DOI: 10.1002/anie.200801863

2D Polymers

Two-Dimensional Polymers: Just a Dream of Synthetic Chemists?

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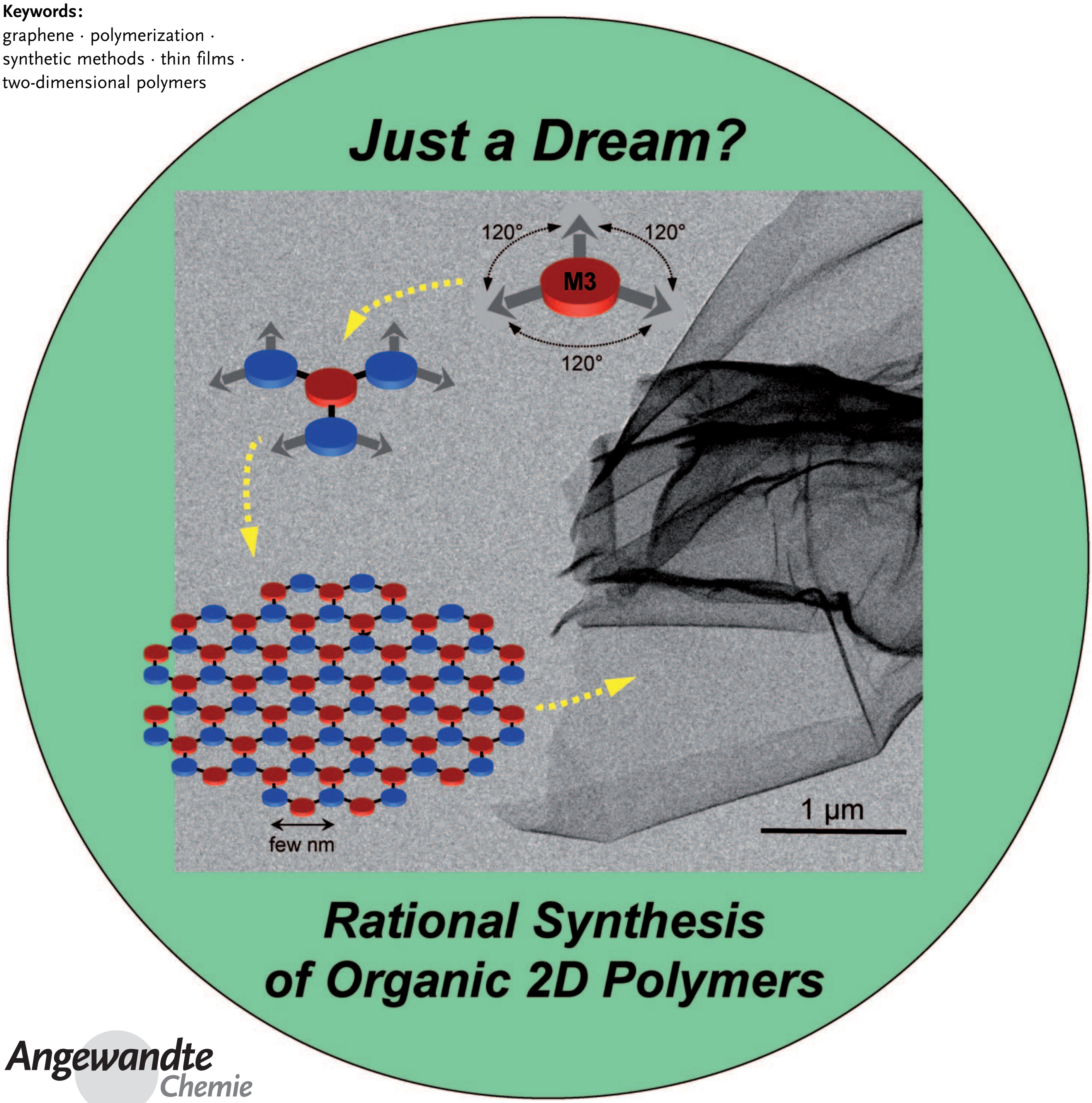
Keywords:
graphene · polymerization · synthetic methods · thin films · two-dimensional polymers



In light of the considerable impact synthetic 2D polymers are expected to have on many fundamental and applied aspects of the natural and engineering sciences, it is surprising that little research has been carried out on these intriguing macromolecules. Although numerous approaches have been reported over the last several decades, the synthesis of a one monomer unit thick, covalently bonded molecular sheet with a long-range ordered (periodic) internal structure has yet to be achieved. This Review provides an overview of these approaches and an analysis of how to synthesize 2D polymers. This analysis compares polymerizations in (initially) a homogeneous phase with those at interfaces and considers structural aspects of monomers as well as possibly preferred connection modes. It also addresses issues such as shrinkage as well as domain and crack formation, and briefly touches upon how the chances for a successful structural analysis of the final product can possibly be increased.

From the Contents

1. Introduction

Take layered crystal-like graphite, rub it onto a solid surface and then search this surface with an optical or an atomic force microscope (AFM) for what has been deposited. What will one find? Practically only multilayered, thick flakes of this material, but with some luck and considerable persistence also a few of its molecular layers.[1,2] What is the evidence for the stunning proposal that this trivial procedure should provide access to such a unique thing as an atomically thin, laterally "infinite", structurally precisely defined, covalently bonded sheet? Firstly, there is a bright-field transmission electron microscopy (TEM) image of such a micrometer-sized object (Figure 1). This was obtained after suspending the sheet from the solid substrate and transferring it to a metallic scaffold.[3a] The signs of the sheet's folded edges, clearly prove it to be a single-layered entity. Secondly, the angle-dependent electron diffraction pattern is fully consistent with the expected honeycomb structure.[3a] Thus, in fact, the image in Figure 1 represents a single graphite layer, a so-called graphene. Graphenes are just one carbon atom thick and, therefore, the thinnest covalent films one can imagine. Graphenes and other natural sheets,[4] because of their long-range order, are often referred to as two-dimensional (2D) crystals. Chemists, who tend to think of compounds and covalent bonds, may instead look at them as 2D macromolecules or 2D polymers and will instantaneously dissect the molecular structure into repeating units and speculate about routes to synthesize these fascinating materials.

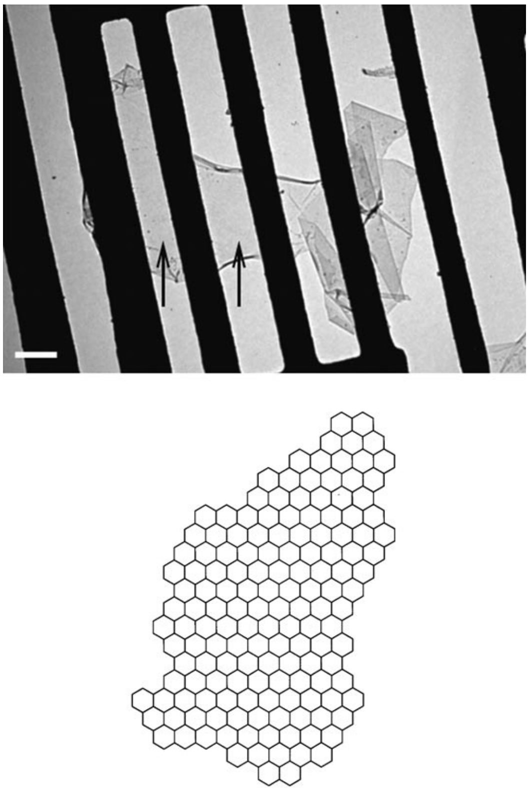


Figure 1. Bright-field TEM image of a suspended graphene sheet (top) and its molecular structure, disregarding the double bonds (bottom). The region indicated by arrows is monolayer graphene. Scale bar: 500 nm. Reprinted from Ref. [3a] with permission from the Nature Publishing Group.

Defect-free graphene has an infinite number of repetitive elements, with the smallest being any of its sp^2-hybridized carbon atoms, whose one p orbital and three sp^2 orbitals are filled with one electron each. These carbon atoms correspond to the smallest repetitive chain segments representing the repeating units of common linear polymers (Figure 2). There are, of course, numerous other options to formally divide graphene into repetitive fragments: for example, the shaded hexagons (benzene-1,2,3,4,5,6-hexayl units) in Figure 2 are

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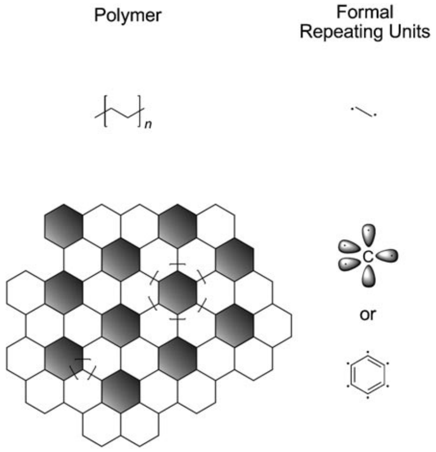


Figure 2. The structure of polyethylene (PE), a typical linear polymer, and of graphene, a 2D polymer with some formal repetitive fragments. The 1,2-ethanediyl unit shown for PE is the repeating unit, whereas for graphene a repeating unit cannot be reasonably defined as long as its mode of synthesis is not known.

alternatives. As for conventional linear polymers, it will also be reasonable in the case of 2D polymers to consider the basic skeleton of the monomer which undergoes polymerization as the repeating unit, even if smaller (or larger) formal units such as in graphene exist.

The fact that one can now isolate and investigate the natural 2D polymer graphene begs the question as to whether such intriguing structures could also be synthesized.[5] This question is not limited to whether one can synthesize graphene—this would be just one target of the entire family of 2D polymers, although admittedly an especially complicated and challenging one. It is meant much more general in the sense: Can one provide reliable and broadly applicable concepts to tackle the synthetic and analytical issues associated with the creation of polymers which meet the structural characteristics of graphene (that is, one repeating unit thick, covalently bonded, and long-range order). Clearly, this would constitute a substantial advance for chemistry in particular, and the molecular sciences in general. Many research groups across the world have developed concepts over several decades on how to possibly solve this issue, but, as yet, there is still no report describing a proven 2D polymer that satisfies these criteria, let alone a general strategy leading to them. Making 2D polymers, shown schematically in Figure 3, is still a dream of many organic and polymer chemists. This Review seeks to strengthen efforts in this direction by first putting the focus on why this class of polymers would be so desirable, before describing the important steps that were accomplished over the years towards their synthesis and characterization. The numerous pitfalls and problems encountered will then form the basis for strategic considerations through which it will hopefully become evident that the dream of periodic, organic 2D polymers is not an illusory one.

Junji Sakamoto, born in Kyoto, Japan in 1973, studied chemistry at Kyoto University (Japan) and earned his PhD in 2002. He carried out postdoctoral research with K. Müllen at the Max-Planck-Institute for Polymer Research (Mainz, Germany), working on the synthesis of polyphenylene-based dendrimers (2002–2004). He then moved to the group of A. D. Schlüter at ETH Zurich, working on the synthesis of shape-persistent macrocycles, where since 2006 he has been group leader for 2D polymer projects. His current research focuses on the synthesis of macromolecules with precisely controlled molecular/supramolecular structures.

Oleg Lukin received his MSc in chemistry at Kiev University (Ukraine) in 1995, and obtained his PhD in 2000 from the Institute of Organic Chemistry, Warsaw (Poland), with H. Dodziuk. After postdoctoral research with J. Leszczynski at Jackson State University (USA), he joined the group of F. Vögtle in Bonn as an Alexander von Humboldt fellow. Since 2004 he has worked in the group of A. D. Schlüter at the ETH Zurich. His research interests include dendritic molecules, two-dimensional polymers, chemo- and regioselective reactions, chemical topology, and theoretical analysis of molecular structures, noncovalent interactions, and reactivity.

Jeroen van Heijst received his MSc in organic chemistry at the Vrije Universiteit Amsterdam (The Netherlands) in 2002. He then joined the group of F. Vögtle at the Universität Bonn (Germany) to work on a combined project in the area of functional dendrimers with L. De Cola (then at the Universiteit van Amsterdam), and in 2006 he obtained his PhD. Since 2007, he has been carrying out postdoctoral research in the group of A. D. Schlüter at the ETH Zurich (Switzerland) on the synthesis of two-dimensional polymers. His interests include the areas of macromolecular chemistry, polymers, and functional organic materials.

A. Dieter Schlüter studied chemistry and geophysics at the LMU Munich, and received a PhD in 1984 with Prof. G. Szeimies. After post-doctoral work with K. P. C. Vollhardt (Berkeley) and W. J. Feast (Durham, England), he joined the MPI for Polymer Research in Mainz in 1986, working on preparative macromolecular chemistry with G. Wegner. In 1991 he habilitated in organic chemistry at the University of Mainz. After a brief stay at the University of Karlsruhe, he became professor for organic and macromolecular chemistry at the Free University of Berlin in 1992. Since 2004 he has been professor of polymer chemistry at ETH Zurich.

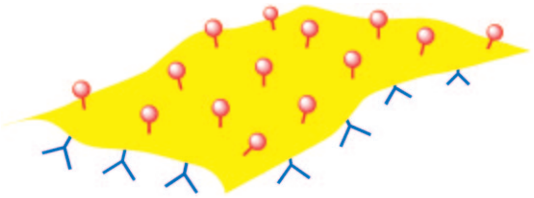


Figure 3. Schematic representation of a 2D polymer with differently functionalized sides. The plane in which the monomers are covalently linked to one another is marked in yellow. The lateral dimensions should be on the order of at least several 100 nm if not μm or even cm. The blue Y-shaped symbols and the red circles indicate, for example, hydrophilic substituents and supramolecular bonding sites, respectively.

2. Why 2D Polymers?

Two-dimensional polymers are fascinating research targets. The development of reliable and robust synthetic routes leading to periodic covalent molecular sheets with rigorously proven structures would open up unique structural, analytical, technological, and theoretical aspects, and are likely to have an almost unimaginable impact on the natural sciences and technology. This section outlines some thoughts underlining this rather strong statement. Let us start with a somewhat abstract consideration of dimensionality in chemistry. Over the years, synthetic chemistry has brought about solutions for many burning questions, including how to achieve stereocontrol in natural product synthesis,[6] to design and synthesize powerful drugs,[7] to develop atom-efficient, environmentally friendly and sustainable processes,[8] and to create polymers with tailor-made properties.[9] Thus, the making and breaking of covalent bonds has been impressively mastered for both "small" compounds, whose sizes typically do not exceed a few nanometers, and single-stranded polymer chains which can attain appreciable sizes. The chemical bonds in all these compounds and polymers are arranged either in typically rather complex but laterally hardly extended geometries or in long zigzag or helical geometries, respectively. Ignoring for a moment the spatial extension each atom has and invoking a somewhat coarser picture of topology, these small compounds could be considered "dotlike", "dimensionless" objects, whereas the polymeric chains could be classified as one-dimensional (irrespective of the entropy-driven tendency of most of them to form coils). Thus, if one analyzes the achievements of covalent synthetic chemistry from dimensionality aspects, it becomes evident that there is substantial space for development, namely in the direction of extended, yet precisely defined 2D and 3D structures. Of course, it has always been at the heart of chemistry to deal with the creation of extended organic matter in the bulk phase, crystals, and thin films, but the tools used here were mainly noncovalent interactions. The recent decades have witnessed enormous progress in understanding how smaller components assemble into larger, defined aggregates, and examples span from artificial membranes and surface patterning to crystal engineering and the generation of functional 3D bulk materials through self-assembly and phase-segregation processes of carefully designed components. The very fact that the creation of these more-complex aggregates was achieved by using weaker forces than covalent bonds suggests that there is a barrier for covalent synthesis to cross the dimensional border between the "zero"- and one-dimensional molecules on one side and extended 2D and 3D structures on the other. Thus, developing methods to progress into this direction holds great promise to advance chemistry.

Besides the somewhat fundamental and abstract reasoning above, there are numerous other aspects which stimulate research on 2D polymers. In the first place it is the curiosity as to which characteristics macroscopic pieces of a one monomer thick sheet will feature. Such sheets could well be several square centimeters large and still represent one single macromolecule. How high will their mechanical stability (that is, their brittleness) be? Can one hang them up on a rope for drying like laundry or feel them with ones fingers? Can one see them with the naked eye?[10] Will they roll up instantaneously or can one roll them up, may be even in a continuous process during the synthesis?[11]

Besides these more intuitive questions, there are fundamental scientific aspects as well. What would the stress/strain curves look like? Are there unexpected effects in the propagation of cracks? Which forces are required to bend the sheets? All these aspects could be directly correlated to the chemical structure because one does not deal with an ultrathin irregularly cross-linked film, where the segments between the netpoints have a length distribution, but in the ideal case with periodic structures with a quantified degree of structural perfection.[3]

Can one put sheet after sheet on top of one another and thus create a gradual transition from a 2D covalent sheet to a (thin) 3D layered material? This would open up the attractive possibility to systematically explore the dependence of the properties on the thickness and compare the results with multilayered stacks obtained both from noncovalently bound monolayers and by the layer-by-layer (LBL) technique, in which oppositely charged polyelectrolytes are deposited on one another in such a way that alternating layers with fuzzy boundaries are obtained.[12,13]

Do the properties change linearly with each added layer? Since such sheets could be used to cover solid surfaces with essentially one layer of organic matter, the question arises as to whether such a process would have any potential advantage over the self-assembled monolayer (SAM) technique, a very potent and established method to do exactly this. The answer is yes. If one is able to place a 2D polymer onto a substrate without crumpling, folding, and tearing (which may not be an easy task), its intrinsic high stability resulting from the covalent nature of the layer could turn into an advantage. If a second layer of certain compounds is placed on it, the liberated heat of condensation associated with this process is less likely to lead to dynamic processes with the possible formation of defects, as can happen with SAMs.[14] Also, for entropic reasons, SAMs have a tendency to form dislocations and islands[15] beyond certain sizes, which should be reduced in the case of their covalently bound congeners, the 2D polymers. Finally, pattern formation in SAMs without any post-treatment is not a trivial task, and this is where 2D polymers with their like or different repeating units (see below) may have another advantage.

In regard to covering solid surfaces with these polymers, a—perhaps even more exciting—thought comes to mind: Could they possibly be used as platforms with positionally defined anchor groups for systematic construction of 3D bulk matter in a true molecular-scale bottom-up approach?[16] Hierarchically structured matter in which such sheets play a key role as a platform, but possibly also as constituents throughout the entire structure, does not sound like mere science fiction. The third dimension may also be reached from single molecular sheets of 2D polymers through "Origami"-type manipulations.[17]

A few words regarding potential applications are in order: The ability of graphene to serve as membranes for small molecules and atoms was recently speculated upon. Similar thoughts were already proposed by Blodgett some 70 years ago[18] and more recently by the research groups of Ringsdorf,[19] Wegner,[20] Regen (see Section 4.2),[21] Duran,[22] and others in connection with ultrathin films. Thus, it makes sense to examine 2D polymers for (molecular) membrane applications once they are available. This specifically holds true if they can be made with high structural fidelity and the flux of matter is confronted with a highly periodic "fisherman's net" with no escape pathway caused by defects. For possible defects, see Section 5. Another application is foreseen when 2D polymers can be placed over cavities without mechanical destruction. These structures should be very sensitive to pressure differences on both sides and could therefore serve as ultrasensitive sensors for pressure changes.[23] Furthermore, 2D platforms with defined anchor groups in the z-direction could be used not only for the construction of structurally well-defined 3D materials, but also for catalysis, electrical circuits, and molecular electronics in general. Lab-on-a-chip applications could profit from such platforms as soon as knowledge is gained on how to decorate 2D polymers with useful sensors and handle them in a controlled fashion.

Finally, the unprecedented structural diversity which is to be expected, even if just two different monomers are used for the synthesis of the 2D polymers, should be mentioned. To illustrate this point we assume for a moment that 2D polymers are synthesized by covalently connecting ordered monolayers of appropriate monomers spread at a gas/liquid interface in a Langmuir trough;[24] in Section 5.2 it will be shown that this is one of many possibilities to create this class of polymers. Figure 4 illustrates some structural options, which are reminiscent of a 2D variant of the continuous forms of order (and disorder) described by Smigelskas and Kirkendall in 1947 for three-dimensional alloys which are formed when two metals are brought in contact, then melted and cooled.[25] The block structure in Figure 4a is the simplest version of gradient 2D block copolymers formed from two or more different monomers.[26] Figure 4b,c show 2D copolymers that result from monomers which do not phase segregate but rather mix by lateral diffusion until they are "frozen-in" at a certain state by an externally stimulated fixation process that leads to a nonrandom formation of covalent bonds. The gradient polymer in Figure 4b represents an early state of this process and the random copolymer in Figure 4c the corresponding thermodynamic minimum. The sequence of repeat units in these two copolymers must be described on the molecular rather than the macroscopic level, despite the macroscopic expansion of the entire macromolcules. The 2D polymers in Figure 4b,c find their counterparts in conventional linear gradient and random copolymers, respectively. The alternating copolymer in Figure 4d requires monomers with a mutually high preference for the other respective monomer.

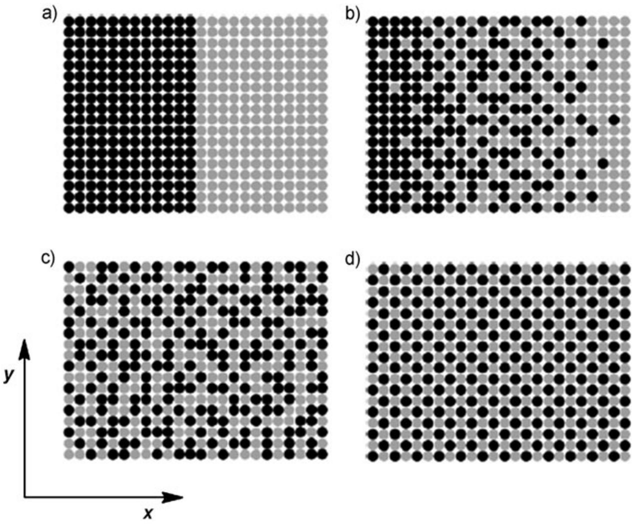


Figure 4. Selected patterns on different length scales of 2D polymers synthesized from two different monomers. The monomers are assumed to have a certain lateral extension and rigidity such that representation as a dot is reasonable. For simplicity, the patterns are shown with tetragonal rather than the more realistic hexagonal symmetry. Options resulting from any treatment after the synthesis are not included.

3. What Is not Considered a 2D Polymer?

The term 2D polymer is widely used in the literature, but apparently no generally accepted definition exists. In an attempt to make the definition and, thus, the scope of the present Review, more precise, we first consider related issues which are important in their own right, but considered outside the scope of this Review. For example, there are numerous materials such as coordination networks[27] and inorganic crystals which consist of layered structures,[28a,b] wherein each layer, when considered separately, fulfills the above criteria to be "classified" as a 2D polymer. There are strong interlayer forces, however, and it is therefore considered to be unlikely that they will be separable from one another. More importantly in the context of this Review, there is no method (yet) which would facilitate creation of just one such layer as a separate entity; typically, three-dimensionally extended matter is obtained.

The focus of this Review, however, is on methods aimed at the preparation of individual molecular sheets and not on layered systems, which would then have to be taken apart in a separate step similar to what one has to do it with graphite (that is, layered graphene)[5v–ba] and some inorganic crystals with layered structures.[28c–m] In a sense, one can say that these layered bulk materials went a step too far.[29] Similar arguments also led to the exclusion of the recent interesting developments in the area of carbon nitrides with graphite-like structural elements.[30,31]

Supramolecular self-assembled structures are held together on surfaces[32] by different noncovalent intermolecular forces such as hydrogen-bonding,[33] π–π stacking,[34] dipolar,[35] or van der Waals interactions.[36] In addition, coordination networks are available, which can also be created as ordered monolayers by vapor-deposition techniques on solid substrates under ultrahigh vacuum conditions.[37] Although the level of order that has been achieved in all these structures is impressive, there does not seem to be a realistic chance to actually remove such monolayers from the substrate and handle them as autonomous molecular units. This of course applies even more so to less laterally binding systems.[38] This is why those studies are also not considered here. Numerous studies dealing with the stabilization of self-assembled entities such as vesicles, micelles, and monolayers by polymerization will only be discussed (Section 4.2) if the process of connecting the individual constituents of the entities leads at least to cross-linked materials. Numerous random-walk polymerizations, for example, in monolayers, are impressive achievements but nevertheless do not belong to the present topic: They produce single-stranded, linear polymers (Figure 5a) which are held in two dimensions only as long as the monolayer stays intact. Upon dissolution, they will attain a three-dimensional coiled shape, as does any other conventional linear polymer.[39] Theoreticians have investigated a related aspect in which linear polymers were artificially confined to two dimensions (Figure 5b). Although the authors referred to these confined macromolecules as "2D polymers", this research will not be considered here.[40] Synthetic studies on Diels–Alder ladder polymers need to be noted in regard to confining polymers to two dimensions. Some of these polymers were referred to as 2D coils. Although their chains confine themselves more or less to two dimensions, the criteria of relevance for this Review are not met.[41]

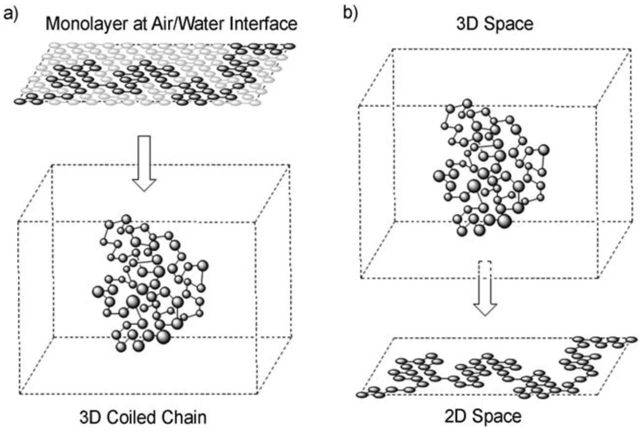


Figure 5. Representation of how a linear polymer confined to two dimensions (for example, within a monolayer) converts into a conventional, coiled linear polymer upon dissolution of the monolayer (left), and the opposite procedure in which otherwise coiled polymers are restricted to two dimensions for theoretical considerations (right). Neither situation is considered in the present Review.

Nature offers beautiful catenated structures which resemble 2D networks but are lacking any covalent connection between the individual monomer units, and will therefore also not be considered here. This "lack" is actually desired by nature because it allows the structures to shrink and expand on demand. Examples are the kinetoplast DNA found in the mitochondria of trypanosomatid parasites[42] and the capsid (shell) of the bacteriophage HK97.[43] The structure of the former was disclosed in the 1990s as a network of multiply interlocked cyclic DNA strands (Figure 6). The capsid consists of 60 hexagonal and 15 pentagonal topologically linked cyclic proteins spanning over the 66 nm icosahedral bacteriophage particle. Studies on 2D crystals from DNA[44] and braided 2D DNA structures show a similar nature.[45]

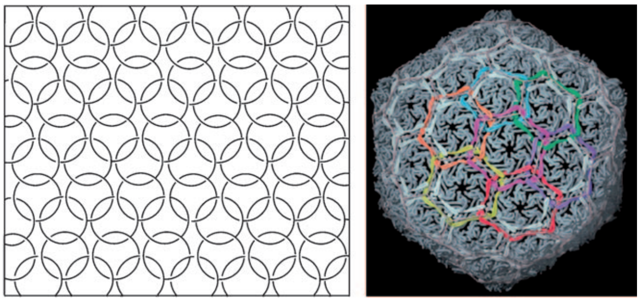


Figure 6. Schematic representation of the medieval chain-mail-like network structure of kinetoplast DNA in its expanded state (left) and the X-ray structure of the bacteriophage HK97 (right). Both are ordered topological 2D networks without covalent bonds between the monomer units [cyclic DNA (left) and cyclic proteins (right)]. Reprinted from Ref. [43] with permission from the American Association for the Advancement of Science.

Rather interesting "quasi-2D polymeric objects" were investigated by Huck and co-workers. These were irregularly cross-linked materials with thicknesses of typically 5–30 nm. They will not be considered here because of their internal irregularity and their thickness, which is well beyond the molecular scale.[46] Similar arguments apply to the impressive work on "2D polymeric nanomaterials" by Gnanou, Duran, and co-workers,[22] and the macroscopic "ordered 2D arrays" of Whiteside and co-workerss.[47]

4. Approaches to 2D Polymers

This section gives an overview of the various strategies that have been applied to approach the ultimate goal of a structurally perfect, infinitely extended and periodic, one monomer unit thick molecular sheet, in other words, a 2D polymer. As will be seen, compromises had to be made in all these studies regarding lateral extension, uniformity of thickness, strictness of periodicity, and—perhaps most importantly—detailed proof of structure on the molecular level.

Nevertheless, all of them give valuable information for successfully obtaining a 2D polymer. This section is divided into two subchapters: Section 4.1 summarizes “flask-type” approaches that take place in solution by using mostly covalent chemistry but in some cases also self-assembly. Although the self-assembly systems do not have covalent coupling between the monomers, they were not excluded right away because they in principle bear the possibility of covalent fixation after the self-assembly step.[48] Section 4.2 introduces various approaches in mono- and multilayered aggregates. Section 5 is devoted to a more rigorous analysis of the advantages and disadvantages as well as an assessment of the future potential of the various methods and attempts, always with the goal in mind to arrive at predictions as to which methods and which monomer design could eventually be successful.

4.1. Flask-Type Organic, Supramolecular, and Polymer Chemistry Approaches

To be a potential building block for covalent 2D polymers, a compound needs to have at least three functional groups (in other words, three latent sites capable of bond formation[49]), through which it can connect to three other (like or different) building blocks during the synthesis. Such a block is 1,3,5-tribromobenzene; the corresponding 1,3,5-benzenetriyl is a repeat unit of the hypothetical corresponding 2D polymer, a small part of which is shown in Figure 7. In principle, this tribromide can give two-dimensional products under cross-coupling conditions.[50] Disregarding for a moment all the rather serious problems associated with such an approach (see Section 5), countless other compounds besides this one would then also have to be considered as potential building blocks. This is outside the scope of this Review, and Section 4.1.1 concentrates only on those oligofunctional compounds which were considered in connection with 2D polymers by the respective authors themselves, and will also show the state-of-the-art regarding combining those into larger fragments.

Section 4.1.2 briefly touches upon model networks that were obtained by self-assembly. Although the structures obtained are not covalent in nature, but instead are reversible coordination networks, they are nevertheless included here because they are considered important examples for the discussion in Section 5 on whether such self-assembly strategies can be expected to be successful for achieving the present goal. Finally, after having dealt with many “small” organic compounds, the structures of which are all more or less isotropic in two dimensions (no preferred extension), approaches based on polymers will be considered in Section 4.1.3.

Two-dimensional polymers can in principle be envisaged as *n*-stranded polymers, and many years ago serious attempts were undertaken to establish a second and perhaps even a third and fourth strand of bonds “parallel” to the first one of a single-stranded polymer. This strategy aims at laterally extending conventional linear polymers either directly during the polymerization event or after a single-stranded polymer has been obtained by laterally synthesizing off the backbone (assumed to define the *y*-direction) to increase its width systematically in the *x*-direction. These strategies will be highlighted by selected double-stranded model compounds prepared by organic synthesis. (These compounds are significantly longer than they are wide.) Figure 8 gives a diagramatic overview of the content of Section 4.1.

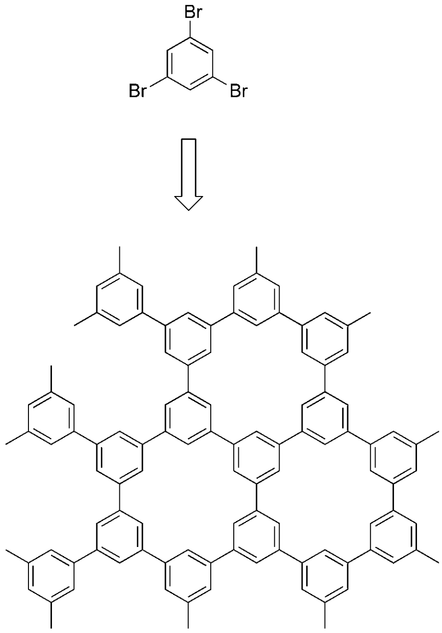


Figure 7. 1,3,5-Tribromobenzene as a hypothetical monomer for hypothetical arylene-based, hexagonal 2D networks, a small fragment of which is shown. The smallest repetitive fragment is a 1,3,5-benzenetriyl unit.

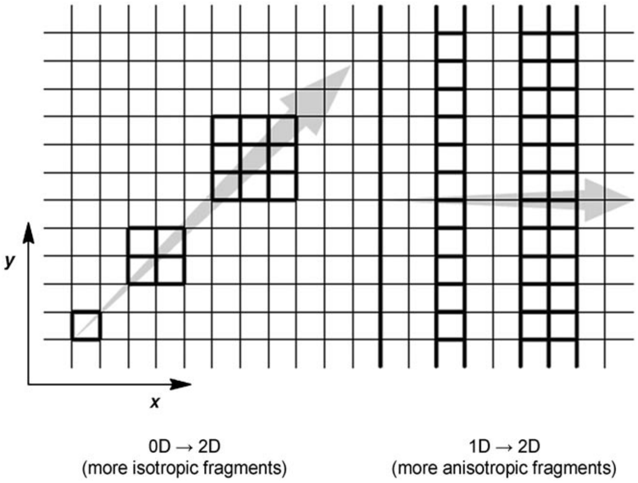


Figure 8. On top of the underlying matrix of a 2D polymer (with tetragonal symmetry for simplicity) are shown products starting from “dimensionless” small compounds (left side) and those aiming at laterally increasing the extension of single-stranded polymers (right side). The still illusive target is the underlying matrix. The resulting compounds on the left side have a more isotropic (disclike) lateral extension whereas those on the right are anisotropic with an almost infinite extension in the *y*-direction.

4.1.1. *The Organic Chemistry Approach: Small Fragments by Covalent Synthesis*

Numerous all-carbon 2D networks were already proposed in the 1980s[51–54] and spurred the interest of synthetic chemists to try to create at least parts of such unusual structures. Although these networks were never actually realized, drawings of them have been published repeatedly. A key role was played by a few, relatively simple looking compounds, such as **1**[55] and **2**[56] (Figure 9), which have the (formal) potential to be coupled to larger flat entities mostly by oxidative or transition-metal-mediated cross-coupling procedures. Whereas differently protected versions of compound **1** were quite intensely used for such purposes, the unprotected hexaethynylbenzene (**2**) could not be reasonably employed because of its high chemical sensitivity. It certainly helped enormously, however, to promote interest in the corresponding networks. There is one report in which a partially protected form of **2** was actually used to create a small 2D fragment.[57] Selected examples of such products are collected in Figure 9, together with those from building blocks other than **1**. Compounds **3**–**6**,[58–60] **7**–**10**,[61–63] and **11**[64] contain butadiyne and ethyne units, and are composed of various numbers of shape-persistent extended trigonal and tetragonal cycles.[65] Compound **12** is based on phthalocyanine building blocks, and is introduced here as a representative for a variety of partially ill-defined related porphyrin- and phthalocyanine-based oligomers which have been synthesized over the years.[66] It should be noted that compound **12**, despite its considerable size in terms of its corresponding infinite network (not shown), plays exactly the same role as the much smaller compounds **3**, **4**, and **7**. They all are just a repetitive element of the corresponding 2D networks which happen to have different mesh sizes.

Müllen and co-workers contributed a whole series of differently sized graphene fragments to this collection of beautiful compounds. Their so-called nanographenes were obtained through the stepwise synthesis of soluble oligophenylene dendrimers, which served as fully characterizable precursors. Their conversion into the corresponding flat polyaromatic hydrocarbons was achieved in a final reaction step by a cascade of intramolecular oxidative cyclodehydrogenations. Scheme 1 shows nanographene C_{222} (**14**),[67] which has a diameter of 3.1 nm and is the largest fragment prepared. It is an intractable and insoluble material which renders structure characterization difficult, if not impossible. According to mass spectrometric evidence, a large portion of the required transformations in the last step could actually be brought about. For AFM and STM characterizations of smaller nanographenes, the reader is referred to the work of Rabe and co-workers[68] and Samori and co-workers.[69]

If it is assumed that the structure of **14** is as shown, this approach allowed the generation of 19 benzenehexayl repeat units plus 18 benzenetetrayl and benzenetriyl end groups in one reaction event. This compound contains the highest number of repeat units in a 2D structure obtained by an "organic chemistry approach in a flask".

Why are experts such as Haley and Müllen still trying to get beyond compounds **5**, **6**, and **14**? The reasons are the enormous synthetic complexity, the elaborate syntheses, and, perhaps most importantly, the insufficient solubility of these products. This latter aspect not only hampers an in-depth structural characterization, but also renders the use of the products as starting materials for further growth impossible.

The complexity of the synthesis is illustrated in the following example: The precursors for **5**, **6**, and **14** were subjected to multiple intramolecular cyclizations in one final reaction step, during which numerous bonds need to be formed at the right place. For relatively small precursors, the number of bond-formation events is limited and the corresponding products can still be isolated as discrete entities. As the precursors become more complex, however, this last step may turn into a nightmare. This point was nicely highlighted recently by Marsden and Haley,[70] in which they comment on the failure of precursor **15** to give the hoped-for target **16** (Scheme 2) by stating: "*Multiple attempts at the construction of the largest planned substructure, hexa[18]annulene **16**, from its precursor **15** were unsuccessful. Despite modifications to the cyclizations conditions, such as addition time, temperature, and concentration, only dark, oligomeric material resulting from intermolecular alkyne couplings was isolated. This result is not surprising, because of the size of the desired DBA (DBA: dodecahydrotribenzo[18]annulene) and the number of simultaneous intramolecular homocouplings necessary for product formation.*"

Of course, in principle, one does not need to risk everything on only one card, namely the last reaction step; stepwise or even repetitive concepts could also be tried, by which the goal would be approached more slowly. This, however, will result in just replacing one rather complex situation by another. The number of overall synthetic steps will very quickly exceed that of even the most demanding natural product synthesis and the amounts of product remaining for the next step will quickly become miniscule. This is not to say that complex precursors cannot be converted in all cases—the synthesis of **14** by Müllen and co-workers is a shining exception. However, it remains questionable as to whether larger precursors than **13** would also become planar, not to mention that already **14** is insoluble like a brick stone. Repetitive attempts cannot easily be pushed further, as unsurmountable barriers arise. These barriers are intrinsic and therefore independent of the special structures and reactions considered. It should be mentioned that this assessment does not automatically hold for step-growth or chain-growth polymerizations in solution, even though the solubility in the initial phase of growth is the same. For a discussion, see Section 5.

4.1.2. *The Supramolecular Approach: Small Fragments by Self-Assembly*

Given the rather considerable effort required for the synthesis of 2D fragments according to the organic chemistry approach, as described in Section 4.1.1., at first glance self-assembly approaches may be considered attractive alternatives. A prominent concept is based on the reversible interaction between properly designed organic ligands and metal ions which under certain conditions equilibrate into the

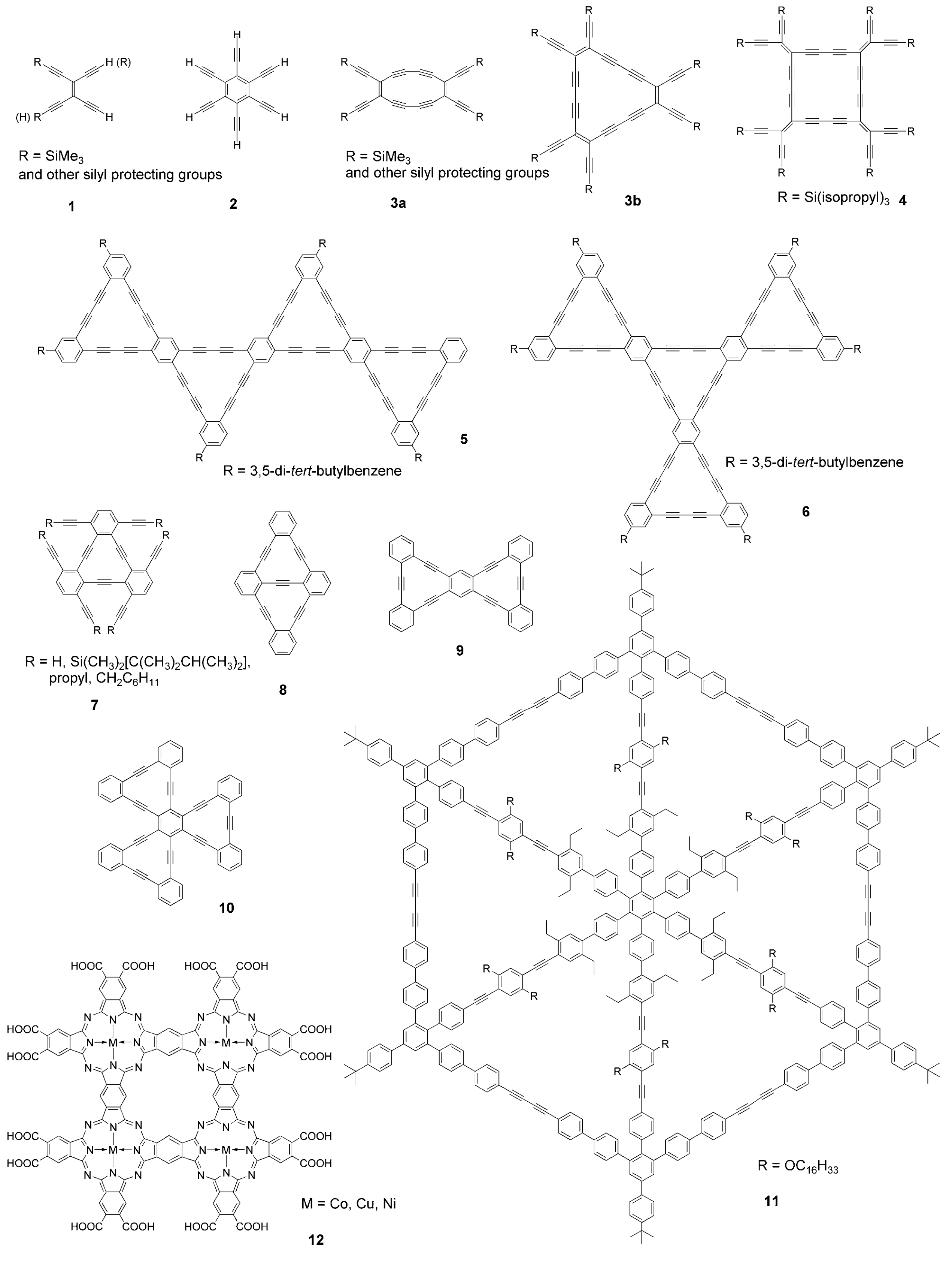
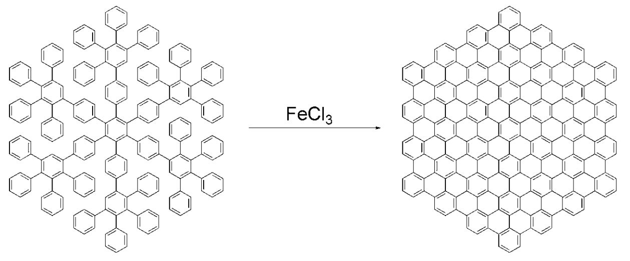
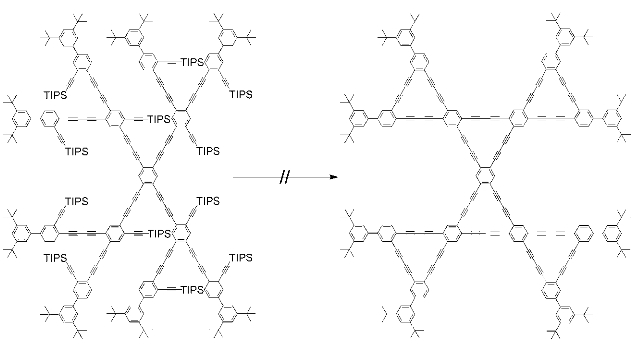


Figure 9. Structures of an actually used (**1**) and a hypothetical building block (**2**) for the synthesis of 2D polymers and of realized fragments (**3**–**12**), partially by using other building blocks (not shown).



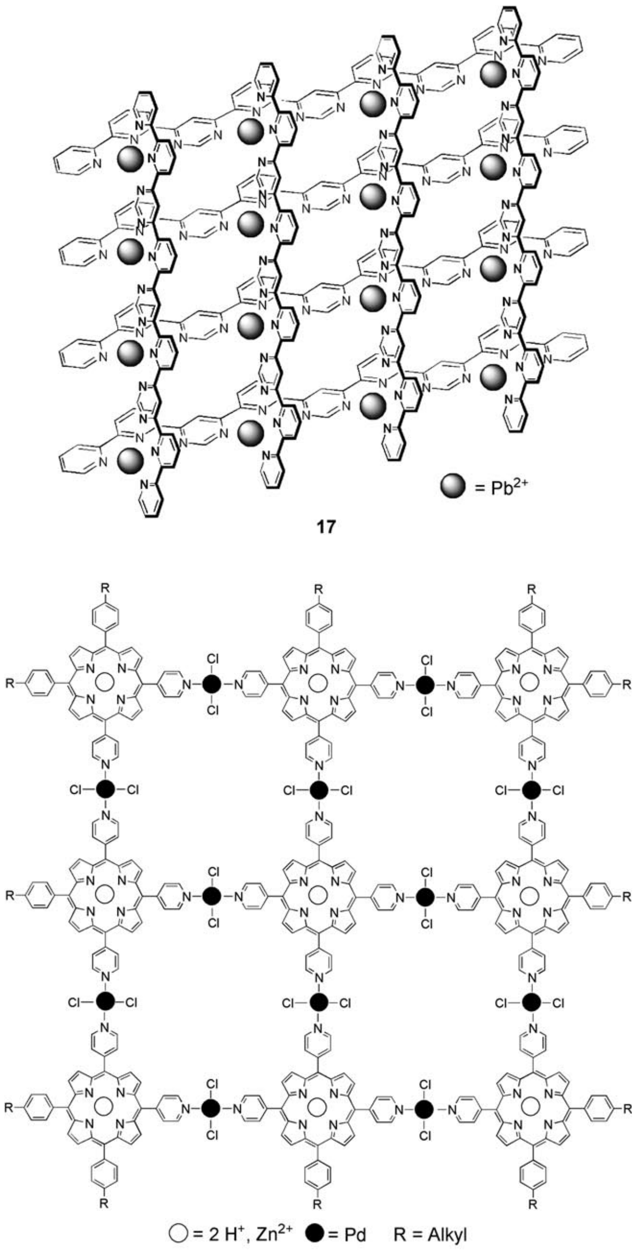
13 **14**

Scheme 1. Proposed transformation of **13** into the disclike fragment **14** of a graphitic plane by a cascade of oxidative cyclo-dehydrogenation steps. Precursor **13**, in contrast to the structure shown, attains a relatively spherical shape which renders it soluble and characterizable, whereas target **14** is completely insoluble under the various conditions tried.



15 **16**

Scheme 2. Precursors can be too complex to allow for the anticipated condensation to give 2D fragments: The unsuccessful attempt to convert **15** into the fully cyclized **16**. Side reactions start to dominate. TIPS = triisopropylsilyl.



17

18

Figure 10. Chemical structures of two prominent metallo-supramolecular grids made from a single kind of ligand (**17**) and three different ones (**18**).

thermodynamic minimum. This results in the complete incorporation of both the ligands and the metal ions into monodisperse, gridlike complexes, such as the ones shown in Figure 10. Depending upon the specific nature of the ligands and metals, two cases can be differentiated: those where the use of one kind of ligand is sufficient and those where the simultaneous presence of different ligands is required. Examples are the $[4\times4]Pb_{16}{}^{32+}$ grid and related ones based on a oligoterpyridine ligand developed by Lehn and coworkers[71] and the pyridinyl-porphyrin squares synthesized by Drain et al., which require the use of L-, T-, and X-shaped ligands in a specific stoichiometric ratio.[72]

The stoichiometry between the metal salts and ligands have to be strictly observed in these cases, otherwise different metallosupramolecular structures may be formed. For example, the $[4\times4]Pb_{16}{}^{32+}$ grid is present in a fast equilibrium with disassembled structures, the ligands of which form helicates; the equilibrium is dependent on the concentration of the metal salt.[73] The addition of the metal salt results in these helicates unwinding and assembling into grids (Figure 11). Thus, the formation of the complexes leads to a change in the shape of the ligand from a helical to a fully extended form.[74] This easily accessible constitutional diversity raises scepticism as to the applicability of metallo-supramolecular strategies to achieve the goal of a 2D polymer. Unfortunately it is not expected that the use of ligands such as the ones developed by Schmittel et al., which are straight and cannot easily form kinks, will make more than a slight difference here.[75]

Although the examples in Figure 10 are beautiful, it is unlikely that such approaches can be used to create "infinitely" large metallo-supramolecular grids. Another indication for this is an analysis of the rather voluminous related literature. There is not a single case in which a structure significantly larger than the ones shown was reported. Although such an analysis is not at all a proof, it nevertheless

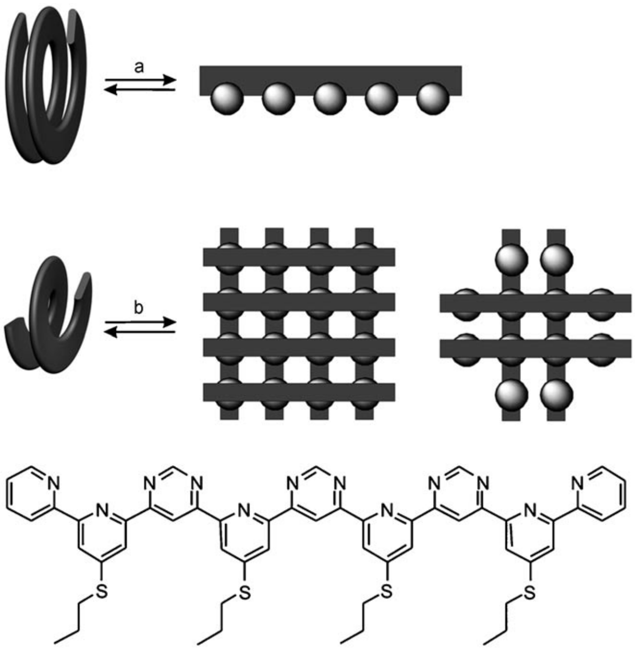


Figure 11. The binding of Pb^{2+} ions to the terpyridine units of the ligand shown leads to a reversible unfolding (a) and self-assembly into gridlike structures (b). This process shows the sensitivity of Pb-based grids to certain parameters such as Pb^{2+} concentration.

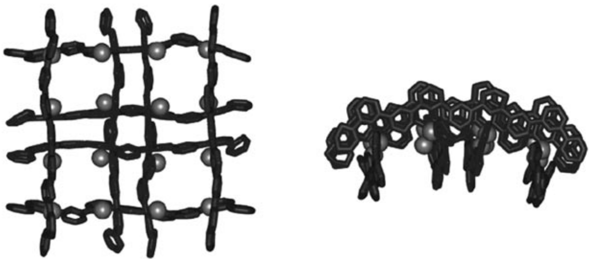


Figure 12. Stick representation of the $[4\times4]Pb_{16}^{32+}$ grid **17** in the single crystal: Top view (left) and side view (right). The angles in the Pb^{2+} complexes do not allow for a flat overall structure. Curvature is observed in several related grids, also with other metal ions. Reproduced from Ref. [73] with permission from the American Chemical Society.

points towards a maximum size of such structures on the order of a few nanometers.[76]

It is also interesting to note that in the various attempts to create porphyrin-based grids such as the one shown in Figure 10, the same few porphyrins were used. This may indicate that as soon as certain substitution patterns (shielding, protecting) are not used, the systems get out of control. Attempts towards larger structures were also undertaken, but have so far met with difficulties,[77] although considerations exist as to how these could be partially circumvented through the use of hierarchical (self-)assembly approaches.[78]

Another critical point is curvature. ChemDraw representations, such as in Figure 10, give the impression that grid **17** has a planar conformation. The single-crystal X-ray structure, however, shows that the geometry of the ligands and the restrictions on coordination imposed by the metal salt do not allow such a conformation (Figure 12). Instead, a sizeable curvature results, which for larger grids (if they were accessible) could lead to the formation of multiwalled helical cylinders and other complex curved structures. Although such structures would be interesting in their own right, curvature clearly poses problems in achieving 2D polymers.

Finally, the kinetics need to be briefly addressed. Given the multitude of docking sites of large ligands and their intrinsic flexibility,[79] it is likely that preferentially disordered aggregates form during the initial phase of complexation. Assuming that 2D self-assembled structures correspond to a thermodynamic minimum—which can not be taken for granted—the repair of all the defects created in the beginning will require countless concerted reorganization steps and therefore will result in a prohibitively high kinetic barrier. When all the arguments are taken together, self-assembly in homogeneous media does not seem to be a useable tool for the anticipated goal.

4.1.3. *Multistranded Compounds with Low and High Molecular Weight*

The right side of Figure 8 illustrates that a 2D network can in principle be considered as an *n*-stranded polymer, in which the strands are covalently connected to one another to generate a periodic structure. Could this be realized synthetically by establishing more and more strands parallel to an already existing one? As long as one can prevent detrimental cross-linking between independent polymer molecules from occurring, one may naively think this could be feasible. This section describes how far research has come in this direction.

We start with some prominent examples of compounds with low molecular weight before the even more challenging double-, triple-, and quadruple-stranded structures with high molecular weight are briefly addressed. Following the famous work on oligoacenes,[80] an important milestone in the chemistry of double-stranded, low-molecular-weight compounds was certainly the multiphenylene synthesis based on the cobalt-mediated trimerization of acetylene by Vollhardt and co-workers.[81] Figure 13 shows the representative compound **19**, which was obtained as a ligand in a cyclopentadienyl-cobalt fragment in a mixture of products. Together with the fused porphyrins prepared by Crossley and Burn (**20**),[82] the open buckybelt from Schlüter and co-workers (**21**),[83] and the fused benzodehydro[12]annulene by Gallagher and Anthony (**22**), [84] these provide an impression of the structural diversity accessible. Recent examples by Moore and co-workers (**23**),[85] and Anderson and co-workers (**24**),[86,87] are noteworthy as they use dynamic covalent chemistry and supramolecular self-assembly, respectively. In the first example, an expansion to larger 2D fragments is explicitly planned;[88,89] the second approach is likely restricted to the oligomeric regime. Irrespective of whether one accepts to call the meso-meso-linked porphyrin ribbons **25** prepared by Osuka and co-workers triple-stranded or not, they clearly represent a step forward in terms of the width achieved.[90] Also their lengths (maximum of 12 repeat units) are quite impressive, although it caused considerable analytical problems and left the characterization of the oligomers

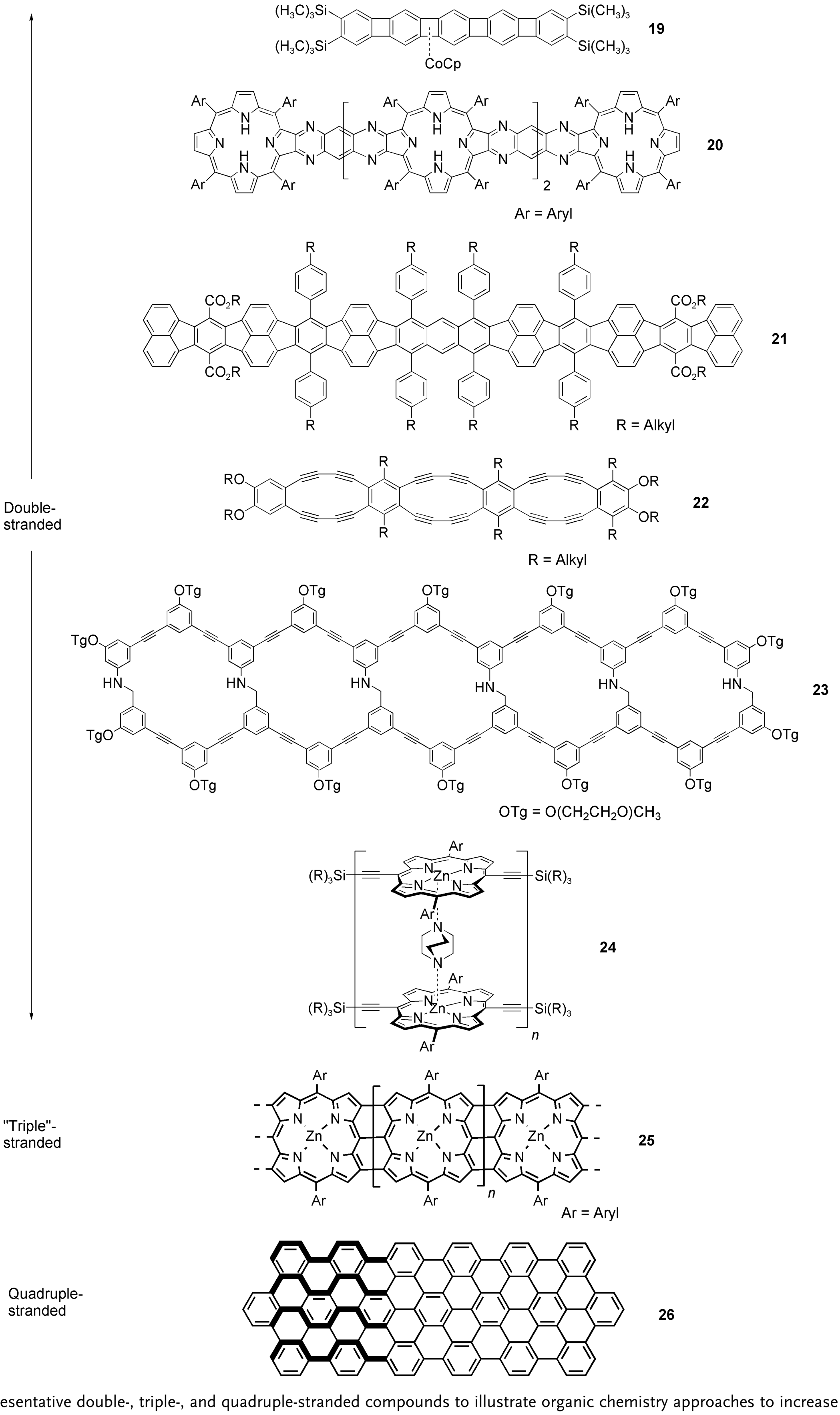


Figure 13. Representative double-, triple-, and quadruple-stranded compounds to illustrate organic chemistry approaches to increase lateral extension. The quadruple-stranded nature of **26** is indicated by highlighting its four independent strands of bonds that neither cross nor merge by bold lines.

beyond $n = 4$ incomplete. The quadruple-stranded compound **26** which was obtained as a mixture of kinked and linear isomers by the Müllen research group rounds up the picture.[91,92]

A collection of double-stranded polymers[93] was made, a few examples of which are shown in Figure 14.[94] They are comprised either of annulated five- and six-membered (**27**–**29** and **31**) or exclusively six-membered rings (**30**). Establishing a second strand of bonds parallel to a first one was a major breakthrough for polymer chemistry, but it is not sufficient in regard to the goal of the present Review. A study which got a bit further as far as lateral extension is concerned was described by Müllen and co-workers, who reported the synthesis of precursor polymer **32a** and its conversion into the quadruple-stranded target **32b**. A comparison of the UV/Vis spectra of **14** (Scheme 1) and **32b** (both recorded in reflection mode) led the authors to conclude that **32b** contains parts with 200 condensed benzene rings. High-resolution TEM images of aggregated products were also provided to support the structural proposal. A full-scale structural analysis, however, was hampered by the extremely low solubility of **32b**. Although not providing structurally defined material, procedures leading to graphene nanoribbons should be mentioned because of the similarity of those ribbons to the compounds described here.[5v,95]

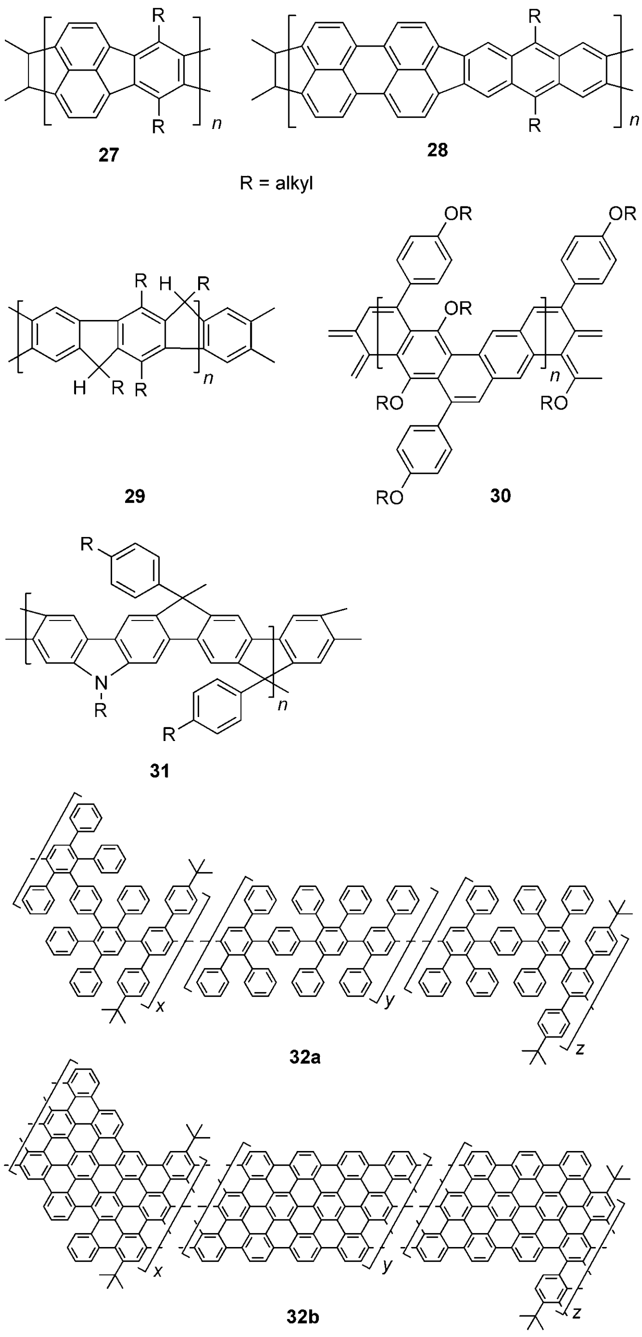


Figure 14. Selected double-stranded (ladder) polymers (**27**–**31**) and a precursor polymer **32a** for the currently laterally most extended macromolecule **32b**.

Although the polymer could be extended lateral in the *y*-direction, this was hardly possible in the *x*-direction. A systematic increase in the lateral extension (*x*-direction) of a polymer chain beyond a few strands is not possible in isotropic solution experiments. The large synthetic effort and insufficient solubility of the products are not the only factors here. One just needs to think in terms of the number of new bond-formation steps that would be required to broaden an initially single-stranded polymer with, for example, 500 repeating units. The range of thousands of transformations per molecule is easily reached, and in a situation where any mistake cannot be removed by purification.

This approach differs in one further important point from the one mentioned above in the same Section: For the first time, the flexibility of long molecules comes into the game. The polymers presented here, irrespective of their numbers of strands, are commonly referred to as rigid rods, but bending their backbones by a few degrees is not costly in energy. The polymers will, therefore, eventually coil in a similar way as conventional polymers. An imaginary observer sitting on a chain following its course will recognize that the chain's memory of its own orientation gets lost after a few nanometers or, at very best, a few tens of nanometers. Thus, even wider chains will not behave like Mikado sticks, with all the consequences this may have on the probability of intrastrand cross-linking and a possibly hindered supply of reagents needed at the site where lateral growth is wanted. Once such chains are no longer dissolved, but arranged in nematic or smectic-like arrays on atomically flat substrates, an interconnection no longer looks like being completely out of range; such an approach has yet to be reported.

In this context it is worthwhile mentioning the attempt by Shinkai and co-workers to produce sheetlike rigid-rod-like conducting polymers (**33** and **34**) by connecting them with porphyrin-based bidirectional "clips" (**35**, Figure 15). This attempt is rather interesting, but also raises questions: Given the low barrier of rotation of the repeating units of the polymers against each other, two clips, when bound to the same chain, can easily attain all possible dihedral angles. This makes it difficult to see why 2D arrays should be favored over, for example, bundle formation.[96]

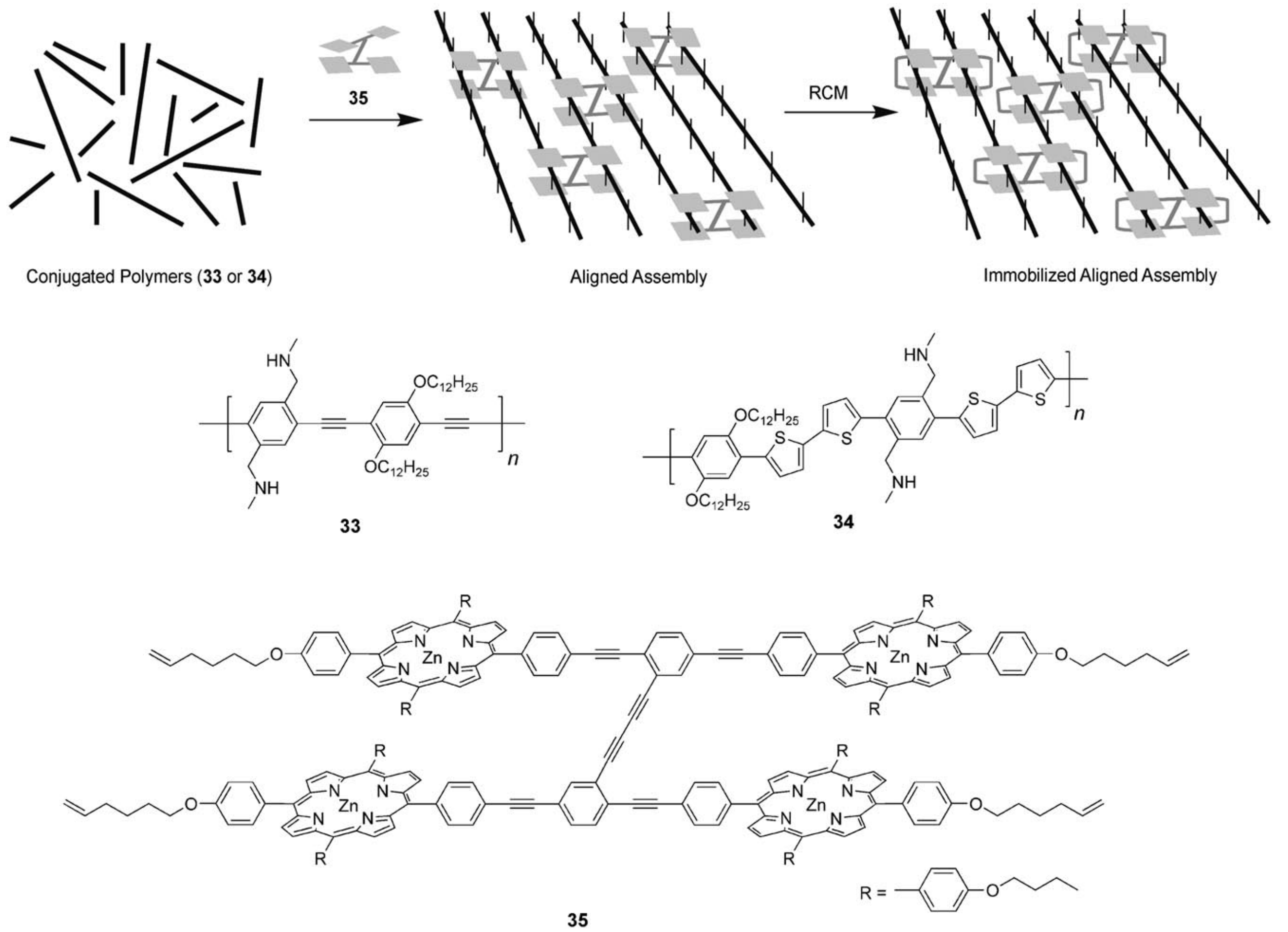


Figure 15. Solution strategies to align rigid-rod conducting polymers into 2D arrays by using supramolecular clips followed by mechanical fixation through formation of a pseudo-polyrotaxane. RCM: ring-closing metathesis.

4.2. Ultrathin Networks by Cross-Linking in Confined Two-Dimensional Space

Up to now small 2D fragments were obtained in solution, as shown in Section 4.1, and the resulting products in the best cases put onto solid substrates for analytical purposes. In this section we describe attempts that make use of confining monomers into 2D geometries prior to cross-linking. This confinement is achieved by spreading the monomers at liquid/gas interfaces, intercalating them into inorganic layered hosts, adsorbing them onto solid substrates, or letting them self-assemble into layered structures. Cross-linking affords covalently connected ultrathin films, whose lateral extensions are orders of magnitudes larger than all those previously discussed. In this sense, the following approaches get substantially closer to the goal of a laterally infinite, one monomer unit thick and periodic structure. One no longer deals with almost dimensionless organic compounds or at best linear polymers with several strands, but instead with infinitely extended films, whose thickness can approach that of a monomer unit. The price to be paid for this increased lateral extension, however, is the loss of structural control on the molecular level. None of the following examples has a periodic molecular structure, but it is nevertheless considered important to provide some insight into what has been achieved in this direction because, in the end, one may be able to devise a strategy to 2D polymers based on the lessons learned both from the approaches previously described in Sections 4.1 and 4.2. Despite the nonperiodic structures produced, many of the authors of the following examples use the descriptor two-dimensional in one form or another. This original terminology is used, even though it is in clear conflict with our definition of a 2D polymer.

4.2.1. Early Results with Monolayers at the Air/Water Interface and in Clays

In 1935, Gee and Rideal made an important first step in this field. Monolayers of β-elaeostearin and its Diels–Alder adduct with maleic anhydride (**36**, Figure 16) were prepared at the air/water interface by using a Langmuir trough; to the best of our knowledge, this is the first report of linear polymerization as well as the cross-linking of such an assembly.[97] Analysis of the force/area curves as well as changes in the surface potential led to the postulation of a process involving primary oxidation at the unsaturated bonds

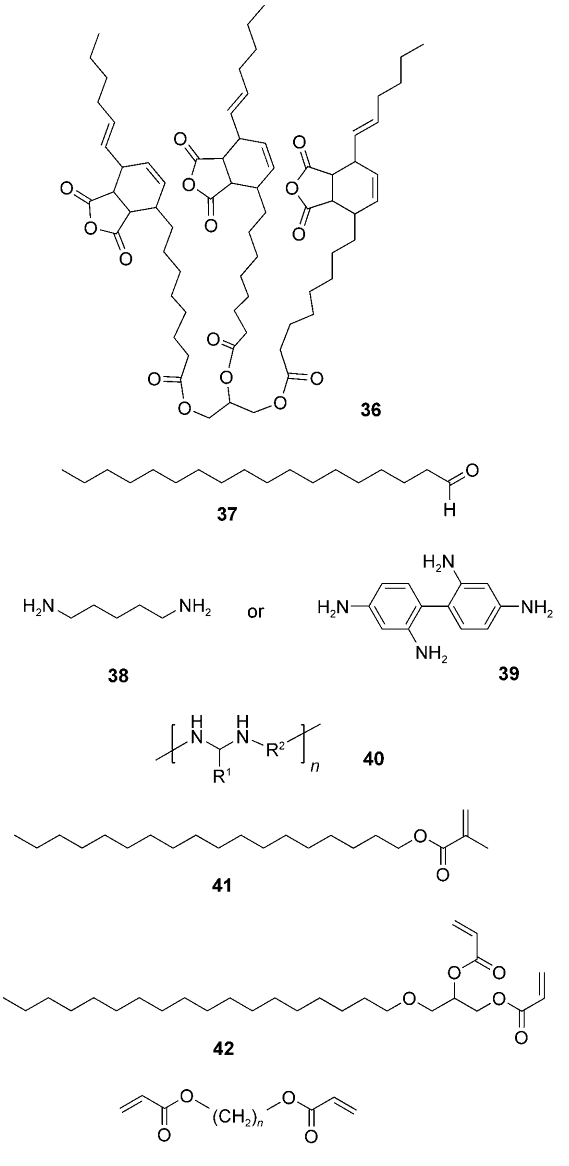


Figure 16. Monomers used for the cross-linking of monolayers at the air/water interface (**36**–**42**) and at the oil/water interface (**43**).

of the lipids followed by polymerization; a molecular mechanism could not be provided at that time because of analytical problems. While a fluid film of β-elaeostearin turned into a continuous gel-like structure during the course of the reaction, monomer **36** gave rise to highly viscous products which broke apart on extension. This difference was ascribed to the more efficient cross-linking in the former case.[98]

In 1941, Bresler et al. reported on mechanical properties of polymerized monolayers and introduced the terms "2D polymerization" and "2D polymer".[99] It was expected that polycondensation should take place between stearic aldehyde (**37**) at the interface and either of the amines **38** or **39**, which were present in the subphase, to give polyaminals **40**.[100] The former combination was supposed to produce "2D linear polymers" (in the terminology of this Review: a linear polymer confined in two dimensions) and actually gave rise to a product that exhibited no elastic properties but only increased viscosity. In contrast, the latter combination afforded a product that behaved as a brittle solid, which was ascribed as a "2D network" (in the terminology of this Review: an irregularly cross-linked monolayer confined in two dimensions). The copolymerization of pepsin with either formalin or a diamine was also studied, which resulted in elastic, rubberlike films. In no case were the degrees of polymerization or any structural analysis of the products provided.

Between the studies by Bresler et al. and the next to be described, research concentrated for quite some time on polymerization in monolayers without cross-linking. As explained in Section 3, such studies will not be treated here (Figure 5).[101,102] Not until 1958 did Blumstein et al. suggest that the adsorption of monomers to form monolayers embedded between lamellar layers of montmorillonite clays would be an interesting approach for the preparation of "sheetlike" macromolecules by cross-linking.[103] They also pointed out that working in clays rather than at the air–water interface would provide access to much larger quantities of product.[104] Surprisingly, however, this study made no attempt to actually realize this idea.[105] It took another three years before systematic studies on such polymerizations were finally published. Methylacrylate (MA) was studied first. It is known that the corresponding polymer, polymethylacrylate (PMA), is sensitive to chain transfer and subsequent cross-linking.[106] The authors studied whether a significant difference could be observed when the polymerization of MA was confined in monolayers and in the bulk phase, with the reaction initiated radically or by γ radiation. The results were compared with methylmethacrylate (MMA) and its corresponding polymer poly(methylmethacrylate) (PMMA), which is less prone to cross-linking. Cross-linking agents were also used in the next step.[107]

These studies involved the isolation of "2D polymers" by dissolving the clay with hydrofluoric acid and dissolving the organic material in common organic solvents. This approach allowed the study of properties such as solubility, viscosity, and sedimentation. For example, PMMA obtained from monolayers in the presence of cross-linkers showed remarkably different surface pressure/area isotherms, which led the authors to conclude: "*The large area at low pressures may indicate the increased rigidity of the cross-linked sheet (of PMMA), whereas the small area at high pressures may indicate the stable ridges are folds in the sheet. This unusually strong film is not entirely unexpected. The polar sheet-like structure should have relatively superior mechanical strengths as well as superior adhesion to the water surface. Moreover, ridges or folds in a compressed sheet should be far more stable than similar ridges or folds in films of polymers that are not cross-linked.*"[107e] Nowadays, when handling single graphene sheets and observing their ridges and folds is routine in many laboratories, Blumstein's statement sounds rather visionary.[108] A report of the first "2D polyelectrolyte" can be found in reference [109].

4.2.2. Cross-Linking in Monolayers at Air/Liquid and Liquid/Liquid Interfaces

Beredjick and Burlant, 30 years after the report by Bresler et al., reported a UV-induced "2D polymerization" at the air/water interface. Oligomeric components were used as monomers which had been prepared from dodecenyl succinic anhydride, maleic anhydride, and propylene glycol by solution condensation such that each oligomer on average carried 1.5 double bonds. These "monomers" were then transferred to the air/water interface and cross-linked by radical polymerization. Unfortunately, little proof was provided in regard to the formation of a 2D cross-linked polymer.[110] Dubault et al. irradiated the better defined monomers **41** and **42** and provided a more in depth characterization of the products that were obtained at the air/water interface.[111] A sharp rise in viscosity was observed after a certain irradiation time onwards for **42**, whereas the increase was continuous for **41**. The solubility of the products also differed: whereas the polymer of bifunctional monomer **42** showed insoluble parts (which is direct evidence for cross-linking) for all stages of irradiation, the polymer from **41** was almost completely soluble at all times. This study is often falsely mentioned as being the first describing a 2D polymerization (in the terminology of this Review: cross-linking polymerization in a monolayer confined to two dimensions). For related studies at the air/water interface, the reader is referred to the studies by Rosilio and Ruaudel-Teixier,[112] Emmerling and Pfannemüller,[113] and Kloepner and Duran.[114] Veyssie and coworkers were able to transfer the cross-linking polymerization of a monolayer from the air/water to the oil/water interface by using diacrylic monomers **43**, and investigated the properties of the cross-linked monolayers comprehensively.[115,116]

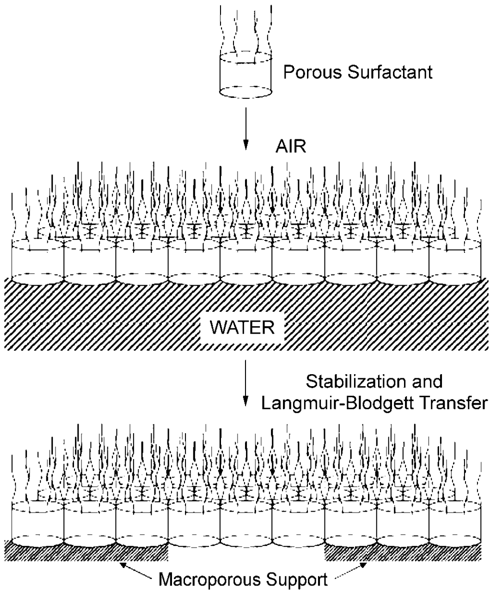
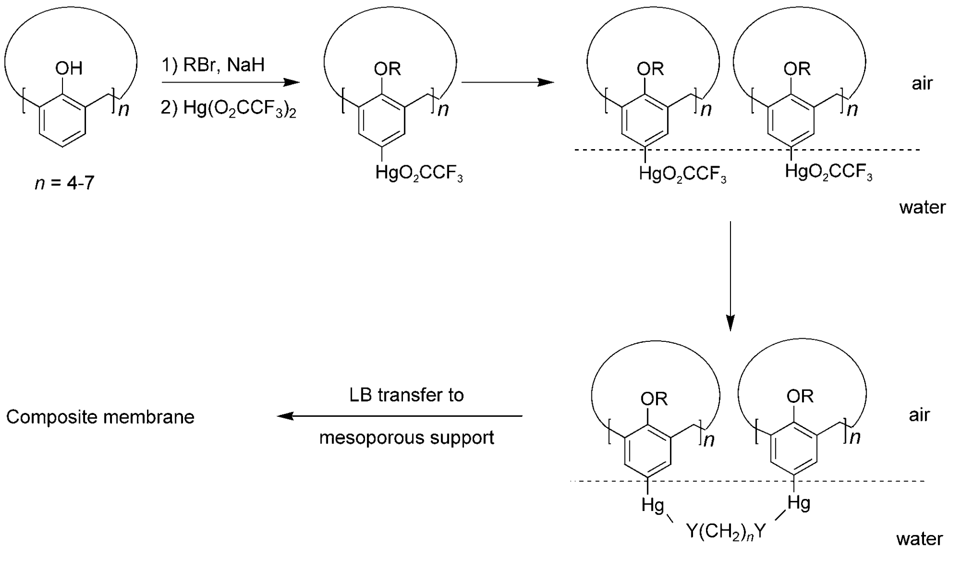


Figure 17. The initial concept of Regen and co-workers for membrane applications of cross-linked monolayers of nanoporous amphiphiles, such as appropriately substituted calixarenes. Spreading the calixarenes at the air/water interface, stabilization of the resulting monolayer (shown in an idealized dense packing) by cross-linking from the subphase, and transfer of the cross-linked monolayer onto a macroporous polymeric support are shown.

The concept of the covalent stabilization of monolayers has also been studied over several decades, mainly with the objective to create stable nanoporous membranes with high permeation selectivity. Regen and co-workers not only investigated monolayers typically supported on macroporous polymeric substrates for increased mechanical stability, but also multilayer arrangements.[21a,117] The main principle was outlined in their 1988 and 1989 publications, in which calix[*n*]arenes ($n = 4$–7)—as nanoporous components—were spread at the air/water interface and then cross-linked prior to Langmuir–Blodgett (LB) transfer of the resulting film onto the macroporous support (Figure 17, Scheme 3). In these initial studies, positively charged mercurated calixarenes were used, which were cross-linked by exchanging their trifluoracetate counterions with the doubly negatively charged malonate ion from the subphase. Later, other chemical cross-linking methods, such as disulfide formation, were developed and the concept of "gluing" LB bilayers was introduced.[21b,118] In this latter concept, cationically charged calixarenes were brought together with water-soluble poly-

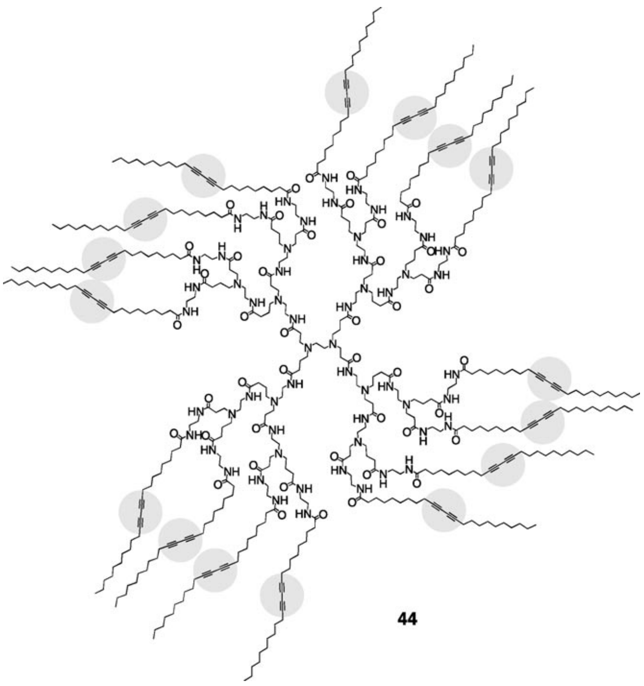


Scheme 3. The synthesis of amphiphilic calixarenes by mercuration at the *para* position, followed by cross-linking from the subphase by exchanging the trifluoroacetate counterion (with a single negative charge) with the malonate (with a double negative charge, $^{-}O_2CCH_2CO_2^{-}$).

anions, such as polystyrene sulfonate, present in the subphase. This "glued together" the compressed monolayer and helped to eventually fill the void space contained in the assembly, "*the net result being enhanced stability, reduced defect formation, and increased permeation selectivity.*"

From the standpoint of an organic chemist, who puts precision of molecular structure as the highest priority, the initial work by Regen and co-workers represents a step closer to the goal of a periodic 2D polymer. Ideally, the nanoporous amphiphiles at the interface end up in domains with a 2D crystalline long-range order (see, however, Section 5). Since the cross-linking and gluing approaches do not occur uniformly, this potential positional order (which still waits to be proven) is not extended to the entire film structure, and irregular films result overall. In addition to this disadvantage, there is no quantitative information available as to how many defects (for example, cracks) are contained in the films and what their exact structural nature is.

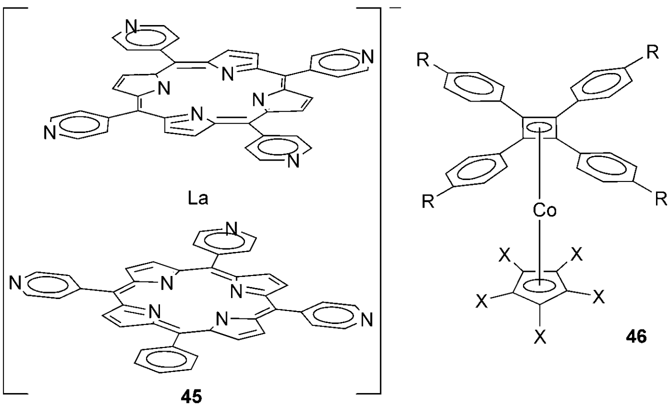
Leblanc and co-workers synthesized the dendrimer-based amphiphile **44** in which sixteen 10,12-pentacosadiynoic acid chains are connected to the periphery of a third generation poly(amidoamine) (PAMAM) dendrimer (Figure 18).[119] A monolayer of this dendritic amphiphile was prepared at the air/water interface, with the peripheral hydrophobic chains lifted up towards the air, while the hydrophilic PAMAM section flexibly changed its conformation and became more compact. Eventually, the hydrophobic chains were (claimed to be) closely packed to one another so that UV irradiation resulted in 2D cross-linking by "topochemical" diacetylene polymerization (see Section 4.2.3). Brewster angle microscopy (BAM) revealed macroscopic defects, but no direct structural information of the product on the molecular level was provided.



44

Figure 18. PAMAM dendrimer **44** with peripheral diacetylene units for use at the air/water interface. The nonpolar termini are presumed to lift upwards upon compression, thus allowing for cross-linking.

Towards the end of this section it seems appropriate to return to an approach which may be considered more rational from an organic chemistry perspective. It was studied by the Michl research group over several years, and is nicely explained in a review article which guides the reader through all of its excitement, but also clearly points out the many problems and potential pitfalls associated with it.[120] Michl and co-workers used double-decker molecules such as the lanthanum and cobalt complexes **45** and **46** (Figure 19), one half of which is designed to adhere to the fluid mercury surface such that the other half sticks freely and unaffected by the surface into the air, and is still able to rotate around an axis perpendicular to the mercury surface. Double-decker **45** actually adsorbed firmly on the mercury under certain electrical conditions, and an IR spectroscopic analysis confirmed that the porphyrin rings of the adsorbed complex were parallel to the surface, thus suggesting that the pyridine substituents on the upper ring would be available for cross-linking reactions.[121] This linking was attempted by the addition of 1,4-bis(bromomethyl)benzene, a potent biselectrophile, and the product still adhered to mercury. Its IR spectra showed that it contained the phenylenebismethylene units as well as the pyridinium rings, and that the porphyrin remained parallel to the surface. Unfortunately it was difficult to prove any long-range order, for example, by scanning tunneling microscopy (STM) as the monolayer had to be first transferred onto atomically flat, highly oriented pyrolytic graphite (HOPG), which caused folding and mechanical damage. Nevertheless, the images revealed a square grid of the anticipated size with some local order. The other monomer with the general structure **46** was synthesized with different substitution patterns. Very recently the adsorption behavior of several representative structures to a mercury surface has been studied in great detail, but the key question is still waiting to be answered: Can they be connected into a 2D polymer?[122]



45

46

Figure 19. Michl-type double-decker monomers **45** and **46** for spreading at the air/mercury interface and subsequent connection to fragments of 2D polymers.

Although this study contains some interesting points which eventually may help to reach the goal of a 2D polymer, it also has a major drawback: Where will the orientation during cross-linking of the double-deckers come from? Even assuming that they themselves can be brought into an ordered assembly, the cross-linking reagent (in this case, 1,4-bis(bromomethyl)benzene) has countless conformational options and will, once reacted with a pyridine group of one monomer, not only react with the pyridine group of the neighboring next monomer, as the concept suggests it will do to get a perfect network structure. Several other motifs (ladders, loops, dangling ends, etc) will unavoidably also form.

Finally, polymerizations of C_{60} monolayers at the air/water interface should be mentioned. A Langmuir film of C_{60} was irradiated at 360 nm and then transferred onto a gold-coated glass substrate by the horizontal lifting method. Analyses were mainly based on infrared reflection absorption spectroscopy and STM. In the former method, the appearance of an absorption band at 1428 cm^{-1} was found, after comparison with the spectra of parent C_{60}, as well as its dimer and trimer, to be indicative of connected monomer units.[123] For the STM method, an iodine-modified gold surface was used, which showed a regular array of what was believed to be the corresponding polymer. Unfortunately, this work does not yet appear in the open literature and deeper insights into the molecular structure of the polymerized film were not provided.[124] C_{60}-based "2D polymers" can also be found in bulk materials.[125]

4.2.3. *Cross-Linking in Multilayers*

So far the studies reported describe irregular (partially random-walk) polymerizations ideally in one plane, the degree to which it is confined to two dimensions depends on the equilibrium structure of the monolayer. Thermal fluctuations may influence the level of confinement, and irregularities caused by them will be captured during polymerization.

Barraud et al. added a new aspect to this type of research by using monomer **47** (Figure 20) not at an interface but in LB multilayers which could polymerize at two different levels relative to the mean interfacial plane.[126] This monomer undergoes a three-step reaction consisting of [2+2] cycloadditions at the butadiene 3,4-positions upon UV treatment, [2+2] cycloadditions at the remaining 1,2-positions under higher energy UV light, and electron beam irradiation induced cross-linking of the remaining single terminal double bond. This study, which in part has to be considered somewhat speculative, was published as a conference preprint only and never further substantiated. Subsequent work by Laschewsky and Ringsdorf using similar monomers (**48** and **49**) arrived at different structural proposals, according to which, irradiation with long-wavelength UV light induced linear polymerization (rather than [2+2] dimerizations) of the butadiene moieties at their 1,4-positions, which was followed by cross-linking of the newly formed 2,3-double bonds by treatment with short-wavelength UV light in air.[127] In contrast to the study of Barraud et al., these polymerizations are not spatially separated.

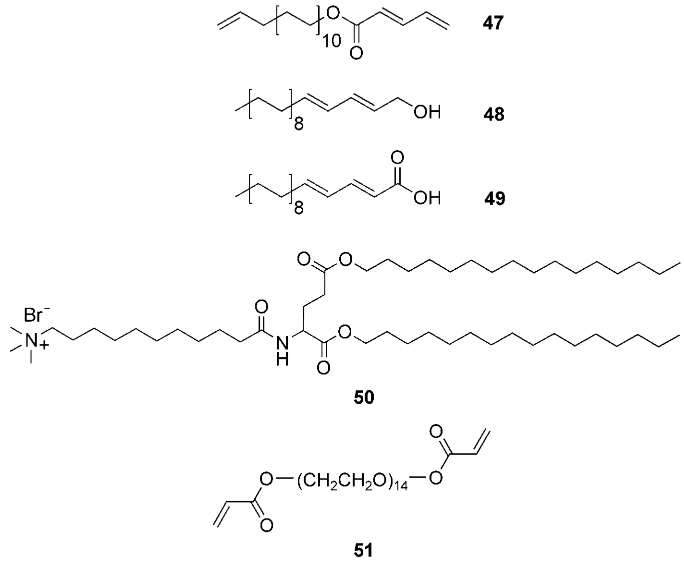


Figure 20. Structures of monomer **47** with two polymerizable groups, monomers **48** and **49**, the synthetic lipid **50**, and monomer **51**.

Interfacial polymerization was influenced considerably by Wegner's finding in the late 1960s that single-crystalline diacetylenes can be topochemically polymerized to polydiacetylenes with conjugated double and triple bonds.[128] Several authors considered this a unique opportunity to not only polymerize monolayers at interfaces or in LB multilayers, but also to generate polymerized ultrathin films with potentially useful properties resulting from the conjugated polydiacetylene backbone. Apart from the polymerizations by Barraud and Ringsdorf described above, topochemical polymerizations proceed in solid-state-like films below the transition temperature to the liquid-like phase, that is, under lattice control. Many of the attempts that used this method with interfacial systems led to linear polymerizations and are therefore not considered here (Figure 5).[10,129–132] Representative 2D cross-linking polymerizations will be described in the following section.[133]

In 1977 Kunitake and Okahata introduced the concept of "synthetic bilayer membranes"[134,135] based on amphiphiles with two long alkyl chains and ammonium head groups. Since then, a large variety of bilayer-forming synthetic amphiphiles have been synthesized and applied to the construction of 2D supramolecular templates for 2D polymerizations.[136] For example, a composite LB cast film with multiple bilayers formed from the artificial lipid **50** and bisacrylate monomer **51** with a photoinitiator was prepared on a fluorocarbon membrane (Figures 20 and 21). In this cast film, the monomer, which because of its ethyleneoxy chains prefers a polar environment, and the initiator segregated into that part of the bilayer assembly where the ammonium head groups of the lipid resided. The thickness of this part was estimated to be approximately 2.6 nm, thus confining the monomers to a pseudo-two-dimensional space. The polymerization was initiated by UV irradiation, and cross-linked polymer films were generated. After rinsing off the template, the residual films were recovered and investigated by scanning electron micro-

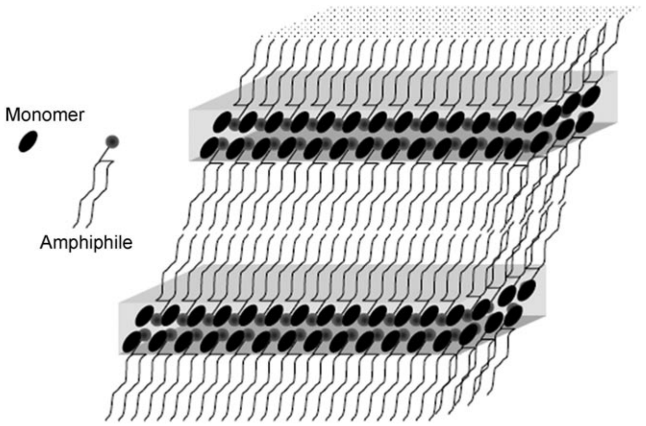


Figure 21. A multi-bilayered film obtained from the synthetic lipid **50**, with monomer **51** intercalated in proximity to the head groups.

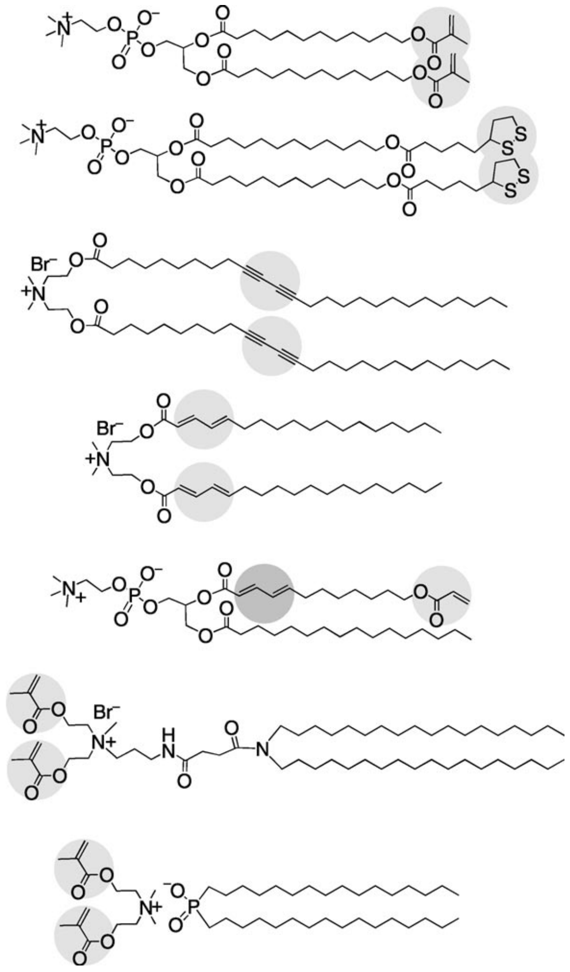

52
53
54
55
56
57
58

Figure 22. Selected monomers for 2D cross-linking polymerizations according to the concepts A–E shown in Figure 23. The assignment of these monomers is as follows: **52**, **53**: A; **54**, **55**: B; **56**: C; **57**: D; **58**: E. The polymerizable units are highlighted by gray circles.

scopy (SEM), which revealed their thickness to be 20–100 nm. This thickness range was clearly beyond the dimensions of a monomer unit and also the estimated thickness of the layer to which the monomers were confined. The authors assumed that some of the initially much thinner films may have aggregated during isolation. This could indicate a general disadvantage of the templating strategy, namely that it does not readily provide an opportunity to isolate the initially formed 2D films prior to their aggregation into thicker objects. At this point the work by Yao et al. should also be mentioned, in which *para*-aminophenyl(trimethoxy)silane was condensed into layered structures stabilized by surfactant.[137]

The concept of Kunitake and Okahata was expanded by integrating polymerizable units directly into the bilayer-forming amphiphiles. Those amphiphiles carrying two polymerizable units are of special interest here.[138] Figure 22 contains a couple of examples with identical such units (**52**,[139] **53**,[140] **54**,[141] **55**,[142] **57** and **58**[143]). A few cases were also reported in which the units differ both in their chemical nature and position in the lipid. Compound **56**[144] serves as an example here. Five different concepts for 2D cross-linking polymerizations were developed (A–E), the main features of which are compared in Figure 23. For more information about structural aspects and applications of these polymerized synthetic bilayers see the excellent reviews by Ringsdorf and co-workers,[19,145] Regen,[146] Fendler and Tundo,[147] Hayward and Chapman,[148] Shimomura,[149] and Mueller and O'Brien.[150]

One example of concept C (Figure 23) deserves more consideration: Stupp et al. reported the bulk synthesis of a "2D polymer" with a thickness of approximately 5 nm (on the order of 100 atoms) and lateral extensions of 10^2–10^3 nm.[151] Compound **59** contains two different reactive groups (acrylate and nitrile) at different positions as well as a smectogen, which generates a smectic phase (Figure 24). The acrylate is positioned at one terminus of **59** and the chiral nitrile somewhere near the center and the smectogen at the other terminus. The polymerization of the acrylates was promoted by interactions between the homochiral nitrile groups; furthermore, the nitrile groups could be at least oligomerized. These two reactive groups were placed far enough apart to avoid the possible formation of ladderlike linear structures. Thus, a 2D object was eventually obtained whose bilayer structure was covalently stabilized by cross-linking of the acrylates at the central main plane and the nitriles in the two additional satellite planes (Figure 25).

At the same time as the studies by Stupp et al., a few reports by the Palacin research group appeared, which described the oxidative coupling of the two-dimensionally preorganized, charged porphyrin derivate **60** (Figure 24).[152] This porphyrin is water soluble and was attracted through Coulomb interactions to the air/water interface spread with a monolayer of the hydrogen dihexadecyl phosphate (HDHP) surfactant. These porphyrin molecules were proposed to form a tetragonal array at the interface, which allowed the coupling of their lateral acetylene functions by copper(I) ions to furnish diacetylenes. These coupling reactions were performed both on HDHP/porphyrin monolayers as well as on LB bi- and multilayers built from them, either by using copper(I) salts from the subphase or by letting solutions of this salt diffuse through to the multilayer, respectively.

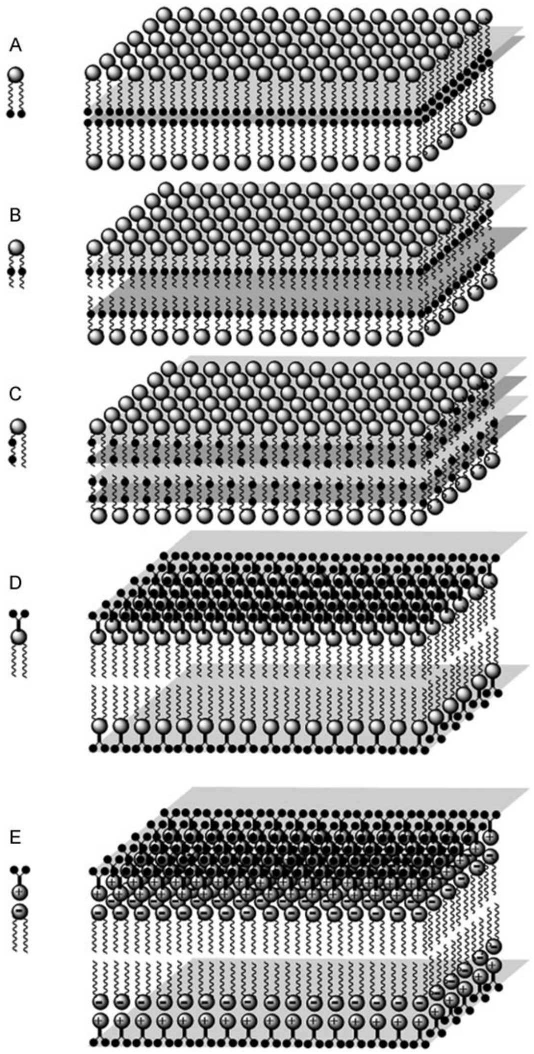


Figure 23. Important modes of 2D polymerization in self-assembled bilayers. A) Polymerizable units (PU, black circle) at the end of a hydrophobic tail. Cross-linking between neighboring monolayers is possible; B: PUs are embedded somewhere in the middle of the hydrophobic tail which avoids any cross-linking with neighboring monolayers; C) two PUs at different but defined positions in the hydrophobic chains so as to allow for two independent polymerization events to occur. Depending on how close one of the PUs is to the chain terminus, this very PU may be involved in cross-linking with neighboring monolayers, whereas the other PU is not involved; D, E) PUs located at the polar head group through covalent (D) or ionic interactions (E). The latter concept provides the option to wash out the cross-linked 2D polymer after polymerization. A–E: It is reasonable to assume that all polymerizations are random-walk processes. For actual monomers, see Figure 22.

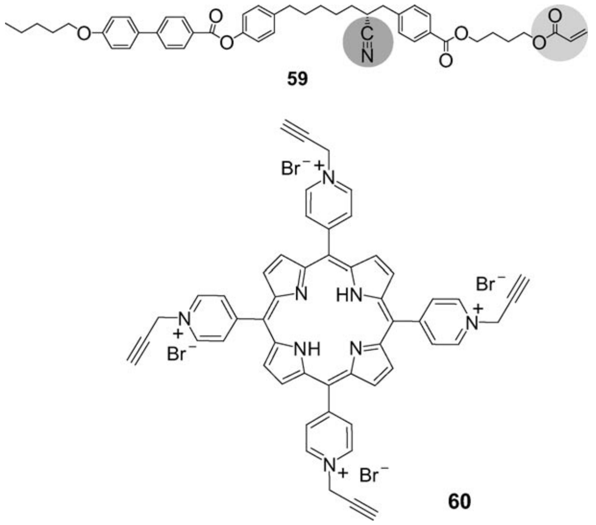


Figure 24. Monomer **59** prepared by Stupp et al. for the bulk generation of "2D polymers", and porphyrin derivative **60** prepared by Palacin et al. for the synthesis of "true 2D polymers".

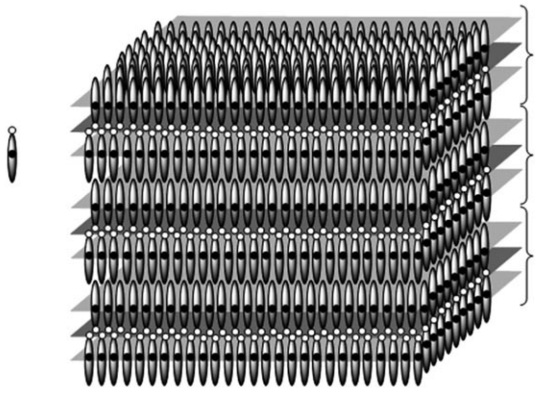


Figure 25. Polymerization in a smectic bulk phase according to Stupp et al. which leads to "2D objects" from **59**. The bilayers are indicated by the brackets. They carry two oligomerizable nitriles (black) in the satellite planes (light gray) and two polymerizable acrylates (white) positioned in the main plane (dark gray). The smectic arrangement is stabilized by cross-linking both in the main plane and the two satellite planes.

Although the characterization of the 2D polymer was rather complex and could not furnish any structural proof at the molecular level, the mechanical stability of the obtained bilayer was rather astounding. After transfer onto a microscopy grid by horizontal lifting, it spanned over holes of approximately 0.003 mm^2. Monolayers were even reported to do the same, which means that approximately 10^9 molecules are involved in such events. These results are clearly interesting, but it remains unclear how one can expect **60** to form a periodic network; the rigid core of the monomer is not used to force the four lateral acetylene functions into a fixed relative geometry. These functions are instead connected to the core through methylene spacers, which enables them to freely attain whatever orientation they prefer. It is thus difficult to see why several other connection motifs were not realized in parallel. This criticism is closely related to that already expressed in a similar case (Figure 19, Section 4.2.2). For the use of transition-metal complexes of porphyrin derivates at interfaces, the reader should see the studies by Qian et al.[153]

4.2.4. *Cross-Linking of SAMs on Solid Substrates*

SAMs have been covalently cross-linked by treatment with electron beams and then removed from the substrates as free-standing films. In an interesting example, electron irradiation of SAMs prepared from biphenyl derivatives **61** and **62** (Figure 26) on solid gold and silicon nitride (SiN_x) substrates, respectively, led to the formation of carbon–carbon bonds between the constituents.[154] Removal of the resulting monomolecular films from the different substrates was achieved by either oxidizing the Au–S bond in a saturated atmosphere of iodine vapor (for **61** on Au; Figure 27) or etching off the silicon nitride layer on a prestructured silicon wafer with hydrofluoric acid (for **62** on SiN_x; Figure 28). The films produced in this way were insoluble in organic solvents. This approach to one monomer unit thick, self-supporting films is rather interesting for materials science, but it can intrinsically not lead to periodic structures because of the random nature of the cross-linking event.

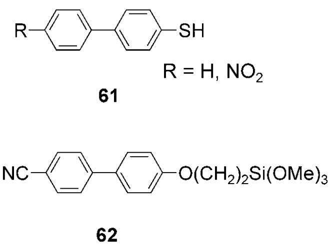


Figure 26. Biphenyl derivatives used for the cross-linking of SAMs by electron beams on gold (**61**) and silicon nitride (SiN_x; **62**).

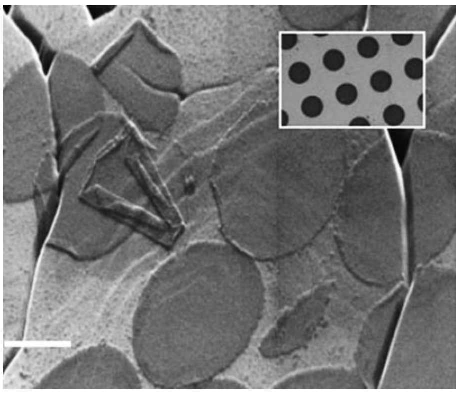


Figure 27. Generation of nanosheets by electron irradiation of **61** (R = H) on gold/mica through a mask with circular holes (diameter: 1.4 μm). After treatment with iodine vapor and rinsing with DMF/ultrasound, the objects have moved on the surface or folded into layered structures. The inset shows the original regular arrangement after rinsing without ultrasound, which leaves the sheets unaffected and dissolves only the non-cross-linked SAMs. The image was recorded by scanning electron microscopy (scale bar: 1 μm). Reproduced from Ref. [154b].

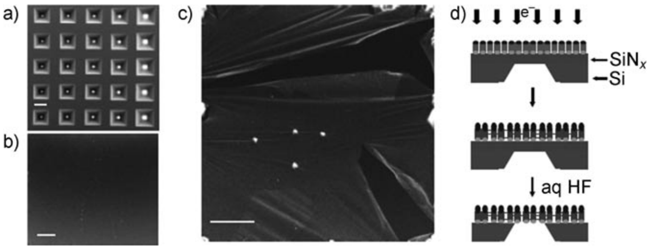


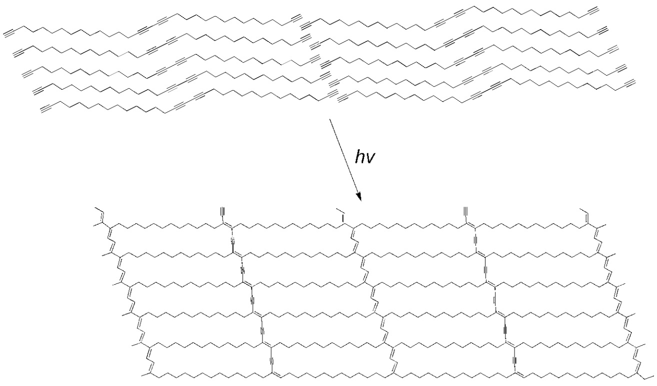
Figure 28. Scanning electron micrographs of free-standing nanosheets obtained by etching off a 30 nm thick SiN_x layer below the cross-linked SAMs of **62** on a prestructured silicon substrate. a) Arrangement of windows in the silicon wafer after removal of the continuous SiN_x layer on the opposite side by etching (scale bar: 200 μm). b) An intact nanosheet (scale bar: 5 μm). c) A ruptured nanosheet (scale bar: 5 μm). d) A schematic representation of the preparation process. Reproduced from Ref. [154b].

4.2.5. *Constructions with Molecules on Solid Substrates*

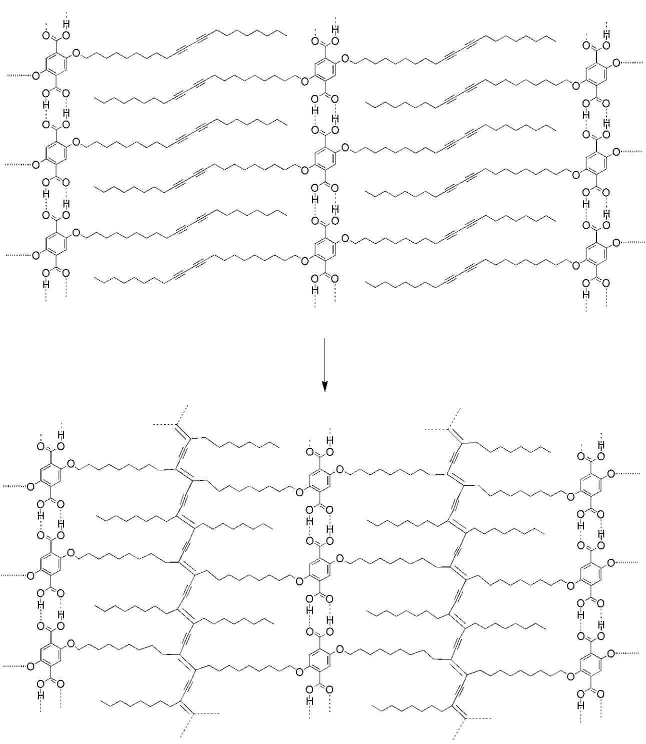
In addition to the rather efficient cross-linking of SAMs with electron beams described in Section 4.2.4, there are also some reports concerning solid substrates, in which more emphasis is placed on the control of the molecular structure. STM and AFM are mostly used for analytical purposes, but have occasionally also been employed as tools to create covalent bonds between molecules adsorbed on appropriate solid substrates. For example, iodobenzenes were coupled to biphenyls in the seminal work of Hla et al.,[155] diacetylene monolayers polymerized to polydiacetylenes by Aono and co-workers[156] and others,[157] and single strands of dendronized polymers[158] "welded" together by Rabe and Schlüter and co-workers.[159] The covalent connection is typically achieved by either activating the precursor components by applying an electrical bias pulse such that transient intermediates are formed which react with one another, or by photochemical treatment after the components have been brought, either manually or by self-assembly, into tight enough contact. The proof of a successful connection normally rests upon experiments, in which the connected molecules are dragged across the surface by the AFM/STM tip. If they do not disassemble, despite the considerable forces applied during this process, weak interactions between the formerly separated components can be excluded. If the electronic state changes considerably during the connection event, for example, by generating conjugation through a polymerization, the connection process may also be read out by the different STM response. There are a few experiments where such considerations have been applied to the "synthesis" of 2D networks. Although the pieces generated are still tiny, these studies may be considered valuable first steps for the synthesis of infinitely extended 2D polymers.

The first such approach in this area was reported by Takami et al., who irradiated monolayers of 1,15,17,31-dotriacontatetrayne under UHV conditions with UV light and investigated the product by STM (Scheme 4).[160] Although the image shows periodic features with reasonable dimensions, it is still questionable how many of the diacetylene units and—perhaps even more so—how many of the terminal acetylene units have actually reacted to give the proposed periodic fisherman's net with a defined mesh size.

A related topochemical polymerization was also reported by De Schryver and co-workers in which a terephthalic acid



Scheme 4. Proposed structure of the product arising from the UV-induced formation of "clothlike" macromolecules by Takami et al. The achieved level of perfection is difficult to conclude from the experimental data provided.



Scheme 5. Proposed structure of the product arising from the STM-induced formation of a small piece of a 2D network.

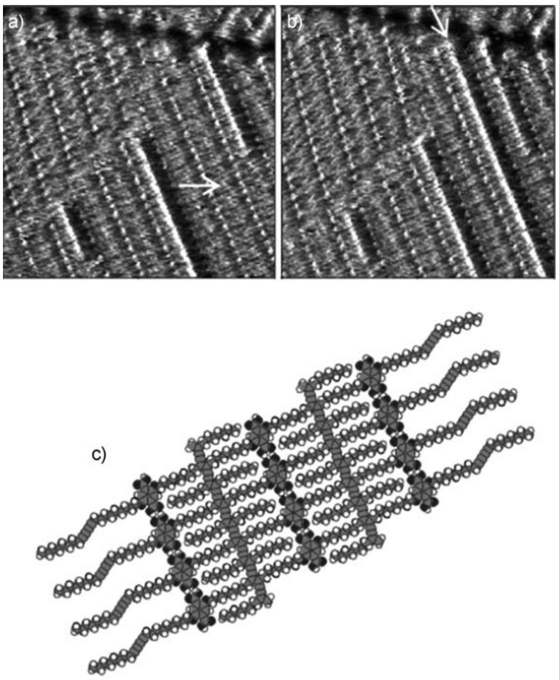


Figure 29. STM image of the monolayer shown in Scheme 5 after UV treatment (a) and after application of a bias pulse (b) at the site indicated with a white arrow in image (a). The molecular model in (c) represents the structure of the small 2D fragment which was generated in the upper right corner of image (b) and indicated by a white arrow. Reprinted from Ref. [161] with permission from the American Chemical Society.

ester carrying two aliphatic chains with internal diacetylene units was used (Scheme 5).[161] This monomer was first spread at the air/water interface and the resulting monolayer then transferred onto HOPG by the horizontal lifting method. The terephthalic acid and diacetylene units formed alternating parallel linear arrays in 2D lamellae, in which the latter units were aligned at a distance and an angle to allow for topochemical polymerization. This was initially induced by UV irradiation, and gave the STM image in Figure 29 a with its three bright parallel lines of different lengths. They resemble the polydiacetylene backbones formed. Two adjacent lines were separated from one another by regular arrays consisting of an alternating sequence of three rows of terephthalic acid ester and two rows of nonpolymerized diacetylene. The polymerization of any of these two rows would result in a piece of a 2D network and was, therefore, tried by applying a bias pulse at the site indicated by the white arrow (Figure 29 a). This pulse initiated another polymerization event which resulted in a fourth polydiacetylene strand, which is marked in Figure 29 b. A part of this new strand in the upper right corner of the image is flanked by the initial polydiacetylene strand; thus, the assembly represents a small part of a 2D polymer. In principle, the size of the 2D network could be increased by polymerizing one diacetylene row after the other.

The most recent case stems from the research groups of Grill and Hecht. Porphyrin derivative **63** was activated thermally before or while being deposited under UHV on a Au(111) surface so that the the carbon–bromine bond was homolytically cleaved.[162] In the absence of any reagent with which the highly active centers of these intermediates could react, and by exploiting their high diffusivity on the surface, some single molecule products such as **64** could be characterized and proven unequivocally by STM (Figure 30). The covalent nature of the products was proven by dragging experiments. Related approaches were recently published by Amabilino, Raval, and co-workers[163] as well as Abel and co-workers.[29d]

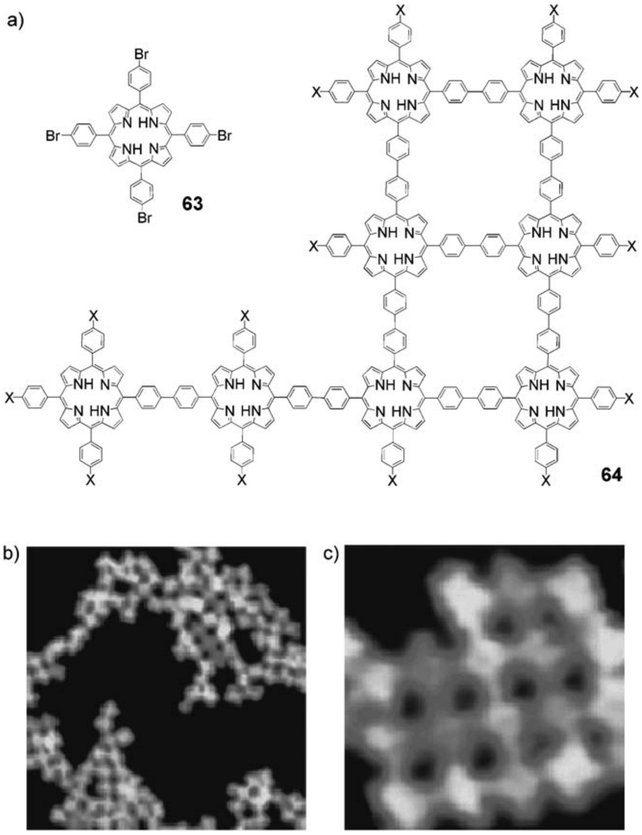


Figure 30. Generation of small 2D fragments such as **64** by heating precursor **63** on a Au(111) surface in an ultrahigh vacuum (a). The precursor is believed to suffer cleavage of the C–Br bond to form highly reactive intermediates (tetraradicals), which then diffuse on the surface until they form intermolecular bonds by collisions which give rise to the formation of larger fragments. The diffusivity of these fragments is reduced to the degree that they become detectable by STM: b) 30×30 nm^2; c) 8.5×8.5 nm^2. The nature of the end groups in **64** is not completely clear and they are therefore denoted as X. Reprinted from Ref. [162] with permission from the Nature Publishing Group.

5. Thoughts on Feasibility

After the focus of Sections 4.1 and 4.2 on chemical synthesis, with scattered specific comments as to the feasibility of the above approaches for the still to be achieved 2D polymer matching the definition given in Section 1, it is time for a few more general comments. They are related to aspects such as monomer design, solubility, shrinkage, and characterization. Some of them specifically refer to either the solution or the interfacial approach, and will be discussed separately wherever appropriate. Finally, approaches in liquid crystals and single crystals will be addressed.

5.1. Solution Approach

5.1.1. Monomer Design

The key difference between solution and interfacial approaches is that the former cannot rely on the ordering power of an interface; monomers are not automatically arranged into the same plane, as occurs if they are just places at a flat liquid or solid surface. Thus, monomer design must account for this disadvantage. It is largely the monomer structure that ensures growth into a nonperturbed 2D geometry. Both the number and positions of the connecting sites and the flexibility of the main skeleton of the monomers have to be carefully chosen.

As pointed out in Section 4.1, the monomers must be equipped with at least three functionalities (latent bond-forming sites) for network formation. To ensure that these functionalities are presented exactly at the predetermined sites, the main skeleton of the monomers should be shape-persistent and the relative conformational play between them and the main frame minimal. Flexible spacers between the bond-forming sites and the skeleton have to be avoided altogether, which is in contrast to the interfacial approach where such linkers may be acceptable under certain conditions (see Section 5.2.1).

One can thus easily imagine that monomers such as **51** with its four bond-forming sites (Figure 20, a double bond can form two bonds) have no chance in homogeneous solutions. These monomers are much too flexible, and there is no force which would direct them into a 2D geometry in the growth step. From this viewpoint, monomer **2** (Figure 9) may be considered a more reasonable candidate. Although it has not yet been employed in the synthesis of 2D polymers because its chemical sensitivity is too high, it was nevertheless selected here as a case study that addresses an important issue to be considered in monomer design: We assume compound **2** polymerizes by acetylene homocoupling. Six such coupling reactions would then have to occur in the same plane for each monomer, with this plane defined by the central benzene rings of the monomers. Even if one believes that all bond formations take place within this same plane for a small fragment (which is unlikely to be so), sooner or later the moment will come when two such fragments couple to one another. Figure 31 illustrates the outcome of such a coupling where fragments A and B, which themselves are assumed to have a perfect structure, become connected at point C. The low rotation barrier of the bond that connects the fragments means they can freely rotate relative to one another, and will do so while growing further at their numerous lateral functional groups. It is unlikely that all critical bond-formation steps, which lead to a structurally homogeneous new fragment, will occur just when the fragments happen to attain a coplanar conformation. Also, depending on the actual growth situation of the respective individual fragments and the relative location of C, it may no longer be possible to covalently capture the in-plane conformation. This inevitably leads to overlapping structures which eventually furnish 3D networks (Figure 32 a). Scheme 2 (Section 4.1.1) provides an example of this effect. The fact that compound **15** cannot be cyclized to **16** is partially due to the ease of rotation of its diacetylenic units which unfortunately do not know what they are supposed to do.

Such defects are actually likely to occur in any solution system. To avoid these problems—or better, to shift them towards the largest possible fragments before failure—the fragments to be connected must be forced automatically into

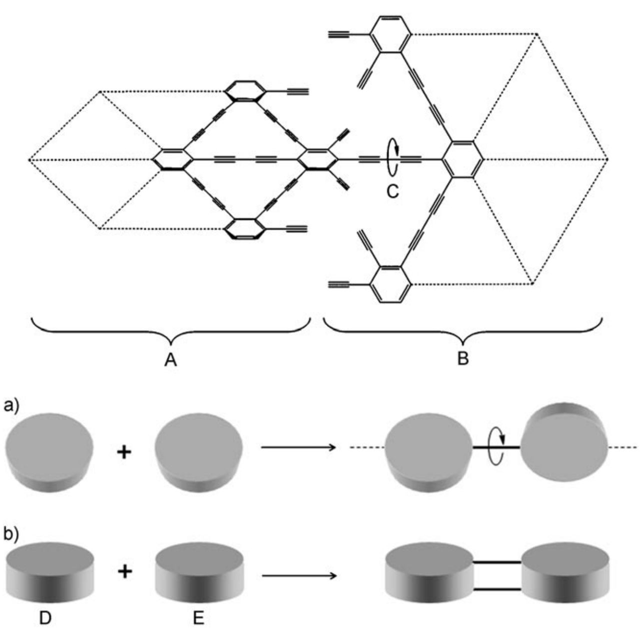


Figure 31. The role of hindered rotation between two connected fragments (A and B) and monomers. Unhindered rotation at C leads to overlapping structures (top) while hindered rotation, which keeps the fragments A and B (now shown as discs) in the same plane, should lead to larger 2D fragments (bottom). There is a clear relationship between the suppression of rotation and attainable size of the 2D fragment which needs to be considered when it comes to monomer design.

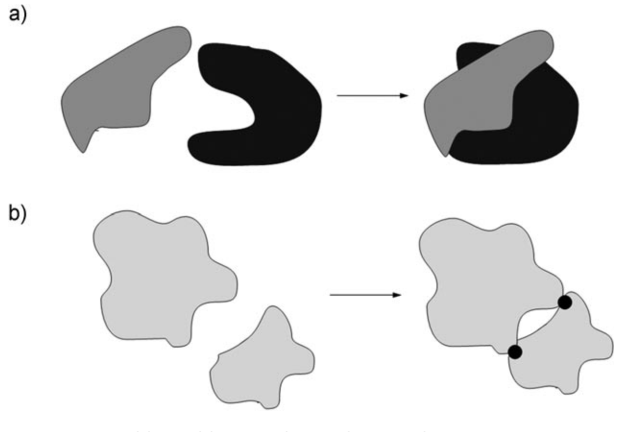


Figure 32. Possible problems with simultaneously growing 2D fragments in solution. The formation of faults by connecting two fragments such that one overlaps the other (a) and upon lateral connection of two fragments at noncomplementary edges (b). The different gray tones in (a) are not meant to indicate chemically different fragments but rather to help illustrate the overlapping.

one plane. In the ideal case, a situation as shown in Figures 31 and 32 a could be avoided simply because the monomers are designed such that the bond-formation event is sensitive to whether or not the fragments are coplanar. In other words, the connection process must not operate unless coplanarity is achieved. Fragments that cannot attain a coplanar arrangement will thus stay independent entities and continue their individual growth. Figure 31 b illustrates the required monomer design for rigid, double-stranded monomers D and E, which are connected to one another through two independent and rigid bonds rather than only one.

When transferring such thoughts into real chemistry, one can think of [2+2] olefin dimerizations, Diels–Alder reactions, and [4+4] anthracene dimerizations. Units enabling such reactions would, of course, have to be incorporated into shape-persistent, possibly cyclic monomers. The rather general structures B and C displayed in Figure 42 (Section 5.2.2) may serve as somewhat more concrete examples here. Under certain circumstances, the modification of such monomers with spatially demanding moieties may help the growing sheets to stay two-dimensional.[164]

Another aspect regarding the connection of fragments in the solution approach still needs to be addressed. Two joining fragments may not only lead to situations discussed in Figures 31 a and 32 a, but also to larger entities with internal holes (Figure 32 b). Such holes are formed whenever two fragments with noncommensurate edges join at two points. It then depends very much on luck whether the resulting holes in the sheet are closed by monomers properly growing inwards. Whereas the overall sheet nature of the resulting polymer would not be disturbed by such defects, properties such as gas permeation or rupture propagation would be influenced, if not dominant. Finally, a word on the expected size of the sheets accessible by the solution approach: Since the ordering power of an interface is not available, any bending motions of the growing sheets, even if they have molecular structures commonly referred to as shape-persistent, will sooner or later lead to deviations from perfection. Thus, if the goal is to synthesize the largest possible 2D polymer with the highest possible structural fidelity, it is advisable to select an interfacial approach.

5.1.2. *Other Aspects*

Another aspect which is rather critical to the solution approach is the enormously fast loss of solubility with increasing size of the 2D objects. Brick-stone-like insolubility is commonly already observed after having reached a few nanometers (see examples in Section 4.1). Rigidity clearly plays a fatal role in this matter, but more decisive may actually be that no appropriate measures were taken (or, could be taken) to keep the 2D discs/sheets in solution. Although structures such as **5**, **6**, and **7** (Figure 9) were actually decorated laterally with flexible chains, they should have rather been facially decorated with "hairs", as nature does with the highly lubricous glycoproteins, the mucins, or even with cells which are protected against aggregation by branched glycolipids and glycoproteins, whose oligosaccharide parts reach out into the surrounding phase.[165] This concept has been successfully mimicked, for example, in the creation of highly lubricous solid surfaces by adsorbing poly(L-lysine-*graft*-polyethylene oxide) onto them[166] or growing polymeric "hairs" off them.[167] If two such "hairy" objects approach each other, a repulsive force will eventually be operative, whose origin is seen in an entropic penalty that builds up as the enforced interdigitation progresses and reduces the conformational freedom of individual hairs (Figure 33).

Besides substituting monomers with hairs such that facially protected 2D fragments result, one may also think in terms of introducing charges spread over the sheet, or a combination of both measures.[168] Sheets facially equipped with (like) charges will, of course, also repel each other. A somewhat speculative aspect regarding solubility of huge flat objects should also be addressed. As mentioned earlier, rigidity is a relative term. We assume that the small 2D fragments discussed in Section 4.1 had dimensions in the micrometer regime. Their mere size means they would automatically be highly flexible sheets showing undulations, foldings, and creases such as seen with graphene sheets.[3] Each chemical bond can be bent by a few degrees with only a small energy penalty. These few degrees quickly add up over the entire structure and thus render all thin objects highly flexible as soon as the object size leaves molecular dimensions. It is thus to be expected that there is a critical size range (which, of course, depends on the system) beyond which this conformational richness is sufficiently dominant to act as a self-protection mechanism against aggregation into an amorphous state of compact, crumpled sheets. If there is, however, a mechanism by which layered structures could form, insoluble flakes would nevertheless be expected. Theoretical studies confirm the existence of crumpled transitions of “tethered surfaces”.[169,170] In this sense, the examples in Section 4.1 unluckily became trapped in insoluble crystal conformations before the fragments could reach crumpled conformations.

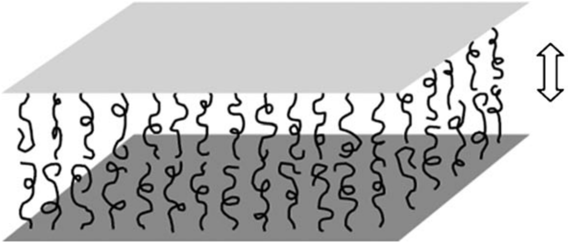


Figure 33. When two hairy surfaces approach each other, an entropic penalty caused by reduced conformational freedom of the hairs hinders interdigitation and thus the formation of the aggregate.

In terms of synthesis, this means that all repetitive approaches have no chance as long as the facial attachment of hairs or the introduction of charges is impossible. Crystallization will be unavoidable after each growth step. If, however, appropriate polymerization procedures could be designed, the situation may no longer be hopeless, even without these attachments, as long as the growth process is significantly faster than precipitation. The polymer will then already have reached a size large enough to form crumples when it “realizes” that it should have precipitated out somewhere along the way should because of its insoluble crystal conformations.[171] Figure 34 illustrates this important point conceptually by showing that crumpled soft tissue paper in water remains crumpled, even though it is well ordered in parallel stacks when still in the box. Although not directly related, it may be of interest to point to a recent report describing the formation of stable aqueous colloids of chemically converted graphene sheets by electrostatic stabilization.[5z] Another interesting topic which is only briefly mentioned here is the conformations of a 2D polymer in solution. For example, such polymers may spontaneously roll up or even form tubes under certain conditions (Figure 35).

Figure 34. Gently crumpled pieces of tissue paper in a loose, fluffy state in water have significantly larger conformational entropy than in a compact crumpled state with little water around the sheets. In contrast to linear polymers, sheets are hence protected against amorphous precipitation by conformational entropy in addition to translational entropy. View from the Department of Materials of ETH Zürich.

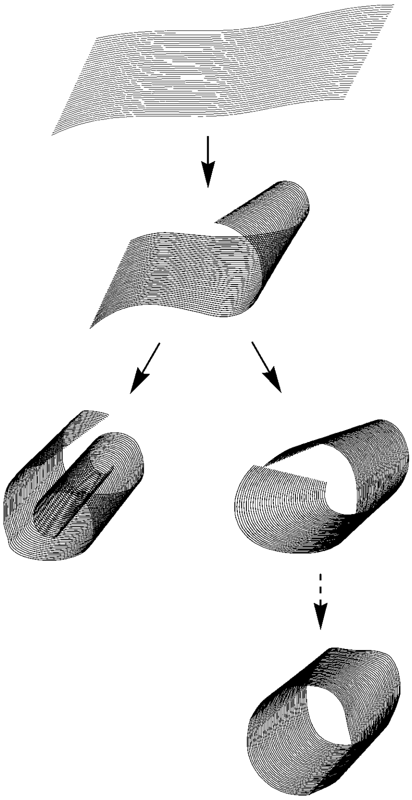


Figure 35. Onset of backfolding caused by theoretically predicted entropy-driven undulations and possible rolling-up processes.

Compared to interfacial approaches, the solution approach offers access to larger quantities of products. When thinking about nano- or micrometer-sized 2D molecular sheets swimming around in a liquid phase, the question arises as to how can these films be fished out, unfolded, and ironed to remove the crumples? The answer to this question is clear: The solution approach is not aimed at preparing individual films for subsequent treatment such as for covering surfaces or for property testing. For such purposes, approaches at the air/water interface are clearly advantageous. The sheets obtained from a solution approach are not meant to be isolated by fishing out one after the other—instead they are designed to be collected by removal of the liquid phase and used as a bulk material, which would be highly interesting in itself. A material consisting of densely crumpled sheets should, for example, have rather unprecedented mechanical behavior compared to conventional linear polymers. The concept of the entanglement of flexible, linear chains which is *the* basis to rationalize the mechanical behavior of polymeric materials clearly does not apply. Hybrid materials where one component is a 2D polymer should also have totally different properties. Metal nanoparticles dispersed in a conventional polymeric matrix would greatly differ, for example, in their catalytic properties from those in a 2D polymeric material, where the particles might be wrapped to some degree and influence their properties. At this point in time, when not even one 2D polymer has been synthesized, one should perhaps not speculate any further; the enormous potential has presumably already become evident from these short comments.

Access to larger quantities of thin films is not restricted to the solution approach discussed here. As has already been mentioned in the context of the studies of Blumstein on layered clays (Section 4.2, see also Section 5.3), "larger" quantities of ultrathin, irregularly cross-linked films could actually be obtained (although the removal of the clay required a rather drastic solvolytic step). If for certain applications a high level of structure perfection is not mandatory, the approach by Blumstein and others would be an alternative that does not require spending time on monomer design and synthesis.

5.2. Interfacial Approach

5.2.1. Monomer Design

Working on fluid surfaces has advantages over solid ones. The 2D polymers, once formed, can in principal be lifted off a fluid surface, dried, and used.[172] For solid substrates this is not impossible either, but is much more complicated than just grabbing the film and hanging it up to dry. This ease of removal constitutes a key advantage of using the air/liquid interface. The monomers at such an interface (mostly air/water[173]) can freely rotate and move around in lateral directions unless they are densely packed. As for the solution approach, the monomer skeletons should therefore be shape-persistent and present the functional groups in the proper relative directions to give a periodic network. Thus, the functional groups of tri-, tetra-, and hexafunctional monomers should be positioned with 120°, 90°, and 60° angles between them, respectively. In addition, the connection units need to be chosen such that a reaction between them is actually possible when confined to two dimensions. Mechanisms of bond formation which require complicated transient relative orientations that can not be realized under the given structural constraints are not appropriate. These requirements suggest the need for rigid cyclic compounds as monomers with functional groups that enable thermal or, perhaps more attractive, photochemical pericyclic reactions such as olefin dimerization, Diels–Alder reactions, and anthracene dimerization. Figure 36 illustrates the expected regular growth of such cyclic monomers equipped with three (M3), four (M4), and six (M6) functional groups at the periphery with the optimal angles.

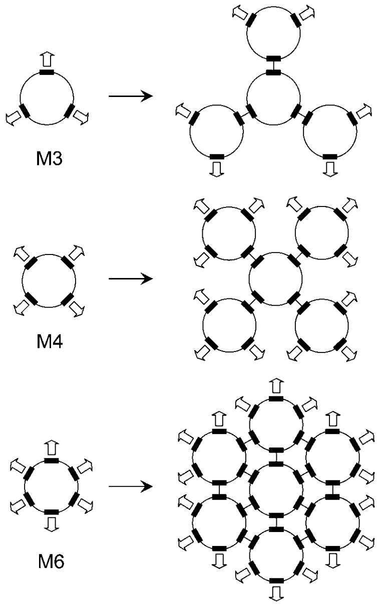


Figure 36. Rigid tri-, tetra-, and hexafunctional monomers M3, M4, and M6, and their ideal growth patterns.

Let us start by considering M6 spread at an air/water interface. Figure 37 illustrates two extreme cases of polymerization. In the first, the noncompressed monomers are confined to two dimensions in a gaslike state and have translational and rotational degrees of freedom. In the second case, they are in a condensed, almost crystalline phase, in which they attain, for example, a hexagonal lattice with no lateral diffusion but with still more or less free rotation. In the first case, this translation and rotation can be enjoyed freely until the first bond-formation step has occurred, and thus a nucleus formed. The structure of the monomer means the next growth step is programmed to furnish a regular network if the growth takes place such that the monomers can diffuse to all the sites they are supposed to occupy. In the gaslike case, spatially separated islands will result and problems arising from noncommensurate edges will be encountered whenever two such islands try to combine. This problem is reminiscent of the rather similar situation discussed for the solution

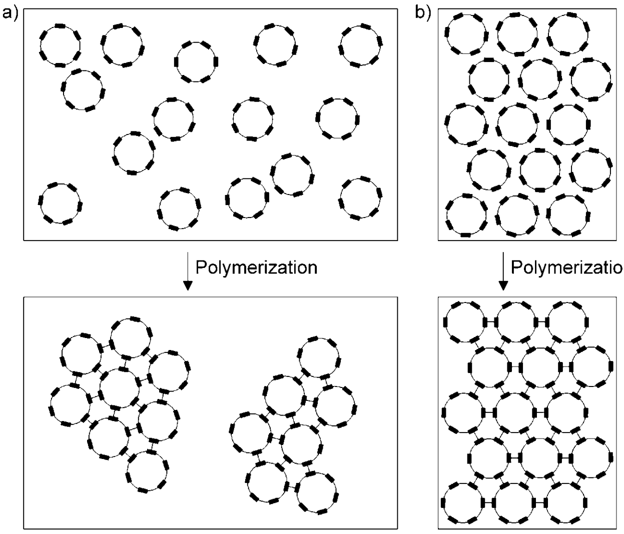


Figure 37. Polymerization at the air/water interface using well-designed M6 monomers with sixfold symmetry in a) a gaslike and b) a condensed phase (after compression with a barrier). In (b) lateral diffusion is no longer allowed, but the monomers are still free to rotate. Aspects such as shrinking are not considered.

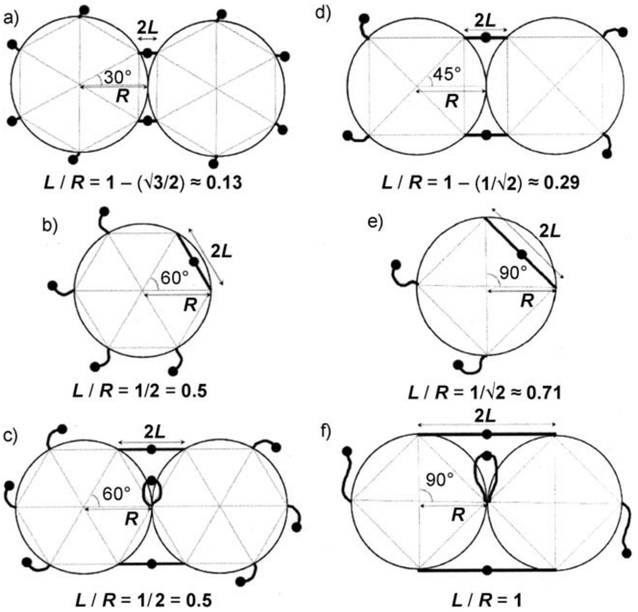


Figure 38. Examples of undesirable bond formation which are explained by the relationship between the size (*R*: radius) of the cyclic main skeleton of a monomer and the length (*L*) of its flexible spacers carrying latent connecting sites at the ends (●): a,d) intermolecular double connections, b,e) intramolecular bond formation, c,f) intermolecular triple connections. Cases (a)–(c) refer to hexafunctional and cases (d)–(f) to tetrafunctional monomers.

approach (see Figure 32 b). In the condensed state, growth can of course also start at different points, but will eventually lead to one large, through-polymerized sheet. This argument holds true only if the compressed monolayer does not contain differently oriented ordered domains and shrinkage can be avoided. Both of these aspects will be dealt with later.

For a better understanding of the importance of having monomers with optimal structures, imagine the situation where similar polymerizations are performed with monomers designed with insufficient care. As an example, a monomer is chosen which also carries six functional groups but they are connected to the main skeleton through flexible spacers. Depending on the length of this spacer relative to the distance between the sites at which two adjacent spacers are connected to the main chain of the monomer, the connecting units may have more options than just the one resulting in a periodic structure.[174] Even if the monomers attain a highly regular order prior to polymerization (high positional order), the non-optimal monomer structure will result in the formation of an irregular network.

This aspect is described in somewhat more depth by using three examples of undesirable bond formation between monomers with flexible spacers for both hexa- (Figure 38 a–c) and tetrafunctional (Figure 38 d–f) monomers. A simple geometric consideration suggests a correlation between undesired connections and the length *L* of the flexible spacers relative to the size (radius *R*) of the main skeleton of the monomer (or the distance between adjacent spacers). For hexafunctional monomers, intermolecular twofold connections between the two monomers are possible if the *L*/*R* ratio is larger than 0.13:1. If this ratio exceeds 0.5:1, then other possibilities of intramolecular bridging and intermolecular triple connections also have to be taken into account. The situation with tetrafunctional monomers is rather similar: *L*/*R* values of 0.29:1, 0.71:1, and 1:1 are critical ratios where intermolecular double connections, intramolecular bridging, and intermolecular triple connections, respectively, may occur. Thus, one can understand that an increased length of the spacer compared to the size of the main skeleton can cause a variety of undesirable bond formations that destroy the periodicity of the 2D polymer. It should be noted at this point that such undesirable connections do not necessarily destroy the positional periodicity of the monomers, a factor which may play a role, for example, for gas permeation. This is the case for several monomers discussed in Section 4.2 for which a positional order may have been achieved (although not proven), but the cross-linking was conducted in a way so as to destroy the overall periodicity.

Let us now return to ideal monomers and consider M4 (Figure 39). Similar to M6 monomers, M4 monomers can also grow into a periodic network in the gaslike phase as a consequence of the programmed structure of the monomer. However, if the same M4 monomer is subjected to polymerization in a condensed phase, a different situation is encountered. Round monomers tend to pack in hexagonal lattices where each single monomer is surrounded by six equidistant ones. The sixfold lattice symmetry and the fourfold monomer symmetry clearly do not match with one another, which has detrimental consequences for the formation of periodic networks. This undesired situation represents a conflict between the monomer design and the pre-assembled structure the monomer attains in the compressed state—a given positional periodicity of the monomers as a result of the molecular packing is incompatible with the positional periodicity necessary for the creation of covalent bonds. There is

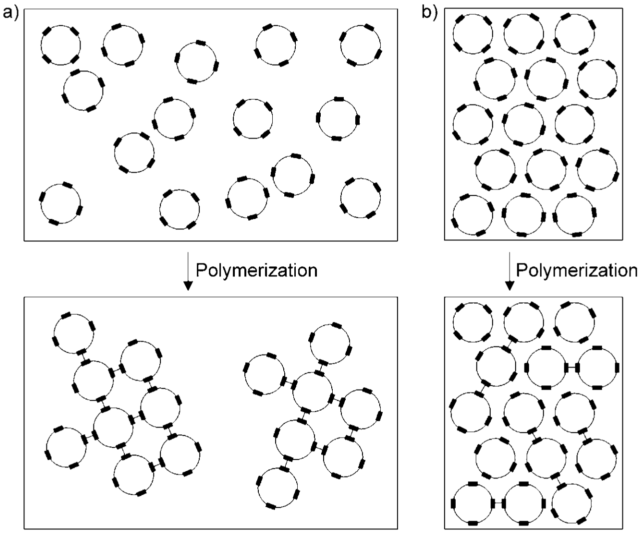


Figure 39. Polymerization of M4 monomers at the air/water interface with fourfold symmetry. In (b) the problems which occur in polymerizations in the condensed state if there is a mismatch between the lattice and monomer symmetry is shown. The lattice decides how many connecting sites a monomer should have in the right symmetry to give a regular 2D polymer. Such problems are not to be expected for polymerizations in the gaslike state (a). Aspects such as shrinking are not considered.

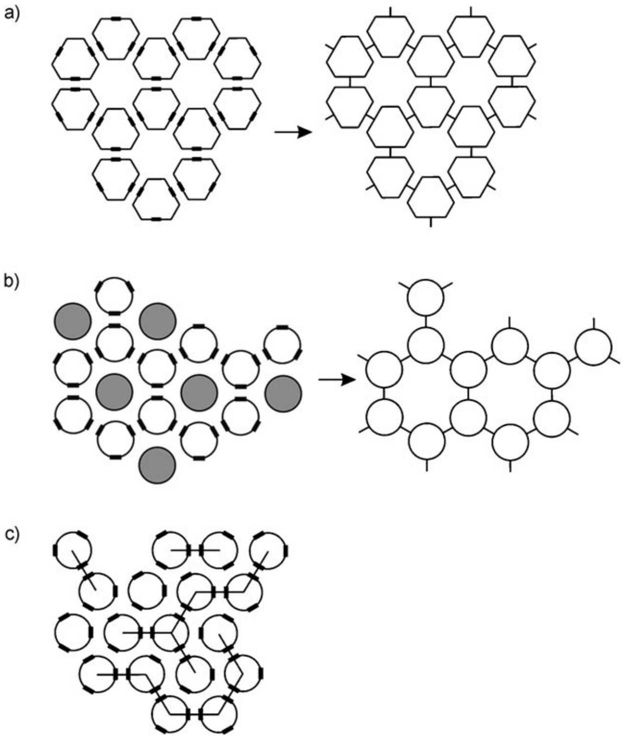


Figure 40. The conversion of monomer M3 into 2D polymers with periodic holes (a,b) and randomly cross-linked monolayers (c). The gray entities in (b) can either be trifunctional monomers with random relative orientation or templates that stabilize the ordered array.

practically only one possibility to circumvent such a problem, which is to find a way to arrange the M4 monomers into a tetragonal packing prior to polymerization.[175] This could perhaps be achieved by using square-shaped or rectangular monomers and/or by equipping them with features for secondary interactions, such as hydrogen bonding, which are most effective in tetragonal lattices.

A periodic network would ideally also be expected for M3 monomers in the gaslike phase. In its hexagonally packed condensed phase, however, the situation is more complicated. The aspect of preferred versus nonpreferred orientation (Figure 40 a,b and Figure 40 c, respectively) leads to different polymers. In the former case, the connecting units always face each other and growth leads to 2D polymers with regularly distributed holes which are either already present in the assembled state (Figure 40 a)[176] or result from unused and more or less freely rotating monomers (Figure 40 b, shaded circles) having been removed from the resulting polymer. The aspect of hole formation appears to be a disadvantage at first glace, but may turn into a real advantage when it comes to characterization (Section 5.4). If the monomers are more or less free to rotate during cross-linking or have random relative orientations to begin with (Figure 40 c), cross-linked polymers will nevertheless be obtained, but the product will not meet the requirements of a 2D polymer outlined in Section 1. Even though the initial monomers will maintain a high and long-range positional order, the bonds connecting them will be random. This argument holds true if no overriding effects come into play, such as slow initiation and fast propagation; in this way, ordered domains could still result in the product. This matter cannot be reasonably treated any further here because the structure of the monomer and its growth mechanism would have to be known.

5.2.2. *Other Aspects*

The main drawback with working at the gas/liquid interface is presumably shrinkage (Figure 41). This phenomenon also applies to gas/solid and liquid/solid interfaces, but presumably less so. Combined with simultaneous growth at many sites in the initially non-cross-linked monolayer, it can lead to the formation of cracks. In the compressed state, the monomers in the very best situation attain a 2D crystalline order, being packed at van der Waals distances. Irrespective of the cross-coupling mechanism, this distance of approximately 3.5 Å will be reduced to that of a covalent bond, which is on the order of 1.5 Å. If one compares a reduction by 2 Å with the cross-sectional diameter of a typical monomer, which is on the order of 5–20 Å, it becomes evident the magnitude of the shrinkage. The formation of cracks may have been a reason why, for example, Regen and co-workers developed the gluing method by which any eventual spaces in the cross-linked monolayers should be filled; the mechanism by which this selective filling of cracks should happen is unclear (Section 4.2). The shrinkage aspect is even more critical if the connection between the monomers requires removal of atoms, such as hydrogen atoms, in oxidative acetylene coupling reactions, for example.

Can one compensate for this shrinkage at least to some degree by means of monomer design? The answer is yes. In

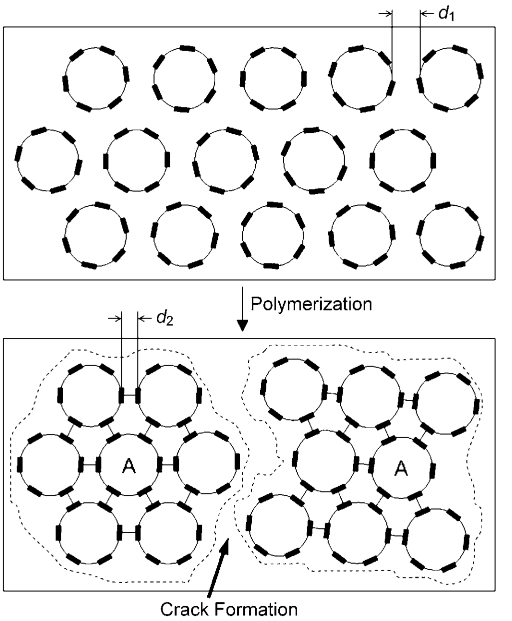


Figure 41. Formation of cracks during the polymerization of a densely packed monolayer at the air/liquid interface caused by the simultaneous growth of nuclei initiated at sites A and the shrinkage during growth. For simplicity the monomers are shown as hexafunctional cycles. d_1 indicates the van der Waals distance (approximately 3.5 Å) and d_2 the length of a C—C bond (approximately 1.5 Å).

topochemical reactions,[177] for example, the space requirement of components in a single crystal is presumed to remain unchanged upon their photochemically induced connection. This aspect was first described by Schmidt for the dimerization of an excited olefin with one in the ground state; this approach relies upon a very specific arrangement of the components and a compensation for the space reduction caused by the bond formation through re-hybridization at the coupling site. This, thus, allows the parts of the components which are not involved in the bond formation to more or less remain where they were before irradiation. The conditions for a perfect topochemical reaction to occur are difficult to realize. It may well be, for example, that the polymerizations of diacetylene derivatives on solid substrates (Figure 29, Section 4.2.5) may have stopped after relatively few growth steps because of a build-up of strain as the polymerization progressed. Tiny mismatches between nonpolymerized and polymerized monolayers may have added up and caused the termination of the growing chains.

Figure 42 shows an example of how to implement compensation for the shrinkage in the monomer design not by using a topochemical reaction in the strict sense but by the well-studied dimerization of anthracene. The van der Waals distance of anthracene is approximately 3.5 Å. Photochemically induced bond formation across the 9,10-positions resulted in a dimer[178] with two bridging single bonds (decrease in the distance between the monomers to ca. 1.5 Å). The side view of the dimer in Figure 42 shows that different shrinkage effects can be programmed into the system, depending on how such a cross-linking unit is incorporated into the monomer.

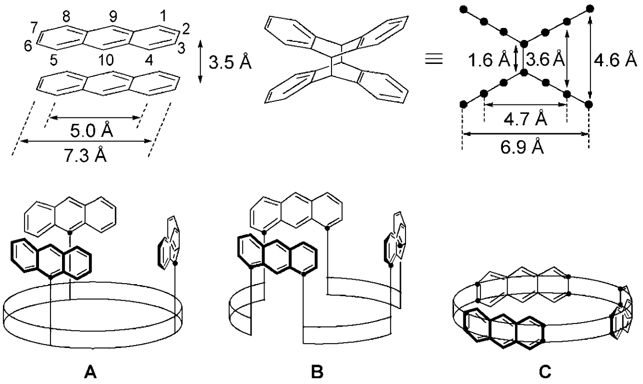


Figure 42. In the anthracene dimer the C atoms 1,4 (and 5,8) are pushed apart by 3.6 Å, which corresponds more or less to the van der Waals distance, while the C atoms 9 (and 10) as well as 2,3 (and 6,7) are pushed apart by 1.6 Å and 4.6 Å, respectively, which is less and more than the van der Waals distance. The hypothetical monomers A and C are expected to be sensitive to such changes in the distance, whereas monomer B may neither show expansion nor contraction. The given values for the distances were estimated by Chem3D Ultra 10.0 (CambridgeSoft).

Three different scenarios can be considered: The anthracene units are built in to the monomer through 1) the 9- or the 9- and 10-positions,[179] 2) the 1- and 8-, or 1,4- and 5,8-positions, and 3) the 2- and 7- or 2,3 and 6,7-positions. These three cases lead to rather different distances between the connected monomers: When the rehybridization associated with the connection is considered, the first mode of connection moves the monomers the closest, the second puts them at 3.6 Å (which more or less resembles the van der Waals distance one started from), and the third puts them at 4.6 Å—which even causes expansion. The monomer design clearly has a substantial impact on the shrinkage and expansion properties. Figure 42 shows trifunctional monomers based on anthracene connecting units which are incorporated into the respective monomers through the 9- (monomer A), 1- and 8- (monomer B), and 2,3- and 6,7-positions (monomer C).[180]

To compensate for possible shrinkage (or expansion) during polymerization, monomers should be designed so that they have "buffers" such as flexible spacers or hinged sections. Such units can help change the space demand of the monomers when subjected to stress. However, the flexible spacers need to be applied with care because of the reasons discussed in Section 5.2.1. In certain cases it may also be helpful to counteract the shrinkage by maintaining a constant pressure on the polymerizing sheet. In a Langmuir set-up this can be achieved by moving the barrier as the polymerization progresses.

There is a final aspect that needs to be addressed in regard to polymerizations at interfaces. It sounds too good to be true that one just has to spread a carefully designed monomer at the air/water interface which is able to compensate for shrinkage, compress it to a certain pressure, polymerize—and the 2D polymer is finished. This polymer has lateral dimensions which are controlled by the size of the compressed monolayer, which can easily be up to 100 cm^2. Unfortunately, this is not true because of entropy. Compressed films tend to consist of a patchwork of domains which in themselves may all have the same order but are placed in different orientations.[20] Thus, the largest achievable 2D polymer has the dimensions of the largest domain. The domain edges will not be commensurate, thereby resulting in free volume and difficult to predict modes of covalent connection between domains.

Some studies have addressed the sizes of domains where the internal order was also proven.[181] Focus here will be put on Langmuir monolayers of *N,N'*-dioctadecyloxacyanine perchlorate (J aggregates), S-layer proteins, and streptavidin 2D crystals. The largest domain size found was for Langmuir monolayers of *N,N'*-dioctadecyloxacyanine perchlorate at the air/water interface. After transfer on to a glass plate, polarization microscopy revealed the layer to consist of a collection of two-dimensional crystals of sizes up to 1 mm and in various orientations.[182] Sleytr and co-workers obtained electron micrographs of recrystallized monolayers of the S-layer protein of *bacillus coagulans* E38-66 prepared at the air/water interface and transferred in to carbon-supported films (Figure 43). These layers consist of numerous randomly oriented crystallites with an average size of 5 to 10 μm.[183,184] The last case to be mentioned is the 2D crystallization of streptavidin at biotinylated lipid interfaces. This approach resulted in largely uniform crystals with sizes of 20–200 μm, as visualized by Brewster-angle microscopy (Figure 44).[185] The long-range molecular order of protein units in the 2D crystals was proven by transmission electron microscopy.

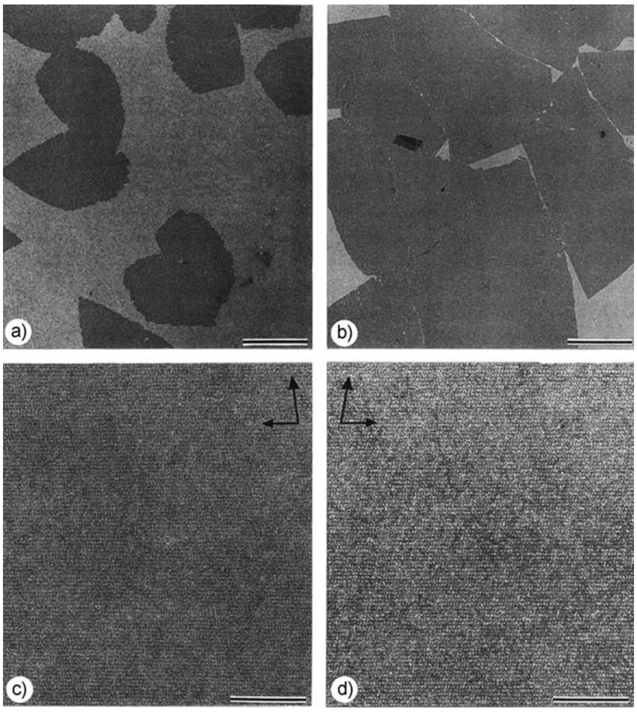


Figure 43. Electron micrographs illustrating the dynamic crystallization process of the S-layer subunits of *bacillus coagulans* E38-66 at the air/water interface (a–c) and on lipid films (d). The scale bars in (a) and (b) are 2 μm and in (c) and (d) 200 nm. Reproduced from Ref. [183a] with permission from the American Society for Microbiology.

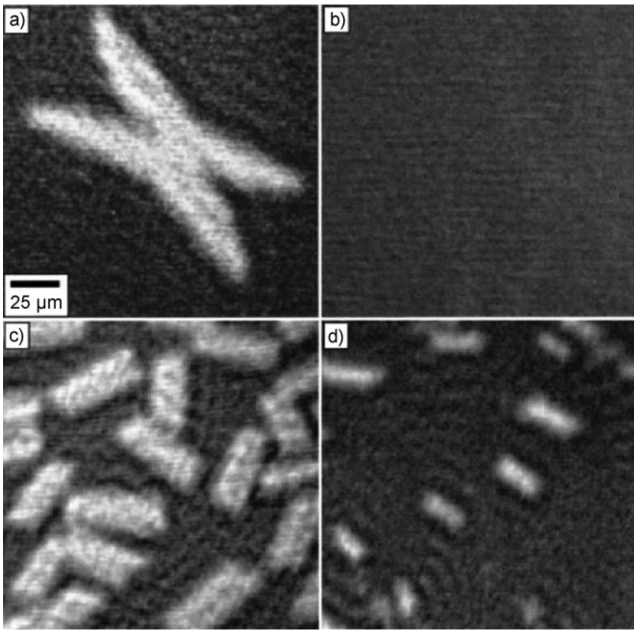


Figure 44. BAM images of wild-type and K132L streptavidin crystals. a) Recombinant wild-type streptavidin forms X-shaped crystals under B-DPPE lipid on 10 mM HEPES, 250 mM NaCl, and 10 mM EDTA at pH 7.8. b) Wild-type streptavidin under B-DPPE in nanopure water. c) K132L forms rectangular crystals under B-DPPE on 10 mM HEPES, 250 mM NaCl, and 10 mM EDTA at pH 7.8. d) K132L forms rectangular crystals on nanopure water. Reproduced from Ref. [185] with permission from the American Chemical Society.

The lesson to be learnt from these three cases is that any interfacial polymerization of a compressed monolayer ideally starts with an analysis of the domain size and the level of internal order. Polymerization only makes sense if large domains of constituents with long-range positional order are observed. To realize the dream of a single-molecule 2D polymer with a size of say 10 × 20 cm^2 it may be necessary to do spreading experiments in a clean-room and with ultrapure monomers. Any surface-active impurities contained in insufficiently purified monomers or dust particles at the surface can cause undesired reorientations of molecules on the surfaces and are therefore limiting factors for domain sizes.

One does not necessarily have to accept, however, the domain sizes obtained even under optimally chosen conditions. The level of order in a compressed layer may be increased by meniscus forces during the transfer onto a solid substrate.[186,187] Mica, for example, is available as single-crystalline material in sizes of up to several cm^2. If a monolayer whose already high order has been further improved during transfer is deposited on such a long-range-ordered substrate, it may be possible to reach 2D polymers in the centimeter range—a wonderful perspective! Such a growth process could be referred to as epitaxial polymerization.

Next, a few comments need to be made on the key issues regarding solid substrates. These are control of the structure of the self-assembled monolayer prior to polymerization by the substrate's crystal lattice as well as the conditions required for lifting cross-linked films off the substrate. The first aspect can be dealt with by a careful choice of substrate. Organic compounds commonly are not adhered strongly on HOPG or MoS_2 and will pack in a dense layer to minimize line tension.[188] On stronger binding substrates (for example, mica, cationized Au, oxidized Si) one may, however, encounter a situation that the substrate controls the structure of the monolayer. If the lattice parameters of the substrate and densely packed monolayer are not commensurate, a less-dense packing of the monomers results, which is detrimental for the formation of a homogeneous 2D polymer without cracks. A couple of techniques are known for the lifting off process which require either harsh chemical or electrochemical treatment with or without simultaneous ultrasound treatment. Alternatively, the substrate can be etched away, which is commonly done with hydrofluoric acid (Section 4.2). All these conditions may work for chemically rather inert films or in cases where damage does not play a role. If structurally perfect 2D polymers, possibly equipped with sensitive functional groups for further modifications, are involved, however, working on solid substrates needs to be carefully considered. If the preparation of 2D sheets on solid substrates requires ultrahigh vacuum (UHV) conditions, an additional disadvantage comes into play. Only a rather limited number of monomers will possibly survive the required preparation conditions. The small fragments shown in Figure 30 (Section 4.2) were obtained because the main framework of monomer **63** survived more than 500 °C while being sublimed onto the substrate; only the C−Br bonds were partially cleaved under these drastic conditions.

Finally, compared to solution approaches, interfacial ones are more limited in regard to the kind of chemical reactions that can be employed for the growth event. This is mainly due to the heterogeneity and the complex nature of the entire reaction system as well as the confined space in which the reactions have to take place. Both aspects have an impact on the rather complex cocktail of factors which finally decide over the outcome of an interfacial reaction. These factors include: molecular motion, transport of reagents/catalysts, concentration, equilibrium, and heat dissipation. Mechanisms may be different and reactions which are otherwise known to be reliable under homogeneous solution conditions can even be rendered impossible at an interface. With such considerations in mind, the structural proposals presented in Figure 42 were made. When two anthracene units of different monomers are forced in to a face-to-face arrangement during compression, they just need to wait until one of them is hit by a photon for an instantaneous dimerization to result, without having to tilt the two monomers relative to each other or any other movement. Transport and supply at the air/water interface will normally be superior to that at the air/solid interface because reagents or catalysts can be supplied through the subphase. Another drawback of interfacial approaches is quantity. A simple calculation shows that if a monomer has a molar mass of 1000 $g\,mol^{-1}$ and a monomer area demand of 4 nm^2, a film of size 10 cm^2 will weigh 4 micrograms. Thus, film preparation would have to be repeated 250000 times to obtain 1 g of the 2D polymer.

5.3. Approaches in Liquid Crystals and Single Crystals

At the beginning of Section 5.1.1 we pointed out that an interface can exhibit an ordering power on monomers. Arranging monomers at liquid/gas, liquid/liquid, solid/gas, or solid/liquid interfaces is of course not the only possibility to pay a large portion of the entropy price associated with the formation of 2D polymers. Important other options to achieve ordered monomer arrays available for 2D polymerization include liquid-crystalline (LC) phases and single crystals. The former can be generated thermotropically or lyotropically either directly by the monomers or by unreactive smectogens (or amphiphiles), serving to template the monomers (see Section 4.2.3). Naturally occurring inorganic crystals with layered structures[103,107–109] and related systems[189] are also available for such a templating purpose (see Section 4.2.1).

Many of the arguments discussed in Sections 5.1 and 5.2 apply also here and are therefore not repeated. There are however potential advantages specifically over the interfacial approach: quantity and facilitated characterization. The first aspect is evident: If ordered arrays form in bulk or from solution, milligram or even gram quantities of 2D polymers could be envisaged. The second aspect becomes specifically apparent in cases where the monomers happen to arrange into lamellar single crystals, ready to undergo topochemical polymerization.[164] This opens the fantastic option to determine the crystal structures before and after polymerization and to compare the two at atomic scale resolution. On the other hand, if individual single sheets are the target, exfoliation techniques would have to be applied to the stacked polymerized products.[5v–ba,28c–m]

5.4. Structure Analysis and Processing

This section is not meant to discuss all the analytical techniques that can be used to obtain information about the surface, such as sheet thickness and homogeneity, orientation of repeating units in a sheet, and periodicity of molecular structure. The arsenal contains ellipsometry, X-ray photoelectron spectroscopy, AFM and STM, high-resolution transmission electron microscopy, grazing incidence infrared spectroscopy, grazing incidence X-ray diffraction, Brewster angle microscopy, and reflectivity. The question is more about what to do if proving the structure on the molecular level turns out to be difficult. Some of the above methods are capable of providing information on the molecular scale. However, sufficient contrast will always be a critical issue and the question is what chemists can do to increase the chance of getting molecular-scale information on the sheets prepared. It is critical to know whether the sheets are just some covalently linked, one monomer unit thick networks with unknown internal structure or proven 2D polymers in the strict sense of the definition in Section 1.

One way to address this issue (although experimentally quite demanding) would be to use homologous series of monomers such as B and C shown in Figure 42. If one had a series with three, four, and six anthracene units available, the resulting sheets would have systematically varied features, which could be assigned with higher confidence than from one set of poorly resolved data from only one kind of sheet. The amplification of patterns is another possibility. Thus, monodisperse metallic nanoparticles could be deposited on a sheet. If the surface ripples of the sheet are sufficiently developed to force the particles into certain patterns, these patterns could be read out by high-resolution TEM or STM and correlated with the underlying periodicity. Of course, the size of these particles should have a reasonable relationship to the lattice spacing of the underlying 2D polymer. In this context, a number of recent attempts should be mentioned, in which self-assembled and highly ordered 2D arrays on solid substrates were "decorated" in a defined manner with other chemical entities (such as C_{60}), which resulted in a lattice on a lattice.[38b,c190] Similarly, dyes with special supramolecular binding capabilities could be added so as to form defined host/guest complexes, and in this way amplify the 2D lattice. Alternatively monomers could be used which by virtue of the symmetry of their connecting units should lead to networks with holes. An illustration can be found in Figure 40. Such sheets would actually have two kinds of holes, the one in the center of each repeat unit and the other in the interstitial sites. These holes would give rise to two different long-range orders in the same sheet, which could possibly be read out by AFM or STM, and their simultaneous presence would reduce considerably the danger of misinterpretation.

Finally, the issue of "further utilization" or "processing" of 2D polymers requires some comments. Given the potential problems of maintaining these large objects in solution, one is faced with the daunting task of manufacturing useful products without destroying them. Whatever their anticipated application, 2D polymers will either be used "as is" (in which case, in situ formation, for example, in the form of monomolecular coatings, would be the route of choice) or these materials may be employed in the form of layers or mixtures or blends with, for example, bulk polymers to possibly provide the latter with enhanced barrier properties; 2D polymers of nonmacroscopic sizes may suffice for this purpose. In this case, exceptional care needs to be taken to avoid undesirable agglomeration by judicious choice of monomer(s), which should yield "self-avoiding" molecular sheets. Finally, the simple rolling up or folding of the 2D polymers as they are created should be mentioned as a route—albeit a far-fetched one—to the macromolecular engineering of novel materials of novel architectures.

6. Conclusion and Outlook

The examples in Sections 4.1 and 4.2 show the current status of research towards 2D polymers. Apart from the few multistranded molecules with high molar weight (Section 4.1.3), which occupy an intermediate position, one either deals with relatively small organic compounds (including self-assembled grids and related structures) or with macroscopically large ultrathin films which are covalently fixed by cross-linking. Whereas the former are structurally well-defined and often fully characterized, the latter have different levels of internal order and are often not precisely characterized. The levels of this internal structural order range from no order at all to a potential positional order of the monomers at least within domains, which has, however, in no case been proven.

It is clear what now has to happen: Either the small molecules have to be forced to grow further or the order in the films has to be increased. In Section 5 an attempt was made to shape these two simple points into a concept including concrete aspects of monomer design. In regard to the first option, the size limitation is best overcome by a polymerization rather than a step by step process. In regard to the second case, the achievement (and proof) of a long-range positional order of monomers was proposed to be mandatory, but insufficient. Furthermore, the entire net which connects the monomers has to be forced into periodicity. This already has to happen during growth and not in some postsynthetic treatment. The concept also has to consider the issue of solubility, the possibility for an in-depth structure analysis, the addition of a component to compensate for shrinkage, and the need for the largest possible ordered domain prior to polymerization.

Is this asking for too much? Or is there a chance to synthesize a monomer of the sort shown in, for example, Figure 42 (Section 5), execute a polymerization-based dimerization of, for example, anthracene, and finally hold an actual 2D polymer in ones hands? Nobody can answer this question at this point in time, but one can say that the M4 monomer **65** (Figure 42, related to type A but with more flexibility)[191] as well as other monomers[192] form reversibly compressible monolayers at the air/water interface, which upon photochemical treatment in the compressed state stay homogeneous in appearance on the micrometer scale (Figure 45). Scratching of the irradiated films with a needle leads to "wounds" which do not heal, and the films can be transferred on to TEM grids with $45\times45\,\mu m^2$ sized holes and imaged by conventional light microscopy with interference contrast. Many of the holes of the grid are spanned without rupture, while macroscopic holes in the film can be seen in some of them (Figure 46). Both findings are clear evidence of a covalent connection throughout the "2D polymer". Without irradiation, the scratches healed instantaneously and holes could not be covered. The thickness of the film was proven to match the height of a monomer, which had been estimated from a structural model. Thus, a mechanically stable, one monomer unit thin, covalently connected film was produced.[10,19,152bc,193]

Is this now a 2D polymer? Possibly not. As long as there is no clear-cut proof of long-range order on the molecular level, one cannot claim more than that about 10^8–10^9 interlinked molecules were placed over a hole and were in a form mechanically stable enough to survive the drying process and remain in the position for at least a couple of weeks. The

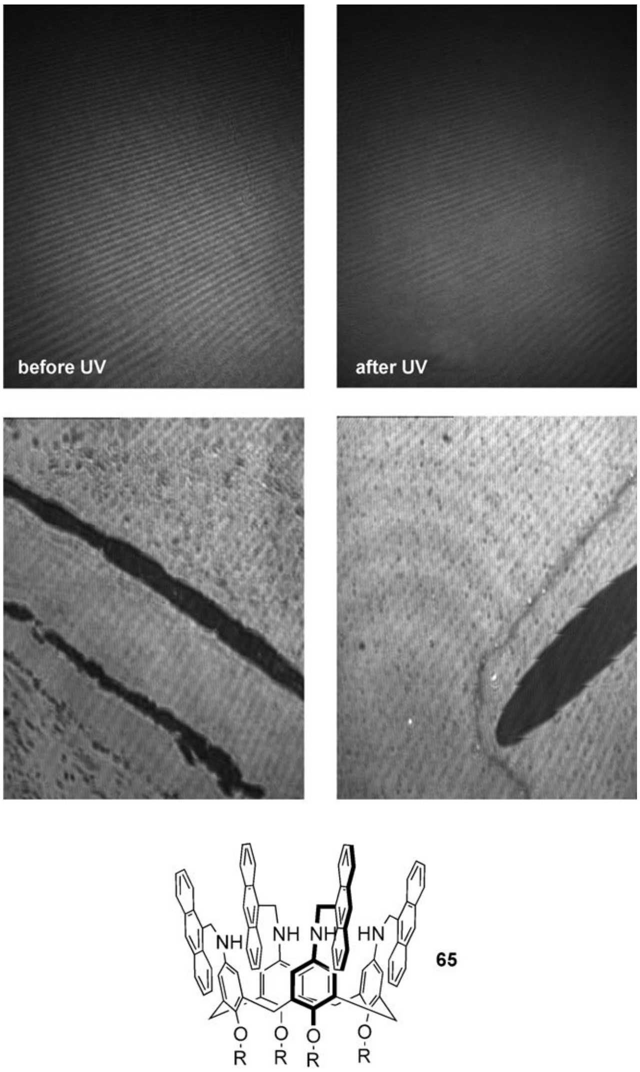


Figure 45. BAM images of a non-irradiated (top left) and UV-irradiated monolayer of monomer **65** [R = $(CH_2CH_2O)_4CH_3$] at the air/water interface (top right). Irradiation does not cause morphological changes or crack formation that is visible by BAM. Bottom left and right: BAM images of UV-irradiated monolayers of **65** after scratching with a needle. The "wounds" stay unchanged even if the film is decompressed. The size of the images is 430×498 μm². Reproduced from Ref. [191].

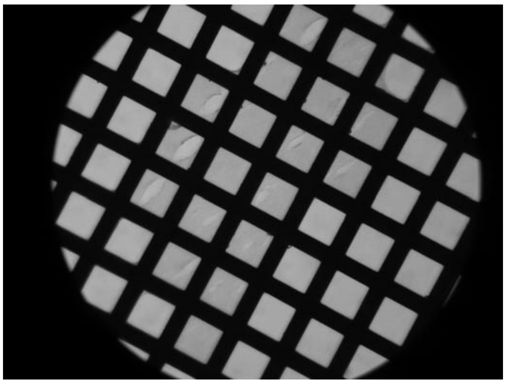


Figure 46. Light microscopy images of UV-treated monolayers of monomer **65** transferred onto a Cu grid with holes of size 45×45 = 2025 μm². Many holes are over-spanned by nonruptured films. Reproduced from Ref. [191].

analysis of this film on the molecular scale is, of course, ongoing, but it is not anticipated that this film could possibly meet the requirements of a 2D polymer; the structure of its monomer is in conflict with the analysis presented in Section 5 in more than one respect. Nevertheless, the fact that these films could be produced so easily in a remarkably short period of time has stimulated an expansive synthesis program. Other monomers, for example, of type B (Figure 42) are currently being synthesized which will meet the above requirements much more closely.[164,192b] Based on the many lessons learned from the examples of Sections 4.1 and 4.2, we believe that the time is now ripe for molecular design and organic synthesis—with the necessary portion of luck—to yield true 2D polymers, the properties and applications of which remain virgin territory.

This work was supported by the Schweizer Nationalfonds (200020-117572 and 200021-111739) and the ETH grant (TH-05 07-1) which is gratefully acknowledged. J.v.H. thanks the Deutsche Forschungsgemeinschaft for a postdoctoral stipend (HE5531/1-1). We cordially thank numerous people who contributed in one or another way to this Review and with whom it was a real pleasure to interact: F. Diederich (ETH Zürich), M. C. Drain (SUNY), H. C. Öttinger (ETH Zürich), J. P. Rabe (HU Berlin), H. Ringsdorf (U Mainz), M. Schmittel (U Siegen), U. B. Sleytr (University of Vienna), P. Smith (ETH Zürich), N. Spencer (ETH Zürich), U. W. Suter (ETH Zürich), T. J. Wigglesworth (ETH Zürich), and V. Vogel (ETH Zürich). Special thanks go to G. Wegner (MPI-P, Mainz).

Received: April 21, 2008

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[1] a) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666–669; b) E. J. Duplock, M. Sheffler, P. J. D. Lindan, *Phys. Rev. Lett.* **2004**, *92*, 225502; c) K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khokevich, S. V. Morozov, A. K. Geim, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 10451–10453; d) Y. Zhang, Y. W. Tan, H. L. Stormer, P. Kim, *Nature* **2005**, *438*, 201–204; e) Y. Zhang, J. P. Small, M. E. S. Amori, P. Kim, *Phys. Rev. Lett.* **2005**, *94*, 176803.

[2] For a short review, see: a) M. I. Katsnelson, *Mater. Today* **2007**, *10*, 20–27; b) A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183–191; c) A. K. Geim, A. H. MacDonald, *Phys. Today* **2007**, *60*, 35–41.

[3] a) J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, S. Roth, *Nature* **2007**, *446*, 60–63; b) J. van den Brink, *Nat. Nanotechnol.* **2007**, *2*, 199–201.

[4] For example: MoS_2, $NbSe_2$, BN, $Bi_2Sr_2CaCu_2O_x$; see also: Ref. [1c].

[5] There is no rational chemical synthesis of graphene yet. The perhaps most convenient way of getting it into ones hands is to mechanically exfoliate it from graphite. This method is not practical for scaling up: a) A. K. Geim, P. Kim, *Sci. Am.* **2008**, *April*, 90–97, and references [1–3]. For approaches to circumvent this problem, see for example: b) O. E. Andersson, B. L. V. Prasad, H. Sato, T. Enoki, Y. Hishiyama, Y. Kaburagi, M. Yoshikawa, S. Bandow, *Phys. Rev. B* **1998**, *58*, 16387–16395; c) Y. Li, S. Xie, W. Zhou, D. Tang, X. P. Zou, Z. Liu, G. Wang, *Carbon* **2001**, *39*, 626–628; d) C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov,

E. H. Conrad, P. N. First, W. A. de Heer, *Science* **2006**, *312*, 1191 – 1196; e) P. R. Somani, S. P. Somani, M. Umeno, *Chem. Phys. Lett.* **2006**, *430*, 56 – 59; f) K. S. Subrahmanyam, S. R. C. Vivekchand, A. Govindaraj, C. N. R. Rao, *J. Mater. Chem.* **2008**, *18*, 1517 – 1523; g) P. W. Sutter, J.-I. Flege, E. A. Sutter, *Nat. Mater.* **2008**, *7*, 406 – 411. A substrate-free synthesis of graphene in the gas phase was also reported recently: h) A. Dato, V. Radmilovic, Z. Lee, J. Phillips, M. Frenklach, *Nano Lett.* **2008**, *8*, 2012 – 2016. Chemical treatment of graphite to graphite oxide has been studied extensively: i) B. C. Brodie, *Ann. Chim. Phys.* **1855**, *45*, 351; j) B. C. Brodie, *Philos. Trans. R. Soc. London* **1859**, *149*, 249 – 259; k) W. Hummers, R. E. Offerman, *J. Am. Chem. Soc.* **1958**, *80*, 1339; l) H. P. Boehm, A. Clauss, G. O. Fischer, U. Z. Hofmann, *Z. Anorg. Allg. Chem.* **1962**, *316*, 119 – 127; m) H. P. Boehm, W. Z. Scholtz, *Z. Anorg. Allg. Chem.* **1965**, *335*, 74 – 79. The oxidation proceeds in the presence of strong oxidizers: n) L. Staudenmaier, *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 1481 – 1487; o) H. P. Boehm, W. Scholz, *Justus Liebigs Ann. Chem.* **1965**, *691*, 1 – 4, and is accompanied by a change of hybridization from sp^2 to sp^3 at the oxidized carbon atoms, and thus increases the interlayer spacing: p) R. J. Beckett, R. C. Croft, *J. Phys. Chem.* **1952**, *56*, 929 – 935; q) H.-P. Boehm, E. Diehl, W. Heck, R. Sappok, *Angew. Chem.* **1964**, *76*, 742 – 751; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 669 – 677; r) C. Hontoria-Lucas, A. J. López-Peinado, J. de D. López-González, M. L. Rojas-Cervantes, R. M. Martin-Aranda, *Carbon* **1995**, *33*, 1585 – 1592; s) H. He, J. Klinowski, M. Forster, A. Lerf, *Chem. Phys. Lett.* **1998**, *287*, 53 – 56; t) A. Lerf, H. He, M. Forster, J. Klinowski, *J. Phys. Chem.* **1998**, *102*, 4477 – 4482; u) T. Szabó, O. Berkesi, P. Forgó, K. Josepovits, Y. Sanakis, D. Petridis, I. Dékany, *Chem. Mater.* **2006**, *18*, 2740 – 2749. Additional thermal v) H. C. Schniepp, J.-L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville, I. A. Aksay, *J. Phys. Chem. B* **2006**, *110*, 8535 – 8539; w) M. J. McAllister, J.-L. Li, D. H. Adamson, H. C. Schniepp, A. A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prud'homme, I. A. Aksay, *Chem. Mater.* **2007**, *19*, 4396 – 4404, ultrasonic x) S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Hamon, R. C. Haddon, *J. Am. Chem. Soc.* **2006**, *128*, 7720 – 7721; y) S. Stankovich, R. D. Piner, X. Chen, N. Wu, S. T. Nguyen, R. S. Ruoff, *J. Mater. Chem.* **2006**, *16*, 155 – 158; z) D. Li, M. B. Müller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. Nanotechnol.* **2008**, *3*, 101 – 105, or chemical aa) S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature* **2006**, *442*, 282 – 286; ab) S. Stankovich, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Carbon* **2006**, *44*, 3342 – 3347 treatment enables exfoliation of the layers as graphene oxide. The obtained single sheets of graphene oxide can then be either reduced back to graphene; ac) S. Gilje, S. Hans, M. Wang, K. L. Kang, R. B. Kaner, *Nano Lett.* **2007**, *7*, 3394 – 3398; ad) C. Gomez-Navarro, R. T. Weitz, A. M. Bittner, M. Scolari, A. Mews, M. Burghard, K. Kern, *Nano Lett.* **2007**, *7*, 3499 – 3503; ae) S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon* **2007**, *45*, 1558 – 1565; af) S. Watcharotone, D. A. Dikin, S. Stankovich, R. Piner, I. Jung, G. H. B. Dommett, G. Evmenenko, S.-E. Wu, S.-F. Chen, C.-P. Liu, S. T. Nguyen, R. S. Ruoff, *Nano Lett.* **2007**, *7*, 1888 – 1892; ag) Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 5856 – 5857; ah) I. Jung, D. A. Dikin, R. D. Piner, R. S. Ruoff, *Nano Lett.* **2008**, *8*, 4283 – 4287 or used or as precursor to design a variety of other graphene derivatives since it possesses functional groups such as epoxide, hydroxyl and carboxyl groups for further chemical modification: ai) S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Haman, R. C. Haddon, *J. Am. Chem. Soc.* **2006**, *128*, 7720 – 7721; aj) Y. Si, E. T. Samulski, *Nano Lett.* **2008**, *8*, 1679 – 1682; ak) J. R. Lomeda, C. D. Doyle, D. V. Kosynkin, W.-F. Hwang, J. M. Tour, *J. Am. Chem. Soc.* **2008**, *130*, 16201 – 16206; al) S. Park, J. An, R. D. Piner, I. Jung, D. Yang, A. Velamakanni, S. T. Nguyen, R. S. Ruoff, *Chem. Mater.* **2008**, *20*, 6592 – 6594. This approach is random and neither leads to a defined degree of functionalization nor a geometrically controlled pattern. Additionally it causes "defects" which cause disruption of the original honeycomb-like sp^2 carbon network of graphene: am) R. Ruoff, *Nat. Nanotechnol.* **2008**, *3*, 10 – 11; J. Zhu, *Nat. Nanotechnol.* **2008**, *3*, 528 – 529; an) V. A. Coleman, R. Knut, O. Karis, H. Grennberg, U. Jansson, R. Quinlan, B. C. Holloway, B. Sanyal, O. Eriksson, *J. Phys. D* **2008**, *41*, 062001; ao) X. Wang, S. M. Tabakman, H. Dai, *J. Am. Chem. Soc.* **2008**, *130*, 8152 – 8153; ap) J. C. Meyer, C. Kisielowski, R. Erni, M. D. Rossell, M. F. Crommie, A. Zettl, *Nano Lett.* **2008**, *8*, 3582 – 3586; aq) D. W. Boukhvalov, M. I. Katsnelson, *Nano Lett.* **2008**, *8*, 4373 – 4379. Studies on exfoilation of graphite via intercalation were also reported: ar) U. Hofmann, W. Rüdorff, *Trans. Faraday Soc.* **1938**, *34*, 1017 – 1021; as) S. F. Makay, *J. Appl. Phys.* **1964**, *35*, 1992 – 1993; at) K. E. Carr, *Carbon* **1970**, *8*, 155 – 166; au) F. Beguin, R. Setton, A. Hamwi, R. Touzain, *Mater. Sci. Eng.* **1979**, *40*, 167 – 173; av) M. Inagaki, K. Muramatsu, Y. Maeda, K. Maekawa, *Synth. Met.* **1983**, *8*, 335 – 342; aw) D. D. L. Chung, *J. Mater. Sci.* **1987**, *22*, 4190 – 4198; ax) D. D. L. Chung, *J. Mater. Sci.* **2002**, *37*, 1475 – 1489; ay) G. Chen, D. Wu, W. Weng, C. Wu, *Carbon* **2003**, *41*, 619 – 621; az) L. M. Viculis, J. J. Mack, O. M. Mayer, H. T. Hahn, R. B. Kaner, *J. Mater. Chem.* **2005**, *15*, 974 – 978; ba) C. Vallés, C. Drummond, H. Saadaoui, C. A. Furtado, M. He, O. Roubeau, L. Ortolani, M. Monthioux, A. Pénicaud, *J. Am. Chem. Soc.* **2008**, *130*, 15802 – 15804.

[6] a) R. S. Atkinson, *Stereoselective Synthesis*, Wiley, New York, **1995**; b) E. M. Carreira, L. Kvaerno, *Classics in Stereoselective Synthesis*, Wiley-VCH, Weinheim, **2008**.

[7] a) *Design of Drugs: Basic Principles and Applications* (Ed.: J. H. Poupaert), Marcel Dekker, New York, **2002**; b) *The Organic Chemistry of Drug Design and Drug Action* (Ed.: R. Silverman), Academic Press, Burlington, **2004**.

[8] a) D. T. Allen, D. R. Shonnard, *Green Engineering: Environmentally Conscious Design of Chemical Processes*, Prentice Hall PTR, **2001**; b) *G. Korevaar Sustainable Chemical Processes and Products: New Design Methodology and Design Tools*, Eburon, Delft, **2004**.

[9] *Macromolecular Engineering: Precise Synthesis Materials Properties, Applications* (Eds.: K. Matyjaszewski, Y. Gnanou, L. Leibler), Wiley-VCH, Weinheim, **2007**.

[10] That this is, in principal, possible was shown for polymerized diacetylene monolayers, the red-orange color of which was visible with the naked eye: D. Day, H. Ringsdorf, *J. Polym. Sci. Polym. Lett. Ed.* **1978**, *16*, 205 – 210.

[11] For the scrolling of graphene sheets during exfoliation attempts, see: a) H. Shioyama, *J. Mater. Sci. Lett.* **2001**, *20*, 499 – 500; b) L. M. Viculis, J. J. Mack, R. B. Kaner, *Science* **2003**, *299*, 1361; c) S. Horiuchi, T. Gotou, M. Fujiwara, T. Asaka, T. Yokosawa, Y. Matsui, *Appl. Phys. Lett.* **2004**, *84*, 2403 – 2405; for related studies with WS_2 sheets, see: d) J.-W. Seo, Y.-W. Jun, S.-W. Park, H. Nah, T. Moon, B. Park, J.-G. Kim, Y. J. Kim, J. Cheon, *Angew. Chem.* **2007**, *119*, 8984 – 8987; *Angew. Chem. Int. Ed.* **2007**, *46*, 8828 – 8831.

[12] G. Decher, *Science* **1997**, *277*, 1232 – 1237.

[13] For biomedical and tissue-engineering applications, see: Z. Tang, Y. Wang, P. Podsiadlo, N. A. Kotov, *Adv. Mater.* **2006**, *18*, 3203 – 3224.

[14] This problem depends, of course, on the method by which compounds are brought on to the surface. Under ultrahigh vacuum conditions, soft-landing mass spectrometric techniques can help reduce the damage caused by impact. For soft-landing,

see: a) V. Franchetti, B. H. Solka, W. E. Baitinger, J. W. Amy, R. G. Crooks, *Int. J. Mass Spectrom. Ion Phys.* **1977**, *23*, 29 – 55; b) H. J. Räder, A. Rouhanipoor, A. M. Talarico, P. Samorì, K. Müllen, *Nat. Mater.* **2006**, *5*, 276 – 280.

[15] a) E. Barrena, C. Ocal, M. Salmeron, *J. Chem. Phys.* **1999**, *111*, 9797 – 9802; b) E. Barrena, E. Palacios-Lidon, C. Munuera, X. Torrelles, S. Ferrer, U. Jonas, M. Salmeron, C. Ocal, *J. Am. Chem. Soc.* **2004**, *126*, 385 – 395; c) S. M. Morgenthaler, S. Lee, N. S. Spencer, *Langmuir* **2006**, *22*, 2706 – 2711.

[16] 2D Coordination networks composed of metal atoms as "connectors" and organic building blocks as "sticks" have been discussed as alternative candidates for such goals. The idea would be to use the "free coordination" site of the metal atoms to attach units, which then point away from the surface into the third dimension. This would constitute a first step towards creating 3D matter from a 2D scaffold. This idea is based on the assumption that the metal connectors can be compared with the metal centers in single-site, for example, octahedral, metal complexes, in which empty coordination sites can in fact be used to dock new ligands to the metal atom at the center. Currently it does not seem that this view is justified.

[17] See for example: T. W. Ebbesen, H. Hiura, *Adv. Mater.* **1995**, *7*, 582 – 586.

[18] For early thoughts on the use of Langmuir–Blodgett (LB) films as filters for molecular separations, see: K. A. Blodgett, *Film Structure and Method of Preparation*, U.S. Patent 2220860, **1940**.

[19] H. Bader, K. Dorn, B. Hupfer, H. Ringsdorf, *Adv. Polym. Sci.* **1985**, *64*, 1 – 62.

[20] See for example: G. Wegner, *Thin Solid Films* **1992**, *216*, 105 – 116.

[21] a) M. D. Conner, S. L. Regen, *Adv. Mater.* **1994**, *6*, 872 – 874; b) D. H. McCullough III, S. L. Regen, *Chem. Commun.* **2004**, 2787 – 2791.

[22] R. Matmour, T. J. Joncheray, Y. Gnanou, R. S. Duran, *Langmuir* **2007**, *23*, 649 – 658.

[23] For a 40 nm thick film used for such purposes, see: W. A. Goedel, R. Heger, *Langmuir* **1998**, *14*, 3470 – 3474. Thinner films that span over the holes can be found in Section 4.2.3 and Section 6 of this Review.

[24] For this technique, see: a) A. Ulman, *An Introduction to Ultrathin films: From Langmuir-Blodgett to Self-Assembly*, Academic Press, New York, **1991**; b) I. Kuzmenko, H. Rapaport, K. Kjaer, J. Als-Nielsen, I. Weissbuch, M. Lahav, L. Leiserowitz, *Chem. Rev.* **2001**, *101*, 1659 – 1696.

[25] A. D. Smigelskas, E. O. Kirkendall, *Trans. AIME* **1947**, *171*, 130 – 142.

[26] Both the block lengths in the *x*-direction and the extension of the 2D polymer in the *y*-direction will be on the macroscopic scale if the Langmuir technique is applied. These block copolymers are therefore not just conventional linear block copolymers whose blocks were almost infinitely expanded in the *y*-direction.

[27] a) L. Carlucci, G. Ciani, D. M. Proserpio, F. Porta, *Angew. Chem.* **2003**, *115*, 331 – 336; *Angew. Chem. Int. Ed.* **2003**, *42*, 317 – 322; b) A. M. Beatty, *Coord. Chem. Rev.* **2003**, *246*, 131 – 143; c) M. J. Hardie, *Struct. Bonding* **2004**, *111*, 139 – 174; d) D. Braga, S. L. Giaffreda, F. Grepioni, L. Maini, M. Polito, *Coord. Chem. Rev.* **2006**, *250*, 1267 – 1285.

[28] a) H. Krebs, *Grundzüge der Anorganischen Kristallchemie*, H. Krebs, Stuttgart, **1968**; b) G. Ferraris, E. Makovicky, S. Merlino, *Crystallography of Modular Materials, International Union of Crystallography Monographs on Crystallography, Number 15*, Oxford University Press, Oxford, **2004**. Note that exfoliation of some inorganic crystals with layered structures has been studied extensively: c) U. Hofmann, *Angew. Chem.* **1968**, *80*, 736 – 747; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 681 – 692; d) R. E. Grim, *Clay Mineralogy*, 2nd. ed., McGraw-Hill, New York, **1968**; e) G. Alberti, M. Casciola, U. Costantino, *J. Colloid Interface Sci.* **1985**, *107*, 256 – 263; f) M. M. J. Treacy, S. B. Rice, A. J. Jacobson, J. T. Lewandowski, *Chem. Mater.* **1990**, *2*, 279 – 286; g) T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada, H. Nakazawa, *J. Am. Chem. Soc.* **1996**, *118*, 8329 – 8335; h) R. Abe, K. Shinohara, A. Tanaka, M. Hara, J. N. Kondo, K. Domen, *Chem. Mater.* **1997**, *9*, 2179 – 2184; i) R. E. Schaak, T. E. Mallouk, *Chem. Mater.* **2000**, *12*, 2513 – 2516; j) R. Ma, Z. Liu, K. Takada, N. Iyi, Y. Bando, T. Sasaki, *J. Am. Chem. Soc.* **2007**, *129*, 5257 – 5263; k) S. Ida, D. Shiga, M. Koinuma, Y. Matsumoto, *J. Am. Chem. Soc.* **2008**, *130*, 14038 – 14039; l) K. Kai, Y. Yoshida, H. Kageyama, G. Saito, T. Ishigaki, Y. Furukawa, J. Kawamata, *J. Am. Chem. Soc.* **2008**, *130*, 15938 – 15943; m) A. Mühlebach, P. Nesvadba, F. Rime, L. Bugnon, *Chimia* **2008**, *62*, 799 – 804.

[29] For impressive works by Yaghi and co-workers in terms of porous, crystalline organic frameworks, see for example: a) A. P. Côte, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, *310*, 1166 – 1170; b) R. W. Tilford, W. R. Gemmill, H.-C. zur Loye, J. J. Lavigne, *Chem. Mater.* **2006**, *18*, 5296 – 5301; c) A. P. Côte, H. M. El-Kaderi, H. Furukawa, J. R. Hunt, O. M. Yaghi, *J. Am. Chem. Soc.* **2007**, *129*, 12914 – 12915. It would be interesting to explore whether the spontaneous assembly of layers into macroscopic 3D objects can be prevented. In this context, see also a recent report attempting to create a single layer of this organic framework on a solid surface: d) N. A. A. Zwaneveld, R. Pawlak, M. Abel, D. Catalin, D. Gigmes, D. Bertin, L. Porte, *J. Am. Chem. Soc.* **2008**, *130*, 6678 – 6679.

[30] a) B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller, W. Schnick, *J. Am. Chem. Soc.* **2003**, *125*, 10288 – 10300; b) F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, *Angew. Chem.* **2006**, *118*, 4579 – 4583; *Angew. Chem. Int. Ed.* **2006**, *45*, 4467 – 4471; c) F. Goettmann, A. Thomas, M. Antonietti, *Angew. Chem.* **2007**, *119*, 2773 – 2776; *Angew. Chem. Int. Ed.* **2007**, *46*, 2717 – 2720.

[31] For a theoretical treatment, see for example: a) A. Y. Liu, M. L. Cohen, *Science* **1989**, *245*, 841 – 842; b) E. Kroke, M. Schwarz, E. Horath-Bordon, P. Kroll, B. Noll, A. D. Norman, *New J. Chem.* **2002**, *26*, 508 – 512; c) D. T. Vodak, K. Kim, L. Iordanidis, P. G. Ramussen, A. J. Matzger, O. M. Yaghi, *Chem. Eur. J.* **2003**, *9*, 4197 – 4203.

[32] a) G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418 – 2421; b) J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness, P. H. Beton, *Nature* **2003**, *424*, 1029 – 1031; c) J. V. Barth, G. Costantini, K. Kern, *Nature* **2005**, *437*, 671 – 679; d) "Two-dimensional Nanotemplates as Surface Cues for the Controlled Assembly of Organic Molecules": F. Cicoira, C. Santato, F. Rosei, *Top. Curr. Chem.* **2009**, DOI: 10.1007/128_2008_2.

[33] See for example: a) M. Sano, D. Y. Sasaki, T. Kunitake, *Science* **1992**, *258*, 441 – 443; b) D. L. Keeling, N. S. Oxtoby, C. Wilson, M. J. Humphry, N. R. Champness, P. H. Beton, *Nano Lett.* **2003**, *3*, 9 – 12; c) M. Stöhr, M. Wahl, C. H. Galka, T. Riehm, T. A. Jung, L. H. Gade, *Angew. Chem.* **2005**, *117*, 7560 – 7564; *Angew. Chem. Int. Ed.* **2005**, *44*, 7394 – 7398; d) R. Davis, R. Berger, R. Zentel, *Adv. Mater.* **2007**, *19*, 3878 – 3881.

[34] R. van Hameren, P. Schön, A. M. van Buul, J. Hoogboom, S. V. Lazarenko, J. W. Gerritsen, H. Engelkamp, P. C. M. Christiansen, H. A. Heus, J. C. Maan, T. Rasing, S. Speller, A. E. Rowan, J. A. A. W. Elemans, R. J. M. Nolte, *Science* **2006**, *314*, 1433 – 1436.

[35] T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, S. Mashiko, *Nature* **2001**, *413*, 619 – 621.

[36] a) J. P. Rabe, S. Buchholz, *Science* **1991**, *253*, 424 – 427; b) V. Stepanenko, F. Würthner, *Small* **2008**, *4*, 2158 – 2161.

[37] a) J. V. Barth, J. Weckesser, N. Lin, A. Dimitriev, K. Kern, *Appl. Phys. A* **2003**, *76*, 645 – 652; b) Y. Wang, M. Lingenfelder, T. Classen, G. Costantini, K. Kern, *J. Am. Chem. Soc.* **2007**, *129*, 15742 – 15743; c) A. Langner, S. L. Tait, N. Lin, R. Chandrasekar, M. Ruben, K. Kern, *Angew. Chem.* **2008**, *120*, 8967 – 8970; *Angew. Chem. Int. Ed.* **2008**, *47*, 8835 – 8838.

[38] See for example: a) K. Tahara, S. Furakawa, H. Uji-I, T. Uchino, T. Ichikawa, J. Zhang, W. Mamdouh, M. Sonoda, F. C. De Schryver, S. de Feyter, Y. Tobe, *J. Am. Chem. Soc.* **2006**, *128*, 16613 – 16625; b) H. Spillmann, A. Kiebele, M. Stohr, T. A. Jung, D. Bonifazi, C. Fuyong, F. Diederich, *Adv. Mater.* **2006**, *18*, 275 – 279; c) S. Furukawa, K. Tahara, F. S. De Schryver, M. Van der Auweraer, Y. Tobe, S. de Feyter, *Angew. Chem.* **2007**, *119*, 2889 – 2892; *Angew. Chem. Int. Ed.* **2007**, *46*, 2831 – 2834.

[39] a) H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem.* **1988**, *100*, 117 – 162; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 113 – 158; b) D. F. O'Brien, B. Armitage, A. Benedicto, D. E. Bennett, H. G. Lamparski, Y.-S. Lee, W. Srisiri, T. M. Sisson, *Acc. Chem. Res.* **1998**, *31*, 861 – 868.

[40] a) J. Tobochnik, I. Webman, J. L. Lebowitz, M. H. Kalos, *Macromolecules* **1982**, *15*, 549 – 553; b) A. Yethiraj, *Macromolecules* **2003**, *36*, 5854 – 5862.

[41] a) V. R. Sastri, R. Schulman, D. C. Roberts, *Macromolecules* **1982**, *15*, 939 – 947; b) T. Vogel, K. Blatter, A. D. Schlüter, *Makromol. Chem. Rapid Commun.* **1989**, *10*, 427 – 430; c) B. L. Schürmann, V. Enkelmann, M. Löffler, A. D. Schlüter, *Angew. Chem.* **1993**, *105*, 107 – 110; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 123 – 125; d) S. W. Thomas, T. M. Long, B. D. Pate, S. R. Kline, E. L. Thomas, T. M. Swager, *J. Am. Chem. Soc.* **2005**, *127*, 17976 – 17977.

[42] a) G. Riou, E. Delain, *Proc. Natl. Acad. Sci. USA* **1969**, *62*, 210 – 217; b) T. A. Shapiro, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 7809 – 7813; c) J. H. Chen, C. A. Rauch, J. H. White, P. T. Englund, N. R. Cozzarelli, *Cell* **1995**, *80*, 61 – 69; d) B. Y. Liu, Y. N. Liu, S. A. Motyka, E. E. C. Agbo, P. T. Englund, *Trends Parasitol.* **2005**, *21*, 363 – 369.

[43] W. R. Wikoff, L. Liljas, R. L. Duda, H. Tsuruta, R. W. Hendrix, J. E. Johnson, *Science* **2000**, *289*, 2129 – 2133.

[44] a) Y. He, Y. Tian, A. E. Ribbe, C. D. Mao, *J. Am. Chem. Soc.* **2006**, *128*, 15978 – 15979; b) C. Zhang, Y. He, Y. Chen, A. E. Ribbe, C. Mao, *J. Am. Chem. Soc.* **2007**, *129*, 14134 – 14135, and references therein.

[45] a) N. C. Seeman, *Nature* **2003**, *421*, 427 – 431; b) B. Samorì, G. Zuccheri, *Angew. Chem.* **2005**, *117*, 1190 – 1206; *Angew. Chem. Int. Ed.* **2005**, *44*, 1166 – 1181; c) U. Feldkamp, C. M. Niemeyer, *Angew. Chem.* **2006**, *118*, 1888 – 1910; *Angew. Chem. Int. Ed.* **2006**, *45*, 1856 – 1876.

[46] a) S. Edmondson, W. T. S. Huck, *Adv. Mater.* **2004**, *16*, 1327 – 1331; b) J. E. Comrie, W. T. S. Huck, *Langmuir* **2007**, *23*, 1569 – 1576.

[47] N. Bowden, A. Terfort, J. Carbeck, G. M. Whitesides *Science* **1997**, *276*, 233 – 235.

[48] One example is the introduction of lateral substituents which could be cross-linked by some well established reactions, for example, ring-closing metathesis.

[49] This differentiation is necessary because, for example, olefins are commonly considered as one functional group, although the two olefinic functional groups of divinylbenzene act as four bond-formation sites in cross-linking events.

[50] For a related hyperbranched polymer, see: Y. H. Kim, O. W. Webster, *J. Am. Chem. Soc.* **1990**, *112*, 4592 – 4593.

[51] The following references are not restricted to 2D networks but may also deal with other allotropes of carbon: a) A. T. Balaban, C. C. Rentia, E. Ciupitu, *Rev. Roum. Chim.* **1968**, *13*, 231 – 247; b) R. Hoffmann, T. Hughbanks, M. Kertész, P. H. Bird, *J. Am. Chem. Soc.* **1983**, *105*, 4831 – 4832; c) R. H. Baughman, H. Eckhardt, M. Kertész, *J. Chem. Phys.* **1987**, *87*, 6687 – 6699; d) K. M. Merz, Jr., R. Hoffmann, A. T. Balaban *J. Am. Chem. Soc.* **1987**, *109*, 6742 – 6748; e) A. T. Balaban, *Comput. Math. Appl.* **1989**, *17*, 397 – 416; f) R. L. Johnston, R. Hoffmann, *J. Am. Chem. Soc.* **1989**, *111*, 810 – 819.

[52] For some property predictions of certain all-carbon networks, see: a) N. Narita, S. Nagai, S. Suzuki, K. Nakao, *Phys. Rev. B* **1998**, *58*, 11009 – 11014; b) N. Narita, S. Nagai, S. Suzuki, K. Nakao, *Phys. Rev. B* **2000**, *62*, 11146 – 11151; c) N. Narita, S. Nagai, S. Suzuki, K. Nakao, *Phys. Rev. B* **2001**, *64*, 245408 – 245414.

[53] For theoretical studies on graphyne substructures, see: K. Tahara, T. Yoshimura, M. Sonoda, Y. Tobe, R. V. Williams, *J. Org. Chem.* **2007**, *72*, 1437 – 1442.

[54] For reviews which, at least in part, contain all-carbon networks, see: a) F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, *104*, 1123 – 1146; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101 – 1123; b) F. Diederich, *Nature* **1994**, *369*, 199 – 207; c) E. L. Spitler, C. A. Johnson II, M. M. Haley, *Chem. Rev.* **2006**, *106*, 5344 – 5386.

[55] J. A. Anthony, C. Bourdon, F. Diederich, J.-P. Gisselbrecht, V. Gramlich, M. Gross, M. Hobi, P. Seiler, *Angew. Chem.* **1994**, *106*, 794 – 798; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 763 – 766.

[56] R. Diercks, J. C. Armstrong, R. Boese, K. P. C. Vollhardt, *Angew. Chem.* **1986**, *98*, 270 – 271; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 268 – 269.

[57] J. D. Tovar, N. Jux, T. Jarrosson, S. I. Khan, Y. Rubin, *J. Org. Chem.* **1997**, *62*, 3432 – 3433.

[58] **3**: J. A. Anthony, C. B. Knobler, F. Diederich, *Angew. Chem.* **1993**, *105*, 437 – 440; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 406 – 409.

[59] **4**: A. M. Boldi, F. Diederich, *Angew. Chem.* **1994**, *106*, 482 – 485; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 468 – 471.

[60] **5** and **6**: J. A. Marsden, M. H. Haley, *J. Org. Chem.* **2005**, *70*, 10213 – 10226.

[61] **7**: a) C. Eickmeier, H. Junga, A. J. Matzger, F. Scherhag, M. Shim, K. P. C. Vollhardt, *Angew. Chem.* **1997**, *109*, 2194 – 2199; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2103 – 2108; b) A. J. Matzger, M. Shim, K. P. C. Vollhardt, *Chem. Commun.* **1999**, 1871 – 1872.

[62] **8** and **9**: a) J. M. Kehoe, J. M. Kiley, J. J. English, C. A. Johnson, R. C. Petersen, M. M. Haley, *Org. Lett.* **2000**, *2*, 969 – 972; b) O. S. Miljanic, K. P. C. Vollhardt, D. G. Whitener, *Synlett* **2003**, 29 – 34; c) M. Iyoda, S. Sirinintasak, Y. Nishiyama, A. Vorasingha, F. Sultana, K. Nakao, Y. Kuwatani, H. Matsuyama, M. Yoshida, Y. Miyake, *Synthesis* **2004**, 1527 – 1531.

[63] **10**: T. Yoshimura, A. Inaba, M. Sonoda, K. Tahar, Y. Tobe, R. V. Williams, *Org. Lett.* **2006**, *8*, 2933 – 2936.

[64] **11**: D. Mössinger, J. Hornung, S. Lei, S. De Feyter, S. Höger, *Angew. Chem.* **2007**, *119*, 6926 – 6930; *Angew. Chem. Int. Ed.* **2007**, *46*, 6802 – 6806.

[65] For an even larger perethynylated dehydroannulene, see: M. Kivala, F. Mitzel, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Asian J.* **2006**, *1*, 479 – 489.

[66] See for example: M. G. H. Vicente, L. Jaquinod, K. M. Smith, *Chem. Commun.* **1999**, 1771 – 1782.

[67] C. D. Simpson, J. D. Brand, A. J. Berresheim, L. Przybilla, H. J. Räder, K. Müllen, *Chem. Eur. J.* **2002**, *8*, 1424 – 1429.

[68] See for example: a) F. Jaeckel, M. D. Watson, K. Müllen, J. P. Rabe, *Phys. Rev. Lett.* **2004**, *92*, 188303; b) T. Boehme, C. D. Simpson, K. Müllen, J. P. Rabe, *Chem. Eur. J.* **2007**, *13*, 7349 – 7357.

[69] H. J. Räder, A. Rouhanipour, A. M. Talarico, V. Palermo, P. Samorì, K. Müllen, *Nat. Mater.* **2006**, *5*, 276 – 279.

[70] J. A. Marsden, M. H. Haley, *J. Org. Chem.* **2005**, *70*, 10213 – 10226.

[71] a) A. M. Garcia, F. J. Romero-Salguero, D. M. Bassani, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 1803 – 1808;

b) M. Barboiu, G. Vaughan, R. Graff, J.-M. Lehn, *J. Am. Chem. Soc.* **2003**, *125*, 10257 – 10265.

[72] a) C. M. Drain, F. Nifiatis, A. Vasenko, J. D. Batteas, *Angew. Chem.* **1998**, *110*, 2478 – 2481; *Angew. Chem. Int. Ed.* **1998**, *37*, 2344 – 2347; b) T. N. Milic, N. Chi, D. G. Yablon, G. W. Flynn, J. D. Batteas, C. M. Drain, *Angew. Chem.* **2002**, *114*, 2221 – 2223; *Angew. Chem. Int. Ed.* **2002**, *41*, 2117 – 2119; for related studies, see: c) M. Schmittel, V. Kalsani, D. Fenske, A. Wiegrefe, *Chem. Commun.* **2004**, 490 – 491; d) C. M. Drain, I. Goldberg, I. Sylvain, A. Falber, *Top. Curr. Chem.* **2005**, *245*, 55 – 88; e) M. Schmittel, V. Kalsani, *Top. Curr. Chem.* **2005**, *245*, 1 – 53; f) K. F. Cheng, N. A. Thai, L. C. Taegue, K. Grohmann, C. M. Drain, *Chem. Commun.* **2005**, 4678 – 4680.

[73] M. Barboiu, G. Vaughan, R. Graff, J.-M. Lehn, *J. Am. Chem. Soc.* **2003**, *125*, 10257 – 10265.

[74] For related cases of dynamic constitutional diversity, see: a) P. N. W. Baxter, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4510 – 4517; b) P. N. W. Baxter, R. G. Khoury, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4140 – 4148; c) A. Marquis, J.-P. Kintzinger, R. Graff, P. N. W. Baxter, J.-M. Lehn, *Angew. Chem.* **2002**, *114*, 2884 – 2888; *Angew. Chem. Int. Ed.* **2002**, *41*, 2760 – 2764; d) S. Hiraoka, T. Yi, M. Shiro, M. Shionoya, *J. Am. Chem. Soc.* **2002**, *124*, 14510 – 14511.

[75] a) M. Schmittel, A. Ganz, *Chem. Commun.* **1997**, 999 – 1000; b) M. Schmittel, U. Lüning, M. Meder, A. Ganz, C. Michel, M. Herderich, *Heterocycl. Commun.* **1997**, *3*, 493 – 498; c) M. Schmittel, A. Ganz, D. Fenske, M. Herderich, *J. Chem. Soc. Dalton Trans.* **2000**, 353 – 359; d) M. Schmittel, V. Kalsani, D. Fenske, A. Wiegrefe, *Chem. Commun.* **2004**, 490 – 491.

[76] For some reviews of metallo-supramolecular chemistry, see: a) M. Fujita, K. Ogura, *Coord. Chem. Rev.* **1996**, *148*, 249 – 264; b) M. Fujita, *Chem. Soc. Rev.* **1998**, *27*, 417 – 425; c) R. V. Slone, K. D. Beckstein, S. Belanger, J. T. Hupp, I. A. Guzei, A. L. Rheingold, *Coord. Chem. Rev.* **1998**, *171*, 221 – 243; d) M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53 – 61; e) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853 – 908; f) M. H. Keefe, K. D. Beckstein, J. T. Hupp, *Coord. Chem. Rev.* **2000**, *205*, 201 – 228; g) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972 – 983; h) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine, J.-M. Lehn, *Angew. Chem.* **2004**, *116*, 3728 – 3747; *Angew. Chem. Int. Ed.* **2004**, *43*, 3644 – 3662; i) F. Wuerthner, C.-C. You, C. R. Saha-Moeller, *Chem. Soc. Rev.* **2004**, *33*, 133 – 146; j) R. Dobrawa, F. Würthner, *J. Polym. Sci. Part A* **2005**, *43*, 4981 – 4995; k) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369 – 378; l) V. Chaurin, E. C. Constable, C. E. Housecroft, *New J. Chem.* **2006**, *30*, 1740 – 1744.

[77] M. C. Drain (SUNY), personal communication.

[78] M. C. Drain (SUNY) and M. Schmittel (University Siegen), personal communication.

[79] As the ligands grow longer and longer, at some stage they will have to be synthesized by polymerization. Such approaches necessarily lead to products with chain-length distributions which would pose another problem here.

[80] E. Clar, *The Aromatic Sextet*, Wiley, London, **1972**.

[81] L. Blanco, H. E. Helson, M. Hirthammer, H. Mestdagh, S. Spyroudis, K. P. C. Vollhardt, *Angew. Chem.* **1987**, *99*, 1276 – 1277; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1246 – 1247.

[82] M. J. Crossley, P. L. Burn, *J. Chem. Soc. Chem. Commun.* **1991**, 1569 – 1571.

[83] B. Schlicke, A. D. Schlüter, P. Hauser, J. Heinze, *Angew. Chem.* **1997**, *109*, 2091 – 2093; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1996 – 1998.

[84] M. E. Gallagher, J. E. Anthony, *Tetrahedron Lett.* **2001**, *42*, 7533 – 7536.

[85] C. S. Hartley, E. L. Elliott, J. S. Moore, *J. Am. Chem. Soc.* **2007**, *129*, 4512 – 4513.

[86] P. N. Anderson, *J. Am. Chem. Soc.* **1999**, *121*, 11538 – 11545.

[87] For similar structures, see: a) T. E. O. Screen, J. R. G. Thorne, R. G. Denning, D. G. Bucknall, H. L. Anderson, *J. Am. Chem. Soc.* **2002**, *124*, 9712 – 9713; b) M. Drobizhev, Y. Stepanenko, A. Rebane, C. J. Wilson, T. E. O. Screen, H. L. Anderson, *J. Am. Chem. Soc.* **2006**, *128*, 12432 – 12433.

[88] C. S. Hartley, J. S. Moore, *J. Am. Chem. Soc.* **2007**, *129*, 11682 – 11683.

[89] For C_{60}-derived double-stranded linear [2+2] cycloaddition oligomers, see: D. Sun, C. A. Reed, *Chem. Commun.* **2000**, 2391 – 2392.

[90] a) A. Tsuda, H. Furuta, A. Osuka, *Angew. Chem.* **2000**, *112*, 2649 – 2652; *Angew. Chem. Int. Ed.* **2000**, *39*, 2549 – 2552; b) A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79 – 82.

[91] J. Wu, L. Gherghei, M. D. Watson, J. Li, Z. Wang, C. D. Simpson, U. Kolb, K. Müllen, *Macromolecules* **2003**, *36*, 7082 – 7089.

[92] For recent related studies, see: a) X. Yang, X. Dou, A. Rouhanipour, L. Zhi, H. J. Räder, K. Müllen, *J. Am. Chem. Soc.* **2008**, *130*, 4216 – 4217; b) H. Qian, F. Negri, C. Wang, Z. Wang, *J. Am. Chem. Soc.*, ASAP.

[93] Only those with planar structure are considered here.

[94] For additional cases, see for example: a) L. Yu, M. Chen, L. R. Dalton, *Chem. Mater.* **1990**, *2*, 649 – 659; b) A. D. Schlüter, *Adv. Mater.* **1991**, *3*, 282 – 291; c) C.-S. Wang, *Trends Polym. Sci.* **1993**, *1*, 199 – 205; d) A. J. Berresheim, M. Müller, K. Müllen, *Chem. Rev.* **1999**, *99*, 1747 – 1785; e) A. C. Grimsdale, K. Müllen, *Macromol. Rapid Commun.* **2007**, *28*, 1676 – 1702.

[95] a) E. Rollings, G.-H. Gweon, S. Y. Zhou, B. S. Mun, J. L. McChesney, B. S. Hussain, A. V. Fedorov, P. N. First, W. A. de Heer, A. Lanzara, *J. Phys. Chem. Solids* **2006**, *67*, 2172 – 2177; b) M. Y. Han, B. Ozyilmaz, Y. B. Zhang, P. Kim, *Phys. Rev. Lett.* **2007**, *98*, 206805; c) A. P. Yu, P. Ramesh, M. E. Itkis, E. Bekyarova, R. C. Haddon, *J. Phys. Chem. C* **2007**, *111*, 7565 – 7569; d) X. Li, X. Wang, L. Zhang, S. Lee, H. Dai, *Science* **2008**, *319*, 1229 – 1232.

[96] a) Y. Kubo, Y. Kitada, R. Wakabayashi, T. Kishida, M. Ayabe, K. Kaneko, M. Takeuchi, S. Shinkai, *Angew. Chem.* **2006**, *118*, 1578 – 1583; *Angew. Chem. Int. Ed.* **2006**, *45*, 1548 – 1553; b) R. Wakabayashi, Y. Kubo, K. Kaneko, M. Takeuchi, S. Shinkai, *J. Am. Chem. Soc.* **2006**, *128*, 8744 – 8745.

[97] a) G. Gee, E. K. Rideal, *Proc. R. Soc. London Ser. A* **1935**, *153*, 116 – 128; b) G. Gee, *Proc. R. Soc. London Ser. A* **1935**, *153*, 129 – 141; c) G. Gee, *Trans. Faraday Soc.* **1936**, *32*, 187 – 195; d) G. Gee, *J. Chem. Soc.* **1937**, 772 – 778.

[98] A kinetic study on a hydrogen peroxide catalyzed polymerization of butadiene at an air/water interface was also reported, although the formation of a 2D network was not discussed: G. Gee, C. B. Davies, *Trans. Faraday Soc.* **1939**, *35*, 1298 – 1311.

[99] S. Bresler, M. Judin, D. Talmud, *Acta Phys.-Chim. URSS* **1941**, *XIV*, 71 – 84.

[100] Given the sensitivity of some aminals, there is a doubt as to whether covalent cross-linking actually took place in the suggested way.

[101] a) A. Baniel, M. Frankel, I. Friedrich, A. Katchalsky, *J. Org. Chem.* **1948**, *13*, 791 – 795; b) G. Scheibe, H. Schuller, *Z. Elektrochem.* **1955**, *59*, 861 – 862.

[102] For a review, see: A. Blumstein, *Adv. Macromol. Chem.* **1970**, *2*, 123 – 146.

[103] A. Blumstein, J. Herz, V. Sinn, C. Sadron, *C. R. Hebd. Seances Acad. Sci.* **1958**, *246*, 1856 – 1858.

[104] 1 g of clay has a surface area of about 780 m^2. An area of at least 3.5 m^2 is estimated for 1 mg of PMMA adsorbed in a monomolecular layer. Thus, 1 g clay should result in 220 mg of PMMA; see Ref. [107c].

[105] For historic reasons it may be of interest that there is a second note in the literature in which predictions are made that

"flexible polymeric sheet molecules" would differ from their linear homologues in various properties such as light scattering, virial coefficients, aggregation, vapor pressure, viscosity, molecular weight distribution, distribution of molecular configurations, phase equilibria, polyelectrolyte behavior, crystallization, sedimentation velocity, and birefringence of flow: T. L. Hill, *J. Polym. Sci.* **1961**, *54*, 58–59. This note however is only one paragraph long, and has neither any experimental section nor any concrete suggestions.

[106] G. Odian, *Principles of Polymerization*, Wiley, New York, **1991**, p. 245.

[107] a) A. Blumstein, *Bull. Soc. Chim. Fr.* **1961**, 899–905; b) A. Blumstein, *Bull. Soc. Chim. Fr.* **1961**, 906–914; c) A. Blumstein, *J. Polym. Sci. Part A* **1965**, *3*, 2653–2664; d) A. Blumstein, *J. Polym. Sci. Part A* **1965**, *3*, 2665–2672; e) A. Blumstein, H. E. Ries, Jr., *J. Polym. Sci. Part B* **1965**, *3*, 927–931; f) A. Blumstein, F. W. Billmeyer Jr. , *J. Polym. Sci. Part A-2* **1966**, *4*, 465–474; g) A. Blumstein, R. Blumstein, *J. Polym. Sci. Part B* **1967**, *5*, 691–696.

[108] Related work on acrylonitrile monolayers in clays is also available: O. L. Glavati, L. S. Polak, *Neftekhimiya* **1964**, *4*, 77–81.

[109] A. Blumstein, R. Blumstein, T. H. Vanderspurt *J. Colloid Interface Sci.* **1969**, *31*, 236–247.

[110] N. Beredjick, W. J. Burlant, *J. Polym. Sci. Part A-1* **1970**, *8*, 2807–2818.

[111] a) A. Dubault, M. Veyssié, L. Liebert, L. Strzelecki, *Nat. Phys. Sci.* **1973**, *245*, 94–95; b) A. Dubault, C. Casagrande, M. Veyssié, *J. Phys. Chem.* **1975**, *79*, 2254–2259.

[112] C. Rosilio, A. Ruaudel-Teixier, *J. Polym. Sci. Polym. Chem. Ed.* **1975**, *13*, 2459–2471.

[113] W. N. Emmerling, B. Pfannemüller, *Colloid Polym. Sci.* **1983**, *261*, 677–687.

[114] L. J. Kloepner, R. S. Duran, *J. Am. Chem. Soc.* **1999**, *121*, 8108–8109.

[115] a) M. Bredimas, M. Veyssié, L. Strzelecki, L. Liebert, *Colloid Polym. Sci.* **1977**, *255*, 975–979; b) M. Bredimas, C. Sauterey, C. Taupin, M. Veyssié, *J. Colloid Interface Sci.* **1978**, *65*, 307–314; c) M. Bredimas, C. Sauterey, C. Taupin, M. Veyssié, *Colloid Polym. Sci.* **1978**, *256*, 459–464; d) M. Bredimas, M. Veyssié, *J. Non-Newtonian Fluid Mech.* **1983**, *12*, 165–174; e) K. Miyano, M. Veyssié, *Phys. Rev. Lett.* **1984**, *52*, 1318–1320; f) H. Rehage, E. Schnabel, M. Veyssié, *Makromol. Chem.* **1988**, *189*, 2395–2408.

[116] For a review, see: H. Rehage, M. Veyssié, *Angew. Chem.* **1990**, *102*, 497–506; *Angew Chem. Int. Ed. Engl.* **1990**, *29*, 439–448.

[117] a) M. A. Markowitz, R. Bielski, S. L. Regen, *J. Am. Chem. Soc.* **1988**, *110*, 7545–7546; b) M. A. Markowitz, V. Janout, D. G. Castner, S. L. Regen, *J. Am. Chem. Soc.* **1989**, *111*, 8192–8200; c) M. Conner, V. Janout, S. L. Regen, *J. Am. Chem. Soc.* **1993**, *115*, 1178–1180; d) L. Zhang, R. A. Hendel, P. G. Cozzi, S. L. Regen, *J. Am. Chem. Soc.* **1999**, *121*, 1621–1622; e) X. Yan, J. T. Hsu, S. L. Regen, *J. Am. Chem. Soc.* **2000**, *122*, 11944–11947; f) X. Yan, V. Janout, J. T. Hsu, S. L. Regen, *J. Am. Chem. Soc.* **2002**, *124*, 10962–10963; for a review, see Ref. [21a].

[118] a) X. Yan, V. Janout, J. T. Hsu, S. L. Regen, *J. Am. Chem. Soc.* **2003**, *125*, 8094–8095; b) J. Li, V. Janout, S. L. Regen, *Langmuir* **2004**, *20*, 2048–2049; c) J. W. Li, V. Janout, D. H. Mccullough, J. T. Hsu, Q. Truong, E. Wilusz, S. L. Regen, *Langmuir* **2004**, *20*, 8214–8219; d) J. W. Li, V. Janout, S. L. Regen, *Langmuir* **2005**, *21*, 1676–1678; e) J. W. Li, V. Janout, S. L. Regen, *J. Am. Chem. Soc.* **2006**, *128*, 682–683; f) J. W. Li, V. Janout, S. L. Regen, *Langmuir* **2006**, *22*, 11224–11229; g) J. W. Li, V. Janout, S. L. Regen, *Chem. Mater.* **2006**, *18*, 5065–5069; for a review, see Ref. [21b]; h) Y. Wang, E. Stedronsky, S. L. Regen, *J. Am. Chem. Soc.* **2008**, *130*, 16510–16511.

[119] G. Sui, M. Micic, Q. Huo, R. M. Leblanc, *Colloids Surf. A* **2000**, *171*, 185–197.

[120] J. Michl, T. F. Magnera, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4788–4792.

[121] a) T. F. Magnera, L. M. Peslherbe, E. Körblová, J. Michl, *J. Organomet. Chem.* **1997**, *548*, 83–89; b) T. F. Magnera, J. Pecka, J. Vacek, J. Michl in *Nanostructured Materials: Clusters, Composites, and Thin Films*, *ACS Symposium Series 697* (Eds.: M. Moskovits, V. Shalaev), American Chemical Society, Washington, **1997**, pp. 213–220.

[122] L. Pospisil, N. Varaksa, T. F. Magnera, T. Brotin, J. Michl, *Langmuir* **2007**, *23*, 930–935.

[123] B. Ma, A. M. Milton, Y.-P. Sun, *Chem. Phys. Lett.* **1998**, *288*, 854–860.

[124] a) M. Kunitake et al., "*Two-dimensional polymer thin film of fullerenes and method for manufacturing the same*", Kokai Tokkyo Koho, Japanese patent 321214, **2003**; see also: b) S. Uemura, M. Sakata, I. Taniguchi, M. Kunitake, C. Hirayama, *Langmuir* **2001**, *17*, 5–7.

[125] a) A. M. Rao, P. Zhou, K.-A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncon, I. J. Amster, *Science* **1993**, *259*, 955–957; b) Y. Iwasa, R. M. Arima, T. Fleming, T. Siegrist, O. Zhou, R. C. Haddon, L. J. Rothberg, K. B. Lyons, H. L. Carter, Jr., A. F. Hebard, R. Tycko, G. Dabbagh, J. L. Krajewski, G. A. Thomas, T. Yagi, *Science* **1994**, *264*, 1570–1572.

[126] A. Barraud, C. Rosilio, A. Ruaudel-Teixier, *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1978**, 179–182.

[127] A. Laschewsky, H. Ringsdorf, *Macromolecules* **1988**, *21*, 1936–1941.

[128] G. Wegner, *Makromol. Chem.* **1972**, *154*, 34–48.

[129] For monolayers at air/water interfaces, see: a) D. Naegele, H. Ringsdorf, B. Tieke, G. Wegner, D. Day, J. B. Lando, *Chem. Ztg.* **1976**, *100*, 426–427; b) D. Day, H. H. Hub, H. Ringsdorf, W. Siol, *Ber. Bunsen-Ges.* **1978**, *82*, 878; c) D. Day, H. H. Hub, H. Ringsdorf, *Isr. J. Chem.* **1979**, *18*, 325–329.

[130] For bilayers, see: a) H. H. Hub, B. Hupfer, H. Koch, H. Ringsdorf, *Angew. Chem.* **1980**, *92*, 962–964; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 938–940; b) D. S. Johnston, S. Sanghera, M. Pons, D. Chapman, *Biochim. Biophys. Acta Biomembr.* **1980**, *602*, 57–69.

[131] For LB multilayers, see: a) B. Tieke, G. Wegner, D. Naegele, H. Ringsdorf, *Angew. Chem.* **1976**, *88*, 805–806; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 764–765; b) B. Tieke, H.-J. Graf, G. Wegner, B. Naegele, H. Ringsdorf, A. Banerjie, D. Day, J. B. Lando, *Colloid Polym. Sci.* **1977**, *255*, 521–531; c) B. Tieke, G. Wegner, *Makromol. Chem.* **1978**, *179*, 1639–1642; d) B. Tieke, G. Lieser, G. Wegner, *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 1631–1644; e) B. Tieke, D. Bloor, *Makromol. Chem.* **1979**, *180*, 2275–2278; f) J. P. Fouassier, B. Tieke, G. Wegner, G. *Israel J. Chem.* **1979**, *18*, 227–232; g) G. Lieser, B. Tieke, G. Wegner, *Thin Solid Films* **1980**, *68*, 77–90; h) B. Tieke, V. Enkelmann, H. Kapp, G. Lieser, G. Wegner, *J. Macromol. Sci. Chem. A* **1981**, *15*, 1045–1058.

[132] For a review, see: B. Tieke, *Adv. Polym. Sci.* **1985**, *71*, 79–151.

[133] For some other such attempts, see: a) B. Armitage, D. E. Bennett, H. G. Lamparski, D. F. O'Brien, *Adv. Polym. Sci.* **1996**, *126*, 53–84; b) K. Morigaki, T. Baumgart, A. Offenhäuser, W. Knoll, *Angew. Chem.* **2001**, *113*, 184–186; *Angew. Chem. Int. Ed.* **2001**, *40*, 172–174.

[134] T. Kunitake, Y. Okahata, *J. Am. Chem. Soc.* **1977**, *99*, 3860–3861.

[135] For a review, see: T. Kunitake, *Angew. Chem.* **1992**, *104*, 692–710; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 709–726.

[136] a) S. Asakusa, T. Kunitake, *Chem. Lett.* **1989**, 2059–2062; b) S. Asakusa, H. Okada, T. Kunitake, *J. Am. Chem. Soc.* **1991**, *113*, 1749–1755; for a recent example, see: c) L. T. Banner, D. C.

Danila, K. Sharpe, M. Durkin, B. Clayton, B. Anderson, A. Richter, E. Pinkhassik, *Langmuir* **2008**, *24*, 11464 – 11473.

[137] a) K. Yao, Y. Imai, L. Y. Shi, E. Abe, Y, Adachi, K. Nishikubo, H. Taeyama, *Chem. Lett.* **2004**, *33*, 1112 – 1113; b) F. T. Yu, K. Yao, L. Y. Shi, H. Z. Wang, Y. Fu, X. Q. You, *Chem. Mater.* **2007**, *19*, 335 – 337; c) K. Yao, X. You, L. Shi, W. Wan, F. Yu, J. Chen, *Langmuir* **2008**, *24*, 302 – 309.

[138] The numerous amphiphiles which contain only one polymerizable unit are not discussed here because they only result in linear polymerization.

[139] A. Kusumi, M. Singh, D. A. Tirrell, G. Oehme, A. Singh, N. K. P. Samuel, J. S. Hyde, S. L. Regen, *J. Am. Chem. Soc.* **1983**, *105*, 2975 – 2980.

[140] J. Stefely, M. A. Markowitz, S. L. Regen, *J. Am. Chem. Soc.* **1988**, *110*, 7463 – 7469.

[141] H. Hub, B. Hupfer, H. Koch, H. Ringsdorf, *J. Macromol Sci. Part A* **1981**, *15*, 701 – 715.

[142] A. Akimoto, K. Dorn, L. Gros, H. Ringsdorf, H. Schupp, *Angew. Chem.* **1981**, *93*, 108 – 109; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 90 – 91.

[143] H. Ringsdorf, B. Schlarb, P. N. Tyminski, D. F. O'Brien, *Macromolecules* **1988**, *21*, 671 – 677.

[144] S. Liu, T. M. Sisson, D. F. O'Brien, *Macromolecules* **2001**, *34*, 465 – 473.

[145] L. Gros, H. Ringsdorf, H. Schupp, *Angew. Chem.* **1981**, *93*, 311 – 332; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 305 – 325.

[146] a) S. L. Regen, *Polym. News* **1984**, *10*, 68 – 73; b) S. L. Regen, *NATO ASI Ser. Ser. C* **1987**, *215*, 317 – 324.

[147] a) J. H. Fendler, *Science* **1984**, *223*, 888 – 894; b) J. H. Fendler, P. Tundo, *Acc. Chem. Res.* **1984**, *17*, 3 – 8.

[148] J. A. Hayward, D. Chapman, *Biomaterials* **1984**, *5*, 135 – 142.

[149] M. Shimomura, *Prog. Polym. Sci.* **1993**, *18*, 295 – 339.

[150] A. Mueller, D. F. O'Brien, *Chem. Rev.* **2002**, *102*, 727 – 757.

[151] a) S. I. Stupp, S. Son, H. C. Lin, L. S. Li, *Science* **1993**, *259*, 59 – 63; b) S. I. Stupp, S. Son, L. S. Li, H. C. Lin, M. Keser, *J. Am. Chem. Soc.* **1995**, *117*, 5212 – 5227.

[152] a) F. Porteu, S. Palacin, A. Ruaudel-Teixier, A. Barraud, *Makromol. Chem. Macromol. Symp.* **1991**, *46*, 37 – 45; b) D. Lefevre, F. Porteu, P. Balog, M. Roulliay, G. Zalczer, S. Palacin, *Langmuir* **1993**, *9*, 150 – 161; c) S. Palacin, F. Porteu, A. Ruaudel-Teixier, *Thin Films* **1995**, *20*, 69 – 82.

[153] a) D.-J. Qian, C. Nakamura, J. Miyake, *Langmuir* **2000**, *16*, 9615 – 9619; b) D.-J. Qian, C. Nakamura, J. Miyake, *Chem. Commun.* **2001**, 2312 – 2313; c) H.-G. Liu, X.-S. Feng, L.-J. Zhang, J. Jiang, Y.-I. Lee, K.-W. Jang, D.-J. Qian, K.-Z. Yang, *Mater. Lett.* **2003**, *57*, 2156 – 2161; d) D. J. Qian, H.-T. Chen, B. Lin, X.-M. Xiang, T. Wakayama, C. Nakamura, J. Miyake, *Colloids Surf. A* **2006**, *284*, 285, 180 – 186.

[154] a) A. Küller, W. Eck, V. Stadler, W. Geyer, A. Gölzhäuser, *Appl. Phys. Lett.* **2003**, *82*, 3776 – 3778; b) W. Eck, A. Küller, M. Grunze, B. Völkel, A. Gölzhäuser, *Adv. Mater.* **2005**, *17*, 2583 – 2587.

[155] a) S. W. Hla, L. Bartels, G. Meyer, K.-H. Rieder, *Phys. Rev. Lett.* **2000**, *85*, 2777 – 2780; b) S. W. Hla, G. Meyer, K.-H. Rieder, *Chem. Phys. Lett.* **2003**, *370*, 431 – 436.

[156] a) Y. Okawa, M. Aono, *Nature* **2001**, *409*, 683 – 684; b) M. A. Kasaya, K. Shimizu, Y. Watanabe, A. Saito, M. Aono, Y. Kuwahara, *Phys. Rev. Lett.* **2003**, *91*, 255501/1 – 4.

[157] a) H. Ozaki, T. Funaki, Y. Mazaki, S. Masuda, Y. Harada, *J. Am. Chem. Soc.* **1995**, *117*, 5596 – 5597; b) S. P. Sullivan, A. Schniederer, S. K. Mougua, T. P. Beebe, *Langmuir* **2005**, *21*, 1322 – 1327.

[158] a) A. D. Schlüter, J. P. Rabe, *Angew. Chem.* **2000**, *112*, 860 – 880; *Angew. Chem. Int. Ed.* **2000**, *39*, 864 – 883; b) A. Zhang, L. Shu, Z. Bo, A. D. Schlüter, *Macromol. Chem. Phys.* **2003**, *204*, 328 – 339; c) H. Frauenrath, *Prog. Polym. Sci.* **2005**, *30*, 325 – 384; d) A. D. Schlüter, *Top. Curr. Chem.* **2005**, *245*, 151 – 191.

[159] a) J. Barner, F. Mallwitz, L. Shu, A. D. Schlüter, J. P. Rabe, *Angew. Chem.* **2003**, *115*, 1976 – 1979; *Angew. Chem. Int. Ed.* **2003**, *42*, 1932 – 1935; b) R. Al-Hellani, J. Barner, J. P. Rabe, A. D. Schlüter, *Chem. Eur. J.* **2006**, *12*, 6440 – 6446.

[160] T. Takami, H. Ozaki, M. Kasuga, T. Tsuchiya, A. Ogawa, Y. Mazaki, D. Fukushi, M. Uda, M. Aono, *Angew. Chem.* **1997**, *109*, 2909 – 2912; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2755 – 2757.

[161] A. Miura, S. De Feyter, M. M. S. Abdel-Mottaleb, A. Gesquiere, P. C. M. Grim, G. Moessner, M. Sieffert, M. Klapper, K. Müllen, F. C. De Schryver, *Langmuir* **2003**, *19*, 6474 – 6482.

[162] L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters, S. Hecht, *Nat. Nanotechnol.* **2007**, *2*, 687 – 691.

[163] M. I. Veld, P. Iavicoli, S. Haq, D. B. Amabilino, R. Raval, *Chem. Commun.* **2008**, 1536 – 1538.

[164] J. Sakamoto, A. D. Schlüter, unpublished results.

[165] D. Voet, J. G. Voet, *Biochemistry*, 2nd ed., Wiley, Chichester, **2003**.

[166] For example, see: T. Drobek, N. D. Spencer, M. Heuberger, *Macromolecules* **2005**, *38*, 5254 – 5259.

[167] a) *Polymer Brushes: Syntheses, Characterization, Applications* (Eds.: R. C. Advincula, W. J. Brittain, K. Caster, J. Rühe), Wiley-VCH, Weinheim, **2004**; b) S. Edmondson, V. L. Osborne, W. T. S. Huck, *Chem. Soc. Rev.* **2004**, *33*, 14 – 22.

[168] Highly polar interactions should also be considered here. Aromatic polyamides can readily be dissolved at room temperature in concentrated sulfuric acid, for example.

[169] a) Y. Kantor, M. Kardar, D. R. Nelson, *Phys. Rev. Lett.* **1986**, *57*, 791 – 794; b) D. R. Nelson, L. Peliti, *J. Phys.* **1987**, *48*, 1085 – 1092; c) Y. Kantor, D. R. Nelson, *Phys. Rev. Lett.* **1987**, *58*, 2774 – 2777; d) L. Radzihovsky, P. Le Doussal, *Phys. Rev. Lett.* **1992**, *69*, 1209 – 1212; e) D. R. Nelson, T. Piran, S. Weinberg, *Statistical Mechanics of Membranes and Surfaces*, World Scientific, Singapore, **2004**.

[170] For the mechanical properties of fluid membranes, see: a) W. Helfrich, *Z. Naturforsch. C* **1973**, *28*, 693 – 703; b) W. Helfrich, *Z. Naturforsch. A* **1978**, *33*, 305 – 315; c) W. Helfrich, *J. Phys.* **1985**, *46*, 1263 – 1268.

[171] This principle is known from linear polymerization. Poly(tetrafluoroethylene)and polyethylene are obtained in very fast processes and "virgin" forms have a crystallinity of virtually 100%.

[172] Lifting a film off a fluid medium with which it is in intimate contact (for example, through hydrophilic chains) is a rather complex process and it is not clear whether the mechanical stability of a one monomer unit thick covalent film is sufficient in all cases for micrometer- or even milimeter-sized pieces. Factors include bending and meniscus forces as well as drying effects.

[173] The oil/water and hydrocarbon/perfluorocarbon interfaces can, of course, also be considered.

[174] S. Weigelt, C. Busse, C. Bombis, M. M. Knudsen, K. V. Gothelf, E. Lægsgaard, F. Besenbacher, T. R. Linderoth, *Angew. Chem.* **2008**, *120*, 4478 – 4482; *Angew. Chem. Int. Ed.* **2008**, *47*, 4406 – 4410.

[175] a) K. E. Plass, A. L. Grzesiak, A. J. Matzger, *Acc. Chem. Res.* **2007**, *40*, 287 – 293; b) A. R. Tao, J. Huang, P. Yang, *Acc. Chem. Res.* **2008**, *41*, 1662 – 1673.

[176] Obtaining such a low density structure upon compression at the air/water interface does not look realistic. Its formation can be made more realistic either by using monomers which fill the non-used space or a second inert component is added in the correct stoichiometry to fill the space.

[177] G. M. J. Schmidt in *Reactivity of the Photoexited Molecule* (Ed.: D. Ginsburg), Wiley Interscience, New York, **1967**, pp. 227 – 288.

[178] a) H. Bouas-Laurent, J.-P. Desvergne, A. Castellan, R. Lapouyade, *Chem. Soc. Rev.* **2000**, *29*, 43 – 56; b) H. Bouas-Laurent, J.-P. Desvergne, A. Castellan, R. Lapouyade, *Chem. Soc. Rev.* **2001**, *30*, 248 – 263.

[179] The latter situation is unlikely to work because the dimer of 9,10-disubstituted anthracene does not normally form.

[180] The discussion of relatively subtle structural aspects may only make sense if it is actually possible to force monomers at an interface into van der Waals distance. If a less dense monolayer is generated upon compression, severe reorganizations could result upon its irradiation, thus rendering structural features of the monomer less important.

[181] For some studies mostly based on grazing incidence X-ray diffraction that address the order in Langmuir monolayers, see: a) R. M. Kenn, C. Böhm, A. M. Bibo, I. R. Peterson, H. Möhwald, J. Als-Nielsen, K. Kjaer, *J. Phys. Chem.* **1991**, *95*, 2092 – 2097; b) G. Brezesinski, E. Scalas, B. Struth, H. Möhwald, F. Bringezu, U. Gehlert, G. Weidemann, D. Vollhardt, *J. Phys. Chem.* **1995**, *99*, 8758 – 8762; c) G. Weidemann, G. Brezesinski, D. Vollhardt, C. De Wolf, H. Möhwald, *Langmuir* **1999**, *15*, 2901 – 2910.

[182] a) Y. Yonezawa, D. Möbius, H. Kuhn, *J. Appl. Phys.* **1987**, *62*, 2022 – 2027; b) J. Ackermann, D. Möbius, unpublished results.

[183] a) D. Pum, M. Weinhandl, C. Hödl, U. B. Sleytr, *J. Bacteriol.* **1993**, *175*, 2762 – 2766; b) U. B. Sleytr, P. Messner, D. Pum, M. Sára, *Angew. Chem.* **1999**, *111*, 1098 – 1120; *Angew. Chem. Int. Ed.* **1999**, *38*, 1034 – 1054.

[184] For a related more recent review, see: U. B. Sleytr, E. M. Egelseer, N. Ilk, D. Pum, B. Schuster, *FEBS J.* **2007**, *274*, 323 – 334.

[185] T. C. Edwards, S. Koppenol, W. Frey, W. R. Schief, Jr., V. Vogel, R. E. Stenkamp, P. S. Stayton, *Langmuir* **1998**, *14*, 4683 – 4687.

[186] a) G. Wegner, *Thin Solid Films* **1992**, *216*, 105 – 116; b) S. Schwiegk, T. Vahlenkamp, Y. Xu, G. Wegner, *Macromolecules* **1992**, *25*, 2513 – 2525.

[187] I. R. Peterson, *J. Chim. Phys.* **1988**, *85*, 997 – 1001.

[188] Surface tension in 2D is referred to as line tension.

[189] For a recent example in which interlayer voids of a redox-active coordination network were used for a linear polymerization of pyrrole, see: N. Yanai, T. Uemura, M. Ohba, Y. Kadowaki, M. Maesato, M. Takenaka, S. Nishitsuji, H. Hasegawa, S. Kitagawa, *Angew. Chem.* **2008**, *120*, 10031 – 10034; *Angew. Chem. Int. Ed.* **2008**, *47*, 9883 – 9886.

[190] a) E. Mena-Osteritz, P. Bäuerle, *Adv. Mater.* **2006**, *18*, 447 – 451; b) K. Tahara, S. Lei, W. Mamdouh, Y. Yamaguchi, T. Ichikawa, H. Uji-i, M. Sonoda, K. Hirose, F. C. De Schryver, S. De Feyter, Y. Tobe, *J. Am. Chem. Soc.* **2008**, *130*, 6666 – 6667; c) S. Lei, K. Tahara, X. Feng, S. Furukawa, F. C. De Schryver, K. Müllen, Y. Tobe, S. De Fyter, *J. Am. Chem. Soc.* **2008**, *130*, 7119 – 7129.

[191] C. Münzenberg, A. Rossi, K. Feldman, R. Fiolka, A. Stemmer, K. Kita-Tokarczyk, W. Meier, J. Sakamoto, O. Lukin, A. D. Schlüter, *Chem. Eur. J.* **2008**, *14*, 10797 – 10807.

[192] a) J. van Heijst, O. Lukin, A. D. Schlüter, unpublished results; b) J. van Heijst, J. Sakamoto, A. D. Schlüter, unpublished results.

[193] For other cases in which holes are spanned by ultrathin but intrinsically more or less irregular films, see: D. Day, J. B. Lando, *Macromolecules* **1980**, *13*, 1478 – 1483, as well as Refs. [10,19] and [152b,c].