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Controlled Polymer Synthesis in Homogeneous and Heterogeneous Processes

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Abstract

Research in polymer synthesis can be oriented toward method or structure. This review is intended to document both approaches. Recent examples from our own work as well as future prospectives will be presented. A general concern is to work out the impact from organic and supramolecular chemistry.
Examples of method oriented work are (i) a unique polycondensation via carbon sulfur-bond formation providing hybrid structures of, e.g., polyphenylenesulfide and polyaniline; (ii) a triazoline additive establishing a novel self-regulation process in controlled radical polymerization; (iii) a metallocene catalyzed polyolefin synthesis which is performed by using "smart", reversibly cross-linked polymer resins as support; and (iv) hydrogen-bonded aggregates suggesting new emulsifiers for emulsion polymerization thus leading to functional nanoparticles.
Examples of structure oriented work are (i) rod-coil block copolymers (1D case) as a „covalently bound combination“ of rigid and flexible segments whereby a key synthetic concern is the chemical modification and quantitative end-functionalization of polyphenylene chains; (ii) discs (2D case) as molecularly defined graphite subunits which are obtained via a remarkably mild intramolecular cyclodehydrogenation; and (iii) dendrimers (3D case) as shape-persistent nanoparticles whose high degree of structural precision results from a new cycloaddition-deprotection protocol.

1. Introduction

Polymer synthesis is a multi-tasking process since it (i) focusses on both structures and methods; (ii) tries to control molecular and supramolecular design, at different length scales and different phases, and (iii) has a strong bias for the active function of polymers, i.e., on their role as materials. With this in mind the outline of the present text appears straightforward: We take a look into quite classical synthetic methods, polycondensation (section 2.1) and radical polymerization of activated olefins (section 2.2), thereby going for

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new ways of repetitive bond-formation and improved control of radical polymerization. While both methods of polymer synthesis can be discussed by restricting the attention to isolated molecules in solution, the following approaches, polyolefin synthesis using supported metallocene catalysts (section 2.3) and emulsion polymerization (section 2.4), have an additional supramolecular aspect since particle formation and bonding through non-covalent effects come into play as well. Needless to say, a spatial confinement of the polymer forming reactions has a profound influence on the synthetic concepts to be applied.

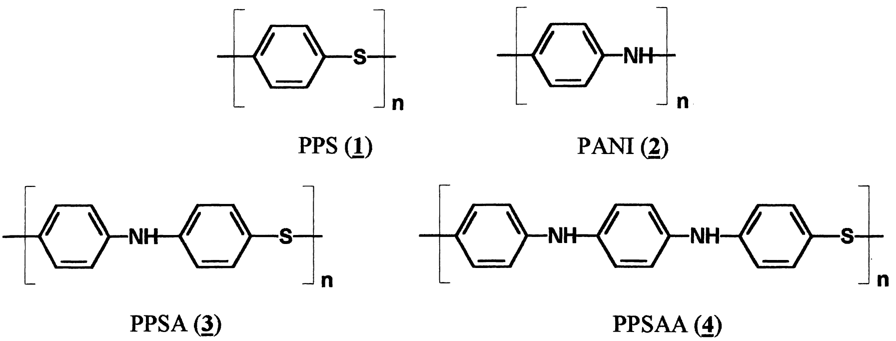
In the search for new, unconventional polymer structures, our starting point will be a classical example, that of polyphenylenes. The dimensionality of polyphenylenes will serve as a guideline, since we proceed from the well known rigid rods, the 1D case (section 3.1), to giant discs, the 2D case (section 3.2), and to dendrimers, the 3D case (section 3.3). Dendrimers which are constructed only from benzene moieties differ significantly from already known dendrimers and can serve as unique functional nanoparticles. It is the astonishing aspect of our design process that a plethora of unique molecular and supramolecular architectures is derived from a seemingly simple chemistry using the benzene ring as modular building block.

The following article is intended to outline our recent work in polymer synthesis aiming at both new synthetic methods and new polymer structures. For details the reader is urged to consult the original publications since this overview is necessarily written in a concise and compact manner. This text is designed to cover quite different topics which at a first glance might even appear somewhat unrelated. These cases are meant to demonstrate, however, how the general needs of controlled polymer synthesis can be met for a diversity of methods and structures. The other advantage of this approach is that it stimulates a fruitful and sometimes surprising combinations of expertise.

2. Methods

2.1. Polycondensation by Carbon-Sulfur Bond Formation

Are there still challenges in polycondensation ? Let us invoke two classical examples of polycondensation products: poly(phenylenesulfide) (PPS, 1) and polyaniline (PANI, 2). Both polymers are obtained by easy procedures and have great practical importance, but suffer from a series of drawbacks, such as low solubility and limited tractability. We thought that we to make a hybrid structure by combining the structural features of PPS (**1**) and PANI (**2**) (*Scheme 1*). [1]

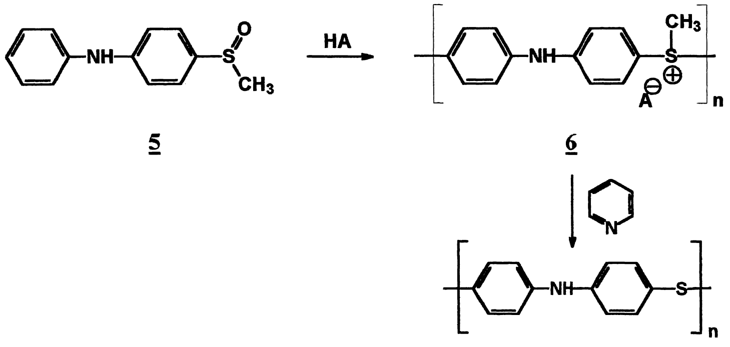


PPS (1) PANI (2)

PPSA (3) PPSAA (4)

Scheme 1: Sulfur and nitrogen-bridged polyphenylenes

Our synthetic concept towards the so-called poly(phenylenesulfide-phenyleneamine) (PPSA, 3) is based on an acid-induced condensation of aromatic methylsulfoxides. Upon treatment of the AB-type monomer 5 with strong acids, polysulfonium salt 6 can be obtained in high yields. Demethylation of 6 with pyridine as the nucleophile gives nearly quantitative access to high-molecular weight PPSA (3) (Mn up to 150.000) *(Scheme 2)*.

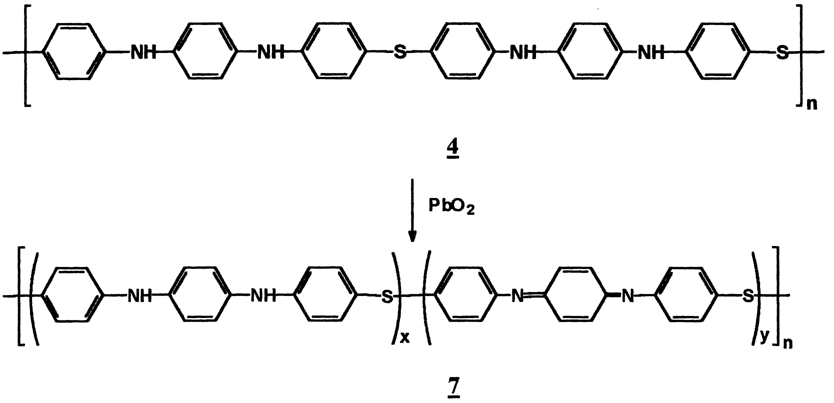


5 6 3

Scheme 2: Synthesis of PPSA

In contrast to the classical polymers PPS and PANI, PPSA is structurally well-defined and exhibits exceptional solubility in organic solvents, such as THF or DMF. Flexible, transparent and colorless films can easily be prepared by spin-coating techniques. Oxidative doping of these films with iron(III)chloride results in electrical conductivities of about 10 S/cm, which remain constant over several months. Apart from promising conductivity, PPSA has turned out to be a very efficient hole-transport material for LED-devices, which, together with its excellent solution processing, defines the material as a prominent candidate for this special application. [2]

The above concept for carbon-sulfur bond formation was extended towards the synthesis of high-molecular weight poly(phenylenesulfide-phenyleneamine-phenyleneamine) (PPSAA, 4), a structure which is attractive due to its close electronic relationship to PANI 3. [3] Chemical oxidation of the as-synthesized, completely reduced form of PPSAA (4) results in different oxidation states of the polymer 7, analogous to PANI (*Scheme 3*).



Scheme 3: Oxidation of PPSAA

Remarkably, PPSAA (7) is soluble in solvents such as THF and NMP through all different oxidation states, and flexible, free-standing films can easily be prepared. Furthermore, by addition of any type of acid to the half oxidized "emeraldine-like" PPSAA ($x = y = 0.5$), spontaneous electron transfer and the formation of semiquinone species are observed. Hence, an acid-type doping without changing the number of π-electrons similiar to PANI is possible.

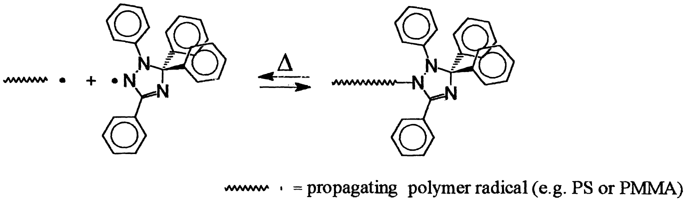
We conclude that a new method of bond formation gives access to high molecular weight polymers without structural defects and allows control of the physical properties of the products. Further opportunities can be highlighted by the synthesis of hyperbranched analogues of PPSA and by an intramolecular version of the carbon-sulfur bond formation which provides access to sulfur containing poly[n]acenes as double-stranded polymers.

2.2. Self-Regulation in Radical Polymerization

In radical polymerization of activated olefins the similar question of rigorous control over the polymer structure goes back to the problem of how we avoid any reactions of the growing free macroradical except chain propagation. Side reactions such as dimerization or disproportionation will not only reduce the thermal stability of the product, but also limit the ability of the free macroradical to participate in block copolymer formation upon reaction with another monomer.

Two methods have recently been established to achieve living species in radical polymerization: the ATRP (atom transfer radical polymerisation) and the NMRP (nitroxide mediated radical polymerisation). Both processes allow the synthesis of block copolymers, but for a technical application some disadvantages have to be solved. In the case of ATRP, molar amounts of Cu catalyst have to be removed, requiring an additional purification step; and, furthermore, polar monomers cause serious difficulties due to the interaction with the metal ion. The most important disadvantage in NMRP for the most common additive TEMPO is the limitation to autopolymerizable monomers such as styrene and styrene derivatives.[4] This is a result of suppressed, but still occurring irreversible side reactions of free polymer radicals such as recombination or disproportionation. [5]

Due to the drawbacks in the existing procedures, metal content and restriction to autopolymerizable monomers, there is still a demand for new additives for controlled radical polymerization.



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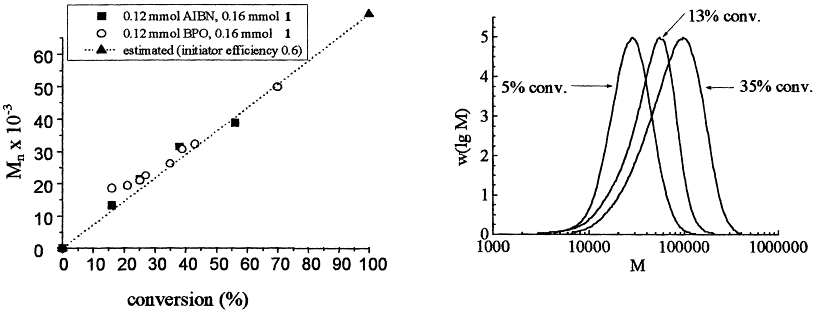
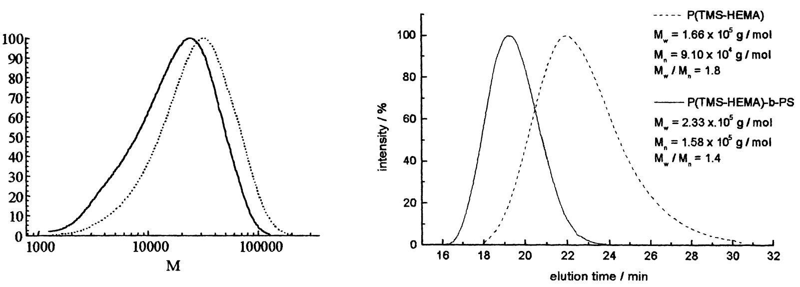
Scheme 4: Equilibrium between active and dormant side with triazolinyl as counter radical

We demonstrate that triazolinyl radicals **8** (*Scheme 5*), first published by Neugebauer [6], fulfill the requirements for a more applicable system.[7] Not only styrene, but also MMA can be polymerized up to high conversions in a well controlled way. Triazolinyl radicals have some significant advantages over TEMPO. The polymerization rates are about four times higher and a broad variety of monomers can be polymerized in a controlled way. While molecular weights in the TEMPO controlled styrene polymerization are limited up to 20000, in the triazolinyl case molecular weights of PS and PMMA of around Mn > 100 000 (*Scheme 5b*) are accessible. *Scheme 5a* clearly indicates the linear increase of the molar mass versus conversion in the polymerization of styrene and in a similar way, (*Scheme 5b*) proves the controlled process by the shift of the GPC traces towards higher masses with increasing conversion.



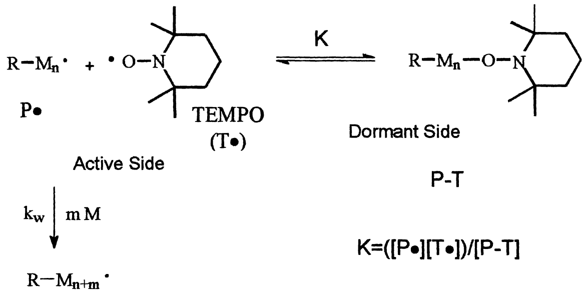
Scheme 5: a) Controlled radical polymerization of styrene in presence of triazolinyl **1** (T = 120 °C, bulk); M_n versus conversion; b) Shifting of the GPC traces towards higher masses with increasing conversion

Via mass spectrometry and UV-spectroscopy a high degree of endfunctionalization can be shown. This results not only in the possibility of chain extension but, more important, in the generation of new types of blockcopolymers such as PS-b-PVAc or Poly(TMS-HEMA-b-PS) (*Scheme 6*).



Scheme 6: a) GPC traces of poly(styrol) macroinitiator versus the resulting poly(styrol)-b-PVAc; b) GPC traces of poly(TMS-HEMA) macroinitiator versus the resulting poly(TMS-HEMA)-b-polystyrene

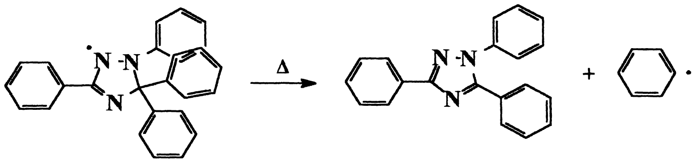
To explain the ability of this radical to control a broad variety of monomers one has to take a closer look into the kinetics of the polymerization. In the TEMPO case it was proven that due to side reactions the number of polymer chains which possess the ability to undergo further chain growth steadily decreases. In order to maintain the equilibrium constant K=([P•][T•])/[P-T] invariant (*Scheme 7*), this loss of „living“ polymer chains is balanced by a simultaneous increase of the number of persistent counter radicals T•, subsequently leading to a shift of the polymerization equilibrium to the dormant side.



Scheme 7: Equilibrium between active and dormant side with TEMPO as additive

This unwanted situation is avoided when the monomer is susceptible to spontaneous (thermal) initiation as it is the case for styrene and styrene derivatives. The thus newly formed radical chains capture the excess of free counter radicals.

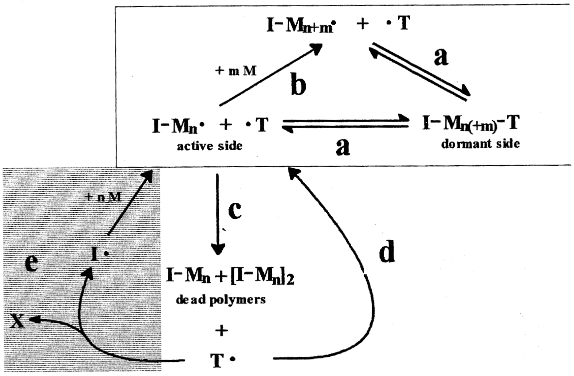
However, in our case not only autopolymerization can generate new growing radicals, but also the triazolinyl radical itself is able to control the amount of macroradicals. This surprising result is an effect of a slow decomposition (half lifetime 20 min / 100°C) of the free radical 8 which is proven by ESR spectroscopy and FD mass spectrometry. The driving force of this reaction which gives rise to a new phenyl radical is the simultaneous formation of an aromatic heterocycle (*Scheme 8*).



8 9 10

Scheme 8: Decomposition of 8

The phenyl radical **10** strongly influences the polymerisation since it initiates new polymer chains. It is important to mention that a triazolinyl group attached to the polymer chain is completely stable because decomposition would not lead to an aromatic heterocycle. In a typical radical polymerization the period during which the counter radical is free is very short and its decomposition is nearly excluded. Decomposition occurs only if an excess of counter radical due to the side reactions.



Scheme 9: Concept of self-regulation

When the number of irreversibly terminated chains increases, the number of free counter radicals **T**· increases as well (**c**). Consequently, the tendency of the counter radical to decompose to **X** by release of new initiating species **I** increases. Half of the amount of the triazolinyl decomposes and forms an initiator (**e**), the other half acts as controlling agent for these newly formed chains (**d**). Accordingly, the counter radical itself possesses the possibility to control its free concentration and therefore the equilibrium **a** (*Scheme 9*). [8]

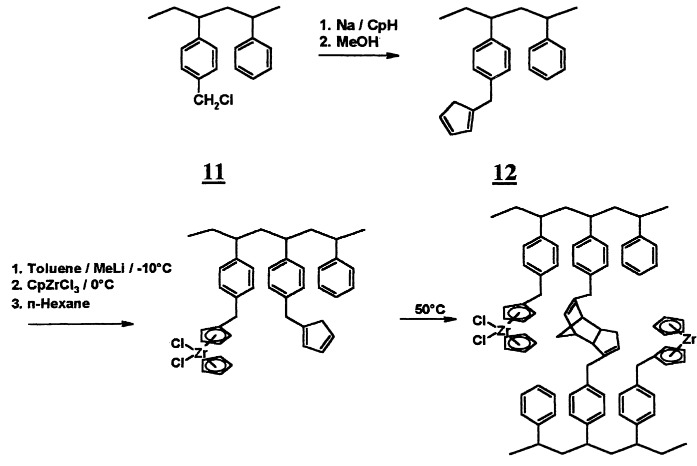
In conclusion, with the triazolinyl radicals, due to a special mechanism, a broad variety of monomers can be polymerized in a controlled, metall free way, autopolymerization like in the case of TEMPO is no longer essential since the system controls itself by the side reactions. In the future, this additives will allow for the synthesis of block copolymers with unusual monomer combinations. Even water-soluble or very polar monomers can be easily incorporated resulting in materials with special morphologies in bulk or agreggation behavior in solution. Especially, for using polymers as emulsifiers, the easy synthesis of amphiphilic block copolymers will be a challenge.

2.3. Supported Metallocenes in Polyolefin Synthesis

It has been emphasized already that the following example of polymer synthesis is different in that it implies a heterogeneous process. The key step is the synthesis of a „smart“ polymer resin which acts as support for catalyst systems. Here again, however, the novelty comes from a concept of organic chemistry since the cross-linking is achieved by a reversible Diels-Alder cycloaddition.

The synthesis of polyolefins is by far the most important industrial polymer-forming process. [9] Compared to conventional Ziegler-Natta catalysts, the metallocene/aluminoxane catalysts offer a number of advantages. In particular, they combine high activity with the possibility to tailor polymer properties such as molecular weight, molecular weight distribution, co-monomer insertion and distribution, as well as the stereoregularity of α-olefins.

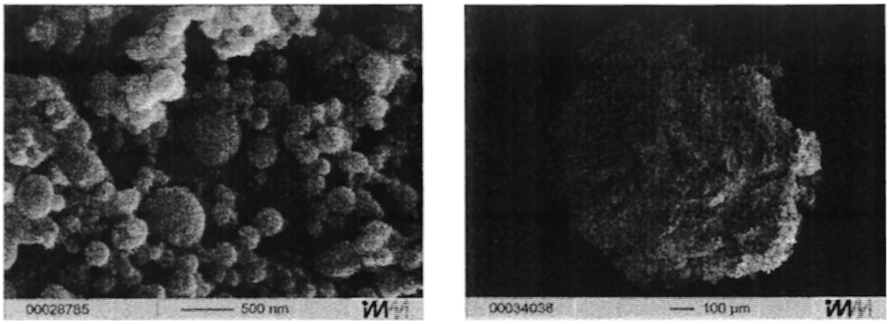
Hitherto, most articles have dealt with the modification of the metallocene ligand sphere in order to generate a series of efficient, soluble metallocene catalysts. [10] For industrial gas-phase and slurry polymerization processes, however, heterogeneous catalyst systems are an important requirement. [11] The catalyst support acts as a template in these particle growth processes and controls the size and morphology of the resulting polymer. Commonly used inorganic supports for metallocenes, such as SiO_2, Al_2O_3 or $MgCl_2$, show a rigid and polar surface structure as opposed to polymer carriers. Hydrocarbon support materials provide a much closer analog to the environment prevailing in homogeneous polymerization. [12, 13] In contrast to polystyrene beads cross-linked with divinylbenzene, where all synthetic steps are performed heterogeneously and only on the accessible surface, our approach involves the formation of the resin following the attachment of metallocenes to the polymer backbone.



13 14

Scheme 10: Synthesis of a metallocene catalyst on a reversibly cross-linked polystyrene

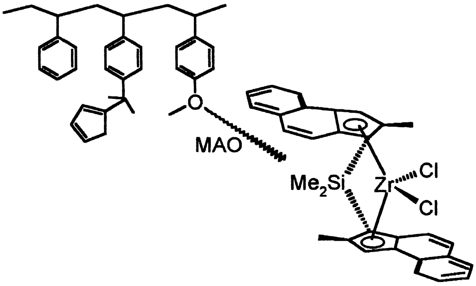
This is expected to provide a more uniform distribution of active centers within the particles (*Scheme 10*). [14] Furthermore, the reversibility of the cross-linking Diels-Alder reaction allows for fragmentation of the catalyst support during the polymerization and polymer processing. The swellable and reversibly cross-linked polymer support which is introduced here, thus, constitutes a closer analog to the soluble metallocene system. It allows for seemingly heterogeneous polymerization to proceed in an isotropic, dynamic and microscopically solution-like environment. [15] This is in sharp contrast to the situation prevailing in rigid, anisotropic surfaces of inorganic supports.



Scheme 11: SEM microscope image of a) a metallated particle (scale bar 500 nm)
b) of a product bead (scale bar 100 µm)

Remarkably enough, despite the easy synthesis of our catalyst the polyolefin product is isolated as nearly spherical beads of millimeter dimension as proven by scanning electron microscopy (*Scheme 11*).

It is quite obvious that this synthetic approach is restricted to cyclopentadienyl containg catalysts. However, to control tacticity in polypropylenes more complicated catalysts have to be applied. Therefore it is not very reasonable to generate them on a polymeric backbone which would require a multi-step synthesis but to synthesize them separetely and combine them on the final stage with the polymeric support.



Scheme 12: Non-covalently attached metallocene

The synthetic approach for such a support is quite straightforward since one starts with a copolymer of styrene, bromostyrene and methoxystyrene, lithiation and addition of fulvene results in a cyclopentadienyl containing polymer. Again, the cyclopentadienyl unit is responsible for the crosslinking. [16]

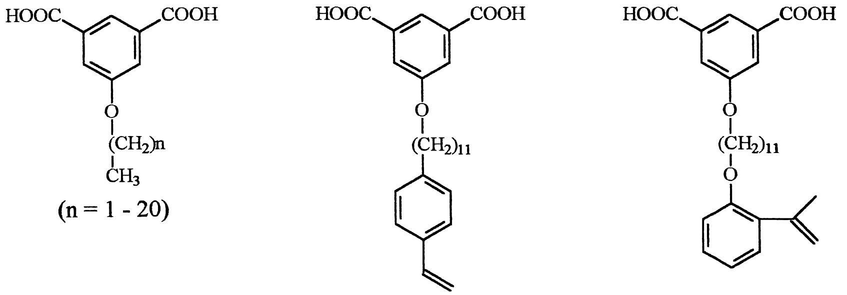
For attaching the catalysts the methoxy group is essential. Due to the high affinity of MAO towards ether groups and to the metallocenes, the catalyst can be non-covalently, but with a high stability, attached on polymeric materials via a "MAO-bridge".

This concept allows, similar to the industrial process using silica, the supporting of a nearly unlimited number of metallocene catalysts on a polymeric material. Polypropylenes with different tacticity can be generated and, furthermore, activity and morphology of product particles optimzed depending on the degree of cross-linking, loading of metallocene and amount of activator. The extension towards copolymerisation with polar monomers is a further task to obtain materials acting as compatibilizers or adhesives.

2.4. Hydrogen-Bonding and Emulsion Polymerization

The formation of particles which is crucial for the above approach toward supported catalysts results from cross-linking of polymer chains via covalent bonding. This suggests an alternative concept for toward the formation of networks and of particles, that via non-covalent bonding.

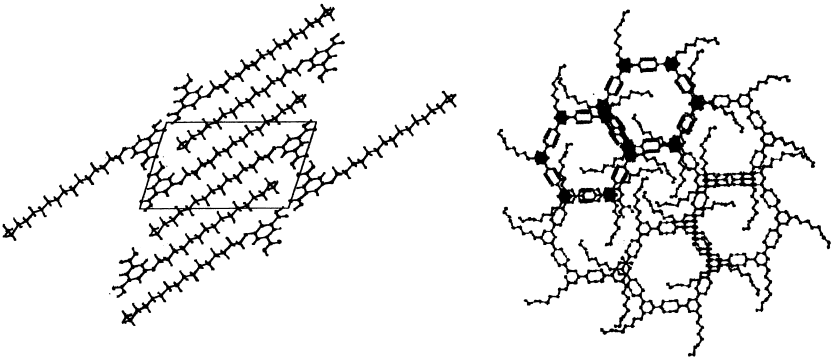
5-Alkoxyisophthalic acids (C_n ISA) *(Scheme 10)* are challenging building blocks for self-assembly processes since they combine two powerful structure-forming principles: alkyl chain packing and hydrogen bonding.



15 16 17

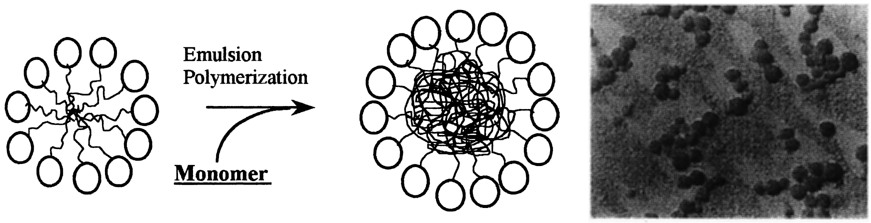
Scheme 13: 5-Alkoxyisophthalic acid (C_nISA) (15), 5-((4-styryl)undecyl)oxy) isophthalic acid (ISA-C_{11}-Sty) (16) and 5-((2-propenylphenoxy)undecyl)oxy) isophthalic acid (ISA-C_{11}-ipr) (17)

When investigating their packing behavior as a function of the alkyl chain length, crystal structure analysis reveals that in the diacids C_nISA, with $n < 6$ or $n > 12$, the alkyl substituents from adjacent molecules of hydrogen bonded strands point towards opposite directions and that infinite sheets with interdigitating alkyl chains are formed (*Scheme 14*). [17] In contrast, the C_n ISA molecules with $6 < n < 10$ form cyclic hexamers in the crystal. [14] Furthermore, the number of motifs in the crystalline lattice can be extended by adding difunctional aromatic bases such as pyrimidine or pyridazine. Here again, strong hydrogen bonded arrays are seen throughout the lattice. An induction of mesophases is also possible.[15] 5-Alkoxyisophthalic acids also form highly ordered monolayers on graphite upon physisorption from solution which can be visualized in real space by scanning tunneling microscopy. This allows a systematic comparison of pattern formation in 2D- and 3D-crystals and paves the way toward chemical transformations of single molecules.



Scheme 14: Crystal structures of $C_{16}ISA$ (**15**) Channel-type crystal structure of C_8ISA

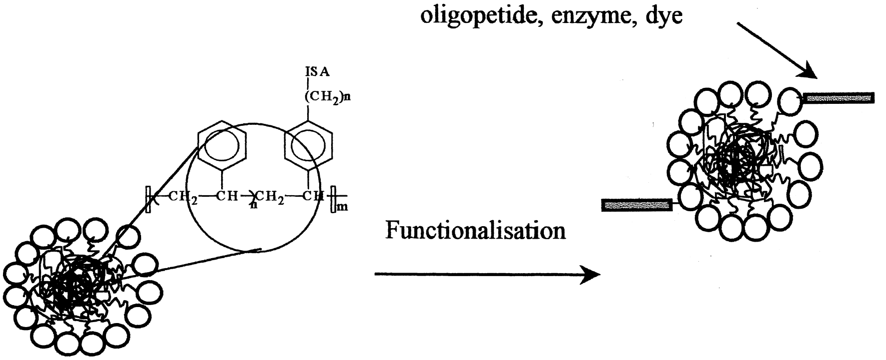
Moreover, the amphiphilic character of the alkoxyisophthalic acid derivatives makes it possible to utilize them as surfactants in emulsion polymerization of different monomers (e.g.: styrene, n-butylmethacrylate and n-butylacrylate) (*Scheme 15*). Indeed, such dicarboxylic acid surfactants increase the electrostatic stabilization of the final latex. The CMC (critical micellar concentration) of these compounds is comparable with the CMC of other dicarboxylic acids [18, 19]. Conventional amphiphilic surfactants used in emulsion polymerization stabilize the final latex particles by adsorption at the polymer/water interface. The major problem of these surfactants appears during the handling of the dispersions. The surfactant is able to adsorb or desorb freely from the latex surface affecting the latex stability and mechanical properties.



Scheme 15: Emulsion polymerisation in the presence of 15 (Monomer: styrene, TEM picture)

One possibility to improve latex stability is the copolymerization with polymerizable surfactants (surfmers). We synthesized different surfmers and copolymerized them with styrene. The ^1H NMR study of the monomer-surfmer conversion ratio showed that ISA- C_{11}-sty (16) and the ISA-C_{11}-i-pr (17) are copolymerized with styrene. The final polymer dispersions are monodisperse and very stable in the presence of mono- and divalent salts (e.g., KCl and $CaCl_2$).

A potential application results from the possibility of functionalizing the latex particles in aqueous media with functional components such as oligopeptides or dyes *(Scheme 13)*. As a result, the carboxylate groups on the surface of the copolymer lattices are involved in the formation of covalent bonds with the functional units. The great number of opportunities for assay formation is obvious. A further challenge comes from a comparison of latices and dendrimers (see below) as functional nanoparticles of different size and stability.



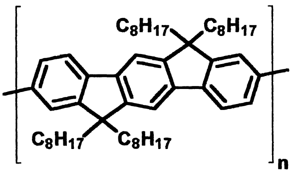
Scheme 16: Functionalisation of latex particles

3. Structures

3.1 Rigid-Rod Polyphenylenes and Rod-Coil Block Copolymers

We have in section 2 dealt with important classical and practical problems of polymer synthesis in both homogeneous and heterogeneous processes and made attempts at introducing new solutions to these problems with a strong influence from organic and supramolecular chemistry.

As mentioned in the introduction, our search for new polymer structures is restricted to polyphenylenes of varying dimensionality. Poly-para-phenylene is the classical case of a rigid-rod and the prototype of a conjugated polymer. Conjugated polymers are of great academic as well as industrial interest since they possess a large application potential [20, 21].



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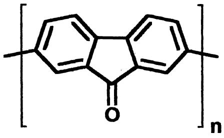

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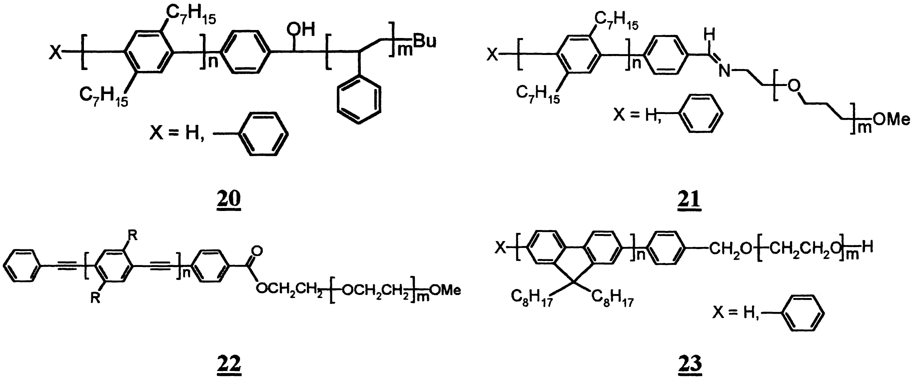
Scheme 17: Examples of polyfluorene-type structures

Recently, our efforts have focussed on bridging the gap between the step-ladder type poly(2,7-(9,9-dialkylfluorene)) and a true ladder-type polyphenylene by the synthesis of poly(2,8-(6,6‘-12,12‘-tetraalkylindenofluorene)) (2,8-PIF) (**18**) which contains three planarized phenylene rings as repeating unit. [22] Polymer **18** exhibits the desired bathochromic shift of absorption and emission bands with respect to the polyfluorenes (**19**). Further, the material posseses excellent film-forming properties, is stable up to 400 °C and forms liquid-crystalline phases.

The device performance of a light emitting diode (LED) depends sensitively upon the balanced injection of holes and electrons into the active layer; therefore, hole-transport as well as electron-transport materials have been used in multi-layer devices. Our efforts towards the development of novel, efficient electron transport materials led to the preparation of poly-(2,7-fluorenone) (**19**) via a precursor route. [23] Cyclic voltammetry measurements revealed a reversible reduction with a $E_{1/2}^0$ of -1.48 V vs Fc/Fc^+ which makes the polymer a promising candidate for the use as the electron transport layer in multi-layer LEDs.

A novel strategy towards controlling the self-assembly, film morphology and hence the opto-electronic properties of conjugated polymers invokes the synthesis of luminescent rod-coil block copolymers. Even short block lengths lead to phase-separated structures in the nanometer regime. [24] The block ratio of the luminescent rods and the non-emissive coils plays an important role, since on the one hand the block lengths should be long enough to seggregate, and on the other hand the length of the flexible coil should be minimized to obtain a material with the highest possible concentration of the conjugated species.



Scheme 18: Some examples of rod-coil blockcopolymers

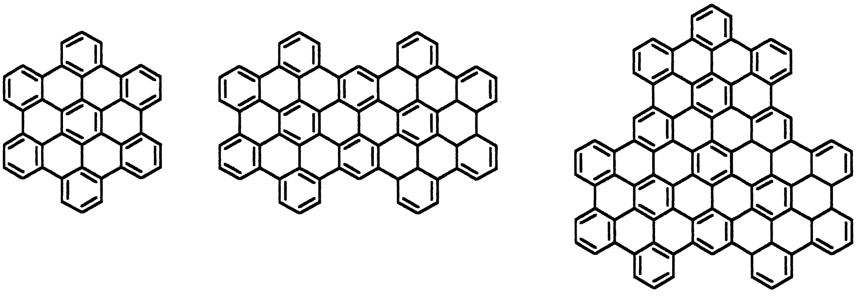
Synthetic strategies towards rod-coil block copolymers involve either a condensation of two pre-formed blocks (grafting-onto process) or polymerization using a macroinitiator (grafting-from process). A quantitative end-functionalization of the desired luminescent rod polymers is a prerequisite for both approaches. We were able to perfectly end-functionalize polyphenylenes by using transition-metal mediated coupling reactions. [25, 26] End-functionalized polyphenylenes (PPPs) and polyphenyleneethynylenes (PPEs) rods were in a second step used as building blocks in conventional condensation protocols followed by careful work-up procedures to obtain the desired rod-coil block copolymers **20** - **23** in good yields. By using a benzylalcohol-terminated poly(2,7-(9,9-dioctylfluorene)) as a macroinitiator for the polymerization of ethyleneoxide we were also able to synthesize the rod-coil block copolymer **23** by a grafting-from procedure (*Scheme 18*).

All the block copolymers show a variety of different phase-separated structures which are dependent on the film preparation. In the case of the poly(2,7-fluorene)-*b*-poly(ethyleneoxide) **23** we could even show a significant change in the optical properties of the block copolymer compared to the corresponding homo-polyfluorene in the solid state due to ordering phenomena. While morphologies of coil-coil block copolymers have long been attracted the attention of polymer scientists, the corresponding rod-coil structures are much less common. Accordingly, it will be the challenge of future synthetic work to provide a broader variety of rod-coil blockcopolymers with different natures and lengths of both components.

3.2. Molecular Graphite Subunits

The chain stiffness of the above rod-like polymers has already served as a powerful supramolecular principle. We now introduce a related approach for 2D- and 3D-molecules. With new molecular topologies of polyphenylenes in hand, the self-assembly of discs and spheres will then create a versatile route to functional nanoparticles.

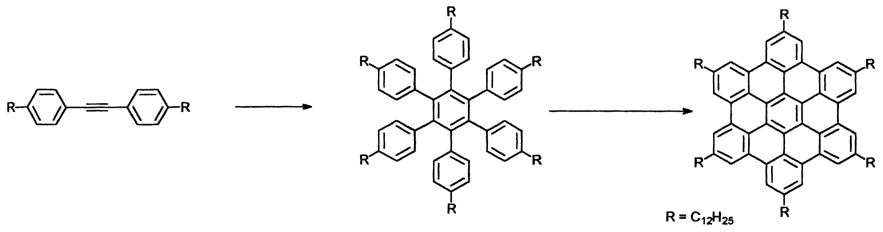
A situation which is electronically different from that in linear polyphenylenes arises if the molecules possess two translational periods such as in disc-type polycyclic aromatic hydrocarbons (PAHs). Looking to capitalize on the interesting electronic properties of graphite, we synthesized topologically distinct graphite-like molecules. Examples of such molecules include hexa-*peri*-hexabenzocoronene (HBC) **24**, supernaphthalene **25** and supertriphenylene **26** *(Scheme 15)*. [27]



24 **25** **26**

Scheme 19: Graphite-like molecules

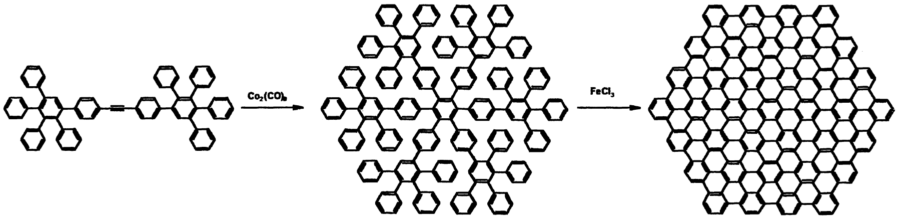
Conceptually, our synthetic method involves synthesis of a branched polyphenylene as precursor, followed by the planarization of the molecule to yield the final two-dimensional product. An important synthetic step to these precursor polyphenylenes is the cyclotrimerization of suitably substituted diarylacetylenes (see *Scheme 16)*, but Diels-Alder cycloadditions between tetraarylcyclopentadienones and diarylacetylenes can be used as well. The construction of polyphenylenes is then followed by their oxidative cyclodehydrogenation and planarization into the final „graphite sheets". [28]



27 **28** **29**

Scheme 20: Synthesis of hexa-*peri*-hexabenzocoronene (HBC)

Another example is molecule **30** which after cyclotrimerization and planarization gives the PAH **32**. Characteristic for this large polyaromatic hydrocarbon is the π-stacking between adjacent layers with insolubility as a consequence.



30 **31** **32**

Scheme 21: Synthesis of the C_{222}-PAH **32**

Unfortunately, it is difficult to fully study the electronic properties of these unsubstituted molecules due to their insolubility. To overcome such problems, we have also synthesized their alkyl substituted derivatives. Interestingly, HBCs such as **19** form thermotropic columnar hexagonally ordered mesophases (Col_{ho}) at higher temperatures. The Col_{ho} mesophase involves the specific arrangement of the disc-like aromatic HBC cores, packed co-facially to optimize π-π interactions of the aromatic cores, into columns and these columns are arranged in a hexagonally close-packed fashion. Typical HBC derivatives are crystalline at room temperature and enter the mesophase at about 110°C. Isotropization temperatures are in excess of 420° C. These mesophases have remarkably large phase widths in comparison to columnar mesophases obtained from conventional disc molecules and are of interest because of their one-dimensional charge-carrier transport properties. To date, these HBC mesophases exhibit world record charge-carrier mobilities of the columnar-type mesophases.[29]

In order to preserve the hexagonally-packed columnar supramolecular ordering down to room temperature, we created cross-linkable HBC derivatives with acrylate and methacrylate functions at the terminus of each alkyl chain. These molecules could be easily thermally cross-linked and indeed, the Col_{ho} arrangement was preserved to room temperature with no distortion of the molecular packing.

To tailor the mesophase behavior (e.g. via H-bonding), mono and difunctionalized HBC molecules were desired. A more flexible route to a variety of substituted HBCs is the above mentioned coupling of diarylacetylenes to functionalized cyclopentadienones.[30] The bromo-substituted compounds can be transformed into a variety of functional groups (e.g. amino, carboxylic acid, cyano), which can affect both the supramolecular packing and the electrochemical potential of the molecule. [31, 32] A potent example of substituents affecting mesophase behavior is the case of HBC carrying six 4-alkylphenyl substituents (HBC-PhC_{12}). The Col_{ho} mesophase of HBC-PhC_{12} exhibits both better packing of each HBC core within one column and longer range hexagonal packing of the columns, as seen in WAXS and NMR spectroscopy, when compared with the standard n-alkyl HBC derivative. [33] Accordingly, the control of the supramolecular order and of the resulting physical properties is a synthesis driven process since in the design of the molecules one includes structural features relevant for the packing behavior.

By making molecular graphene sheets increasingly larger, polymer synthesis approaches the world of carbon-rich materials in which, e.g., graphitic or tubular structures are produced by unselective high-temperature methods. As part of this merger of different fields we are introducing a precursor route in which graphene sheets are made on substrate surfaces with the latter serving as chemical template.[34]

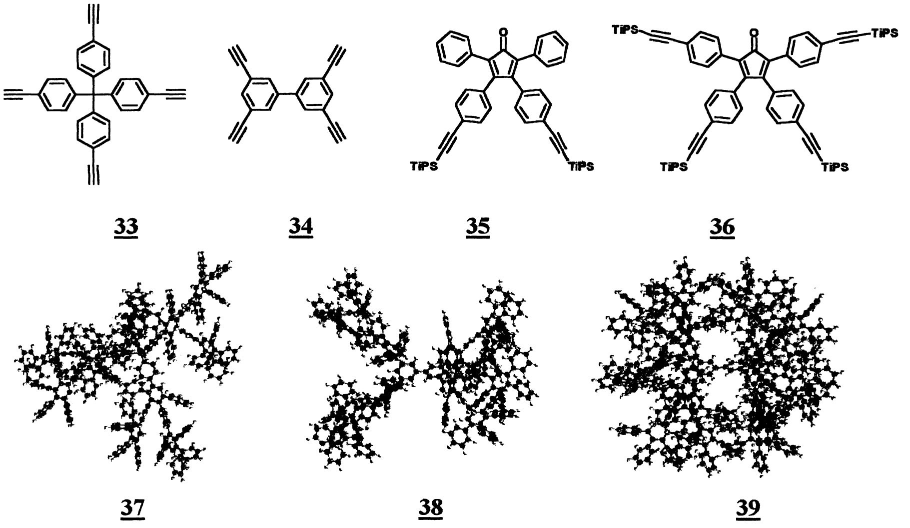
3.3 Dendritic Polyphenylenes

In section 3.2 branched polyphenylenes have served as precursors for fully conjugated PAHs. Surprisingly enough, the principles used in their synthesis also lead to a new type of dendritic 3D-polyphenylenes.

We have recently described a rapid access to hyperbranched and dendritic polyphenylenes that contain pentaphenylbenzene repeating units and can be synthesized in high yields by a repetitive Diels-Alder cycloaddition. [30] It is the beauty of this synthetic method that even high molecular weight polyphenylene dendrimers can be obtained as monodisperse species without any structural defects. Further, by the use of different ethynyl-substituted aromatic cores **33** and **34** and ethynyl-substituted cyclopentadienones as branching monomers, **35** and

36, we were able to obtain dendritic 3D-polyphenylenes of different shapes and densities as well as with diameters varying between 2 and 8 nm (*Scheme 22*). To conclude the relevant results, the 3D-polyphenylenes

- are colorless, chemically inert and thermally stable (> 450°C),
- have good solubility in organic solvents, but are easily precipitatable in polar solvents,
- can be thoroughly spectroscopically characterized, and
- are shape persistent.



33 **34** **35** **36**

37 **38** **39**

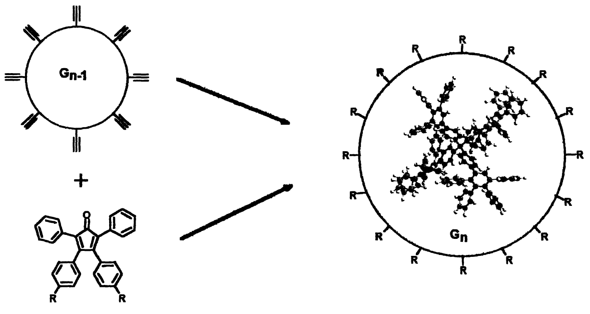
Scheme 22: Cores, building units and the second generation dendrimers resulting therefrom

While a detailed discussion of physical properties is beyond the scope of the present text it should be mentioned that the new dendrimers are particularly rewarding objects for the visualization and manipulation of single nanomolecules by, e.g., electron microscopy and atomic force microscopy. The latter methods also support the description of the polyphenylene dendrimers as stiff 3D-particles.

Because of their stiff and dense structure, the branches of the polyphenylene dendrimers cannot interpenetrate, as has been seen from crystal structures of first generation dendrimers. [35] The pores between the dendrimer molecules are larger than 10 nm and can be filled with solvent molecules. This result is important with regard to catalysis, since many catalytic reactions are diffusion controlled and strongly dependent on pore size.

By *in-situ* deprotection and polymerization of 35, it is possible to obtain polydisperse hyperbranched polyphenylenes with high molecular weights up to M_w = 96000 $gmol^{-1}$, but with less well-defined shapes.

For catalysis, carrier properties and supramolecular chemistry, the dendrimers can be chemically functionalized. The first approach is simple, but unselective. By sulfonation reactions it is possible to obtain a water-soluble dendrimer. The number of attached sulfonic groups depends on the molar ratio of sulfonic acid and the dendrimer used. Chloromethyl groups are very important substituents for attaching catalysts or as initiators for polymerization. Due to electronic as well as steric reasons, by chloromethylation one can attach up to 60 chloromethyl groups on a second generation dendrimer, thus, yielding a randomly surface-functionalized nanoparticle that allows further manipulations.



40

Scheme 23: Functionalization of polyphenylene dendrimers, cycloaddition of functionalized cyclopentadienones in the last generation

The second concept is to use the controlled functionalization of ethynyl substituted dendrimers (section 3.2) with substituted cyclopentadienones in the last step. This method allows a topologically defined functionalization of the dendrimer surface, but requires the synthesis of specifically substituted cyclopentadienones for each functional group. The substituents **R** of cyclopentadienones 40 can be halide, cyano, methoxy, thiomethoxy, methyl, N,N-dimethylamino or hydroxymethyl groups. In polymer-analogous reactions, the substituted dendrimers can then be further modified. Suitably functionalized dendrimers allow the synthesis of core-shell polymers via various grafting-from processes. The resulting particles are unique in that they possess a particularly rigid core.

Dendrimers with sulfonic or carboxylic groups are soluble in water and can, e. g., act as drug deliverers. The polyphenylene dendrimers are also well suited as catalyst carriers. The high surface-to-volume ratio allows very high catalyst densities together with easy product separation by ultrafiltration of the dendrimer after reaction.

Using dyes on the surface of the dendrimer, unique nanoemitters can be synthesized which are exciting objects for single molecule spectroscopy. Physics has recently provided methods for the direct visualization and manipulation of single molecules or aggregates consisting of few molecules. This is where polymer synthesis comes into play since future nanoscientific developments require molecular nanoobjects of well-defined size, shape and complex functionalization.

4. Conclusion

A typical point of issue when looking at approaches toward polymer synthesis concerns the degree of sophistication: one school, mostly with a background in organic chemistry, goes for somewhat unconventional polymer structures and for a high degree of stuctural precision, while another school, mostly with an application orientation, stresses the need for practical solutions. The present article was meant to demonstrate that these approaches are not necessarily in conflict. A good case can be made when looking at dendrimers. Polymer scientists feeling closer to "classical structures and to sound "bread-and-butter-chemistry" might tend to regard monodisperse dendrimers as somewhat exotic species requiring overly demanding synthetic methods of synthesis. When attempting to immobilize active components with chemical, physical or biological functions on suitable support systems, it is highly appropriate to compare dendrimers, hyperbranched polymers, latices and polymer resins. Along this sequence one will always relate the necessary degree of structure control to the synthetic effort and to the ultimate desired function.

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References

[1] a) L. Wang, T. Soczka-Guth, E. Havinga, K. Müllen, *Angew. Chem. Int. Ed. Engl.* **35**, 1495 (1996); b) J. Leuninger, C. Wang, T. Soczka-Guth, V. Enkelmann, T. Pakula, K. Müllen, *Macromolecules* **31**, 1720 (1998)

[2] Y. Tak, H. Bässler, J. Leuninger, K. Müllen, *J. Phys. Chem. B* **102**, 4887 (1998)

[3] J. Leuninger, J. Uebe, J. Salbeck, L. Gherghel, C. Wang, K. Müllen, *Synth. Met.* **100**, 79 (1999).

[4] a) T. Fukuda; T. Terauchi, A. Goto, Y. Tsujii; T. Miyamato, Y. Shimuzu, *Macromolecules* **29** 3050 (1996); b) I. Li, B.A. Howell, D.B. Priddy, P.B. Smith, *Polym. Prep. (Am. Chem. Soc., Div. Polymer. Chem.)* **37(1)** 612 (1996); c) B. Keoshkerian, M.K. Georges, D. Boils-Boissier,. *Macromolecules* **28**, 6381 (1995); d) C.J. Hawker, E. Elce, J. Doer, W. Volksen, T. Russel, G. Barclay, *Macromolecules* **29**, 2686 (1996)

[5] a) Y. Zhu, B.A. Howell, D.B. Priddy, *Polym. Prep. (Am. Chem. Soc., Div. Polymer. Chem.)* **38(1)**, 652 (1997); b) M. Steenbock, M.Klapper, K.Müllen, N.Pinhal, M. Hubrich, *Acta Polymer.* **47**, 276 (1996)

[6] a) F.A. Neugebauer, H. Fischer, C. Krieger, *Angew. Chem. Int. Ed. Engl.* **28**, 491 (1989); b) F.A. Neugebauer, H. Fischer, *Tetrahedron* **51**, 12883 (1995)

[7] a) D. Colombani, M. Steenbock, M. Klapper, K. Müllen, *Macromol. Rapid Commun.* **18**, 243 (1997); b) M. Steenbock, M. Klapper, K. Müllen, *Macromol. Chem. Phys*, **199**, 763 (1998); c) D. Colombani, M. Steenbock, M. Klapper, K. Müllen, M. Fischer, J. Koch, W. Paulus, *Pat.* DE 196 36 99.7

[8] M. Steenbock, M. Klapper, K. Müllen, *Acta Polymer.* **49**, 376 (1998**);** M. Steenbock, M. Klapper, K. Müllen, C. Bauer, M. Hubrich, *Macromolecules* **31**, 5223 (1998)

[9] a) H. H. Brintzinger, D. Fischer, R. Mühlhaupt, B. Rieger, R. Waymouth, *Angew. Chem. Int. Ed. Engl.* **34**, 1143 (1995) b) W. Kaminsky, *Macromol. Chem. Phys.* **197** 3907 (1996)

[10] a) J. Okuda, *Nachr. Chem. Tech. Lab.* **41**, 8 (1993) b) M. Aulbach, F. Küber, *Ch. i. u. Z.* **4**, 197 (1994) and references therein

[11] F. Langhauser, J. Kerth, M. Kerstin, P. Kölle, D. Lilge, P. Müller, *Angew. Makromol. Chem.* **223**, 155 (1994)

[12] a) S. C. Hong, H. T. Ban, N. Kishi, J. Jin, T. Uozumi, K. Soga, *Macromol. Chem. Phys.* **199**, 1393 (1998), b) S.C. Hong, T. Teranishi, K. Soga, *Polymer* **39**, 7153 (1998)

[13] H. Nishida, T. Uozomi, T. Arai, K. Soga, *Macromol. Chem., Rapid. Commun.* **16**, 821 (1995)

[14] e.g. a) Y. Qian, K. Hong, H. Zong, J. Huang, *Polym. Adv. Tech.* **7**, 619 (1996); b) T. Kamfjord, T. S. Wester, E. Rytter, *Macromol. Chem., Rapid. Commun.* **19**, 505 (1998)

[15] a) M. Stork, M. Koch, M. Klapper, K. Müllen, H. Gregorius, U. Rief, *Macromol. Chem. Rapid Commun.* **20**, 210 (1999); b) M. Stork, U. Wiesler, M. Klapper, K. Müllen, *PMSE,* **80**, 8 (1999); M. Stork, M. Koch, M. Klapper, K. Müllen, H. Gregorius, U. Rief, M.O. Christen, *Pat.* DE 198 219 49.0

[16] M. Koch, M. Stork, M. Klapper, K. Müllen, *Macromolecules*, submitted

[17] S. Valiyaveetil, V. Enkelmann, G. Moeßner, K. Müllen, *Macromol. Symp.* **102** 165 (1996)

[18] P. Reb, K. Margarit-Puri, M. Klapper, K. Müllen, *Macromolecules submitted*

[19] K. Shinoda, *J. Phys. Chem.* **59**, 432 (1955)

[20] D. Marsitzky, T. Brand, Y. Geerts, M. Klapper, K. Müllen, *Macromol. Chem. Rapid Commun.* **19**, 385 (1998)

[21] a) A. Kraft, A.B. Holmes, A.D. Grimsdale, *Angew. Chem Int. Ed. Engl.* **37**, 110 (1998); b) T. Skotheim, A.B. Holmes, A.D. Grimsdale, *Handbook of Conducting Polymers,*.Marcel Dekker (1998) c) D. Marsitzky, K. Müllen, *Synth. Metals* (1999), *in print*; d) K. Ziemelis, *Nature,* **393**, 619 (1998); e) C. Kallinger, M. Hillmer, A. Haugeneder, M. Perner, W. Spirkl, U. Lemmer, J. Feldmann, U. Scherf, K. Müllen, A.Gombert, V. Wittwer, *Adv. Mater.* **10**, 920 (1998); f) F. Hide, B.J. Schwartz, M.A. Diaz-Garcia, A.J. Heeger, *Synth. Metals,* **91**, 35 (1997)

[22] a) S.R. Forrest, P.E. Burrows, M.E. Thompson, *Chem. & Ind.* 1022 (1998); b) J. v. Haaren, D. Broer, *Chem. & Ind.* 1017 (1998); c) T. Jüstel, H.Nikol, C.Ronda, *Angew. Chem. Int. Ed. Engl.* **37**, 456 (1998)

[23] S. Setayesh, D. Marsitzky, K. Müllen, *Adv. Mater.* (1999) *submitted*

[24] F. Uckert, S. Setayesh, K. Müllen, *Macromolecules* (1999) *in print*

[25] G. Mao, C.K. Ober, *Acta Polym.* **48**, 405 (1997)

[26] a) V. Francke, H.J. Räder, Y. Geerts, K. Müllen, *Macromol. Rapid Commun.* **19**, 275 (1998); b) D. Marsitzky, M. Klapper, K. Müllen, *Macromolecules* **32**, 8685 (1999)

[27] V.S. Iyer, M. Wehmeier, J.-D.Brand, M.A. Keegstra, K. Müllen, *Angew. Chem. Int. Ed. Engl.* **36,** 15 (1997)

[28] P. Herwig, C.W. Kayser, K. Müllen, H.W. Spiess, *Adv. Mater.* **8**, 6 (1996)

[29] A.M. Van de Craats, J.M. Warman, K. Müllen, J.D. Brand, *Adv. Mater.* **10**, 1 (1998)

[30] a) F. Morgenroth, E. Reuter, K. Müllen *Angew. Chem. Int. Ed. Engl.* **36**, 631 (1997); b) F. Morgenroth, K. Müllen, *Tetrahedron* **53**, 15349 (1997) c) F. Morgenroth, C. Kübel, K. Müllen, *J. Mater. Chem.* **7**, 1207 (1997) d) F. Morgenroth, A.J. Berresheim, K. Müllen, *Chem. Comm.* 1139 (1998) e) U.-M. Wiesler, K. Müllen Chem. Comm., 2293 (1999)

[31] A. Stabel, P. Herwig, K. Müllen, J.P. Rabe, *Angew. Chem. Int. Ed. Engl.* **34**, 15 (1995)

[32] J.D. Brand, K. Müllen, *in preparation*

[33] A. Fechtenkötter, K. Saalwächter, M.A. Harbison, K. Müllen, H.-W. Spiess, *Angew. Chem. Int. Ed. Engl.* **38**, 3039 (1999)

[34] K. Weiss, G. Beernink, F. Dötz, A. Birkner, K. Müllen, Ch. Wöll, *Angew. Chem. Int. Ed. Engl.* **38**, 3752 (1999)

[35] U.-M. Wiesler, V. Enkelmann, K. Müllen, *in preparation*