Macromol. Symp. **2003**, *201*, 1–9

Shape Persistence as a Concept in the Design of Macromolecular Architectures

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Summary: Shape persistent macromolecules are objects defined by a time independent overall shape. In most cases such macromolecular objects are characterized by an exterior surface structure and an internal architecture giving coherence to the shape and topology. Shape persistent macromolecules are essential to the development of a polymer based nanotechnology and serve as constitutive units of larger scale architectures either via self-organization or via processes in which they are assembled to give constructs of nanoscale defined patterns.

Keywords: nanocomposites, nanotechnology, self-organization, stiffness, supramolecular structures

Introduction

Most of the industrially important polymer materials are composed of flexible macromolecules. Their solutions, melts, glassy and even semi-crystalline forms are characterized by the random flight nature of the chain trajectory. Important properties like rubber elasticity and the viscoelastic behavior of their melts find explanation in the most probable random distribution of the bond vectors along the chain trajectory and the time/temperature dependent changes and fluctuations of that distribution when external forces are exerted.

Contrary to that biomacromolecules derive their biological function from shape persistence that is a non-fluctuating positioning of chain segments within the volume filled by segments of the individual macromolecules; chain segments far apart from each other along the trajectory have a fixed spatial relationship ("topochemistry"). Although long recognized as an important principle in the world of biomacromolecules, "shape persistence" was only relatively recently accepted and put forward as a concept in the design of synthetic macromolecules and as an objective towards large scale architectures beyond the individual macromolecules.[1-5]

It needs to be mentioned, however, that H. Staudinger already in the late 20^s of the last century has put forward the idea that rod-like and, therefore, shape-persistent macromolecules are at the origin of the strength of certain fibres, in particular poly (oxymethylene) and

DOI: 10.1002/masy.200351101

cellulose.[6] This opinion was not shared by many of his contemporaries and was in fact not based on good experimental evidence but bears visionary potential.

Definition of Shape-persistence

Shape-persistent macromolecules are defined as objects characterized by a time independent overall shape. They have an exterior – that is surface – structure and an internal architecture which gives coherence and stability to the shape but also contributes to the function of the macromolecular object. Restricted fluctuations of the internal or external (surface) structure may be possible and necessary to provide functional properties as long as the overall shape persists.

Figure 1 describes the salient features by which linear flexible and rod-like chains decorated by a dense population of flexible side-groups – so called hairy-rod macromolecules (HRM) – differ in terms of physical concepts.[2, 7, 8]

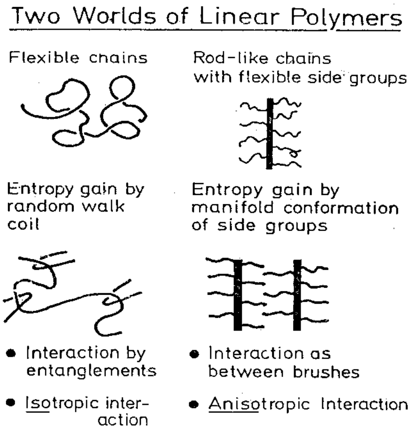

Fig. 1. Comparison between flexible and "hairy-rod macromolecules" (HRM). The latter are prototypes of shape-persistent linear polymers.

The meaning of persistence is exemplified by Figure 2 comparing a (flexible) Kuhn-chain with a worm-like Porod-chain.

The salient magnitude, the persistence length P, is a statistical description of the average shape of the worm-like chain. P is related to the ratio of the work needed to achieve a certain bending of the trajectory and the average thermal energy acting on the chain as given by *T. Odijk*:[9] $P = \pi d^4 E/(64 k_B T)$ and $K = \pi d^2 E/4$ where d is the diameter of the rod-like chain having a Youngs-modulus per unit length of E at temperature T, K is the elastic module of the whole worm-like chain.

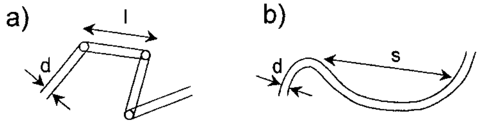

Fig. 2. A flexible Kuhn-chain (a) characterized by random fluctuation of the directors of the statistical elements of the chain of length l and thickness d; A worm-like (Porod-Kratky) chain (b) characterized by continuous variation of the director along the contour.

We note in passing that *Odijk*'s formulation tells us how to improve the stiffness of the individual chain by understanding that the diameter of the segment is the most important parameter. This may be an important consideration for further work aiming for chemistry and physics with individual macromolecules at the level of nanotechnology.

Shape persistence is achieved by direct synthesis of a bond pattern of the constitutive elements of the chain which prevents randomisation of the bond directors. Hairy-rod macromolecules (HRM) are a good example. Here, flexible side-chains act like a polymer bound solvent shell, disguise the backbone elements and help to achieve processability.

Figures 1 and 6 summarize what has been learned in the past 15 years on the relation between chemical structure and persistence in linear HRM. Substituted poly (p-phenylene)s[10] and cellulose derivates[11] are key examples where persistence is achieved by fixing the conformational angle between constitutive units.

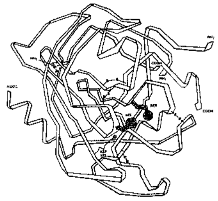

Fig. 3. Example of a shape persistent fold-structure of a globular protein (chymotrypsin) exhibiting fixed spatial relationships between segments far apart on the chain trajectory.

Phthalocyaninatopoly(siloxane)s have attracted interest as examples in which the very dense packing of the constitutive units prevents random fluctuations of the chain trajectory. P is therefore as large as one micrometer.[12] Similarly, helical polypeptides, e.g.

copolyglutamates[13] have very large persistence length. Shape persistence envisages – in fact – any defined shape of an object. The synthesis can be directed such that severe steric hindrance between the constitutive units enforces a particular shape: this is the case for dendrimers of high generation number, dendronized linear macromolecules and the like. A further approach is folding of linear flexible macromolecules into a secondary or tertiary structure then characterized by rigidity. The best known example is the folding of proteins, that is linear biogenic polypeptides into three-dimensionally well defined globular structures for which Figure 4 gives a schematic outline.

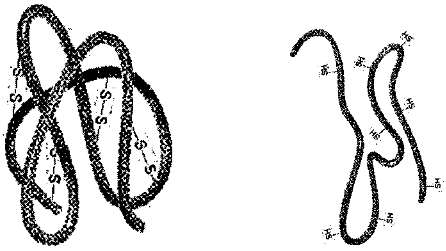

Fig. 4. Folding and unfolding of linear (bio) macromolecules: How to achieve a precise and non-random fold pattern in <u>synthetic</u> macromolecules is problem and challenge.

But also in the field of DNAs and RNAs we find many examples of regularly folded structures. The processes of folding and unfolding remain essentially a puzzle. So far no synthetic analogue exists in which a linear (co-)polymer has been demonstrated to undergo a regular random-coil to specific globule transition as indicated by Figure 4.

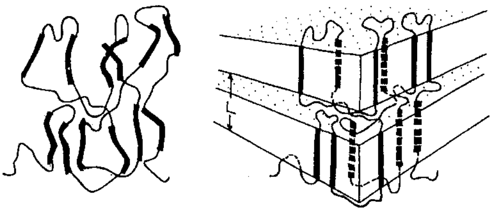

Fig. 5. The solidification model of polymer crystallization as an example how structure in the globular macromolecule relates to supramolecular texture in semicrystaline polymers.[4]

It remains a major challenge to macromolecular chemistry to design polymers which would undergo such transitions and would yield identical fold structures every time the transition is made. The underlying theory on inter- and intramolecular interactions and the molecular dynamics controlling the trajectory of folding are not sufficiently developed to predict progress in the near future. More theory is clearly needed. And yet, it needs to be reminded, that folding mechanisms and consequenses of folding processes are of outmost importance to the field of the industrially important polymers.

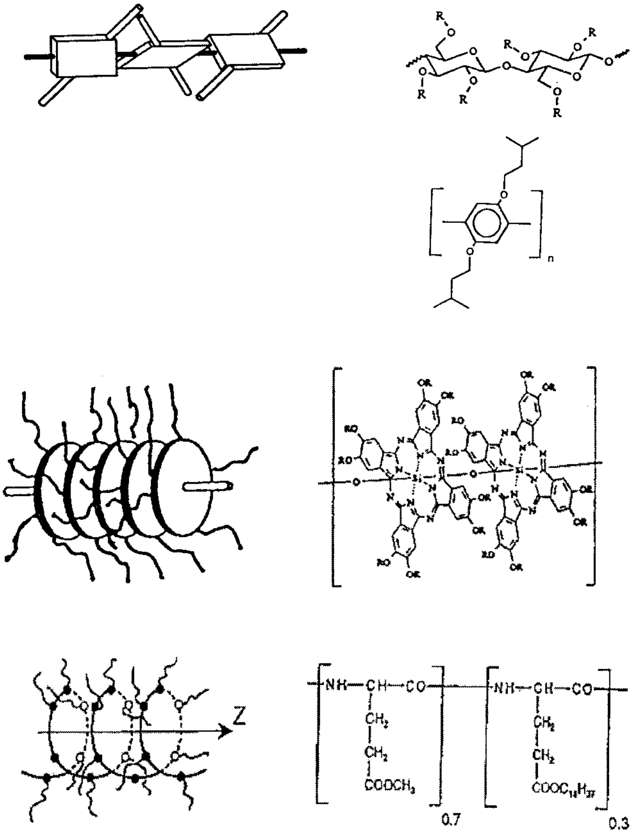

Fig. 6. Structure of HRMs obtained by suppressing bond fluctuations; from top to bottom: Fixation of the connective bond conformational angle; steric hindrance of bond fluctuations along director axis; stabilization of a secondary (helical) structure by weak bonds (H-bridges) along trajectory.[16]

Even here, there remain many open questions as to what precisely determines the fold-length and – thereby – the degree of crystallinity in ordinary semicrystalline polymers and fibres manufactured from such polymers. The "solidification-model"[14] as sketched in Figure 5 has been widely accepted, but its chemical consequences in terms of fixing crystallinity by copolymer structure has not been properly exploited.

Assemblies and Constructs

Although it is very important to understand the chemistry and physics of individual macromolecular objects, the final goal is, nevertheless, to use them as building blocks for large scale "molecular devices" or materials. It is important to differentiate between "macromolecular architecture" and "supramolecular assembly". The former refers to the topology of the individual macromolecule and comprises all stable fold-structures where as the latter refers to the interaction and topology of two or many of the individual objects. Depending on methods and conditions macromolecular objects will undergo mutual interactions and reactions leading to new structures composed of the constituent objects in a process sometimes called "self-organization". Examples for supramolecular assemblies or – what is used as a synonym – supramolecular architectures of HRM are shown in Figure 7.

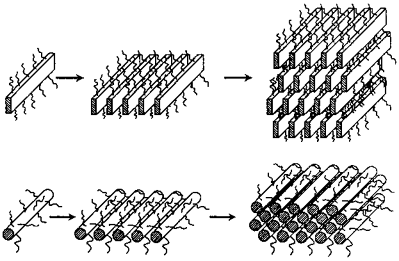

Fig. 7. Forms of supramolecular architectures of HRM.

The relation between the shape of the constituent HRM and the symmetry of packing is self-evident. In this context the word "self-organization" needs to be used with caution. In most cases structures described in literature are merely one out of many phases which can be obtained from the same constitutive units depending on the phase diagram and the parameters described therein. In other words, it remains to be clarified what the precise set of parameters (temperature, solvent, pressure, further components) are under which a specific supramolecular structure can be obtained. The hope[15] that one can make "programmed" (macro)molecules to achieve "programmed" functional architectures remains somewhat elusive on closer inspection.

More interesting are so-called constructs, that is super-structures to be obtained by processing (macro) molecules on the nanoscale level. The methods used for this purpose could be called "synthesis of supra-molecular architectures". The Langmuir-Blodgett assembly of HRM serves as a model case.[11, 16]

Figure 8 shows the principle of the process by which layered assemblies of HRM can be constructed with a deliberately chosen sequence of layers differing in both chemistry and the relative orientation.[17]

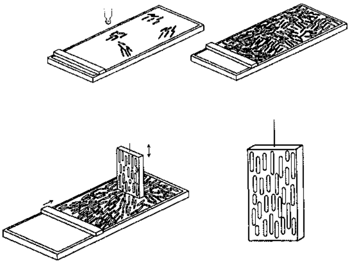

Fig. 8. Processing of HRM by the Langmuir-Blodgett Method to obtain layered assemblies.[2,16-18]

An actual example of a model construct which has been "synthesized" accordingly from two different cellulose derivates, namely isopentylcellulose and pentenylcellulose, is shown in Figure 9 together with the X-ray evidence (grazing incidence diffractograms) which proves the success in achieving a specific pattern of the layer sequence.[11]

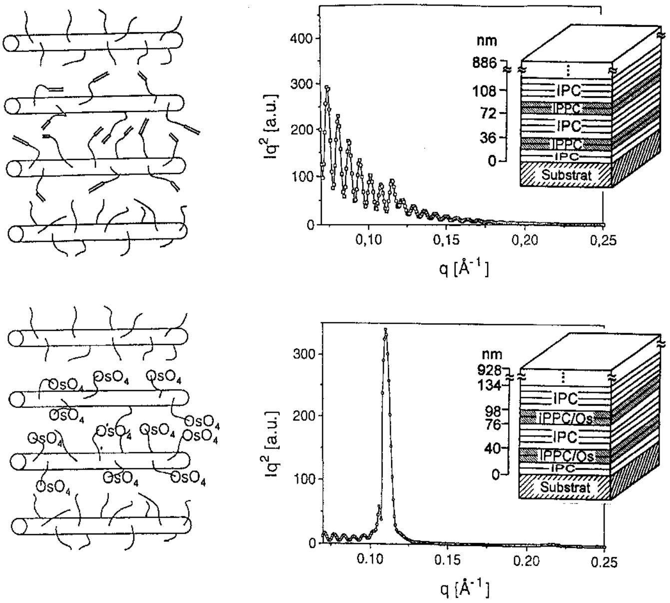

Fig. 9. Example of a construct obtained by processing cellulose based HRM via the LB-Method (above) and subsequent topochemical modification.[11]

The construct obtained was treated with osmium tetroxide which reacted topochemically with only those layers containing double bonds. As a consequence a new architecture was obtained exhibiting the expected diffractogram. Many interesting architectures can be obtained by this combination of molecular design (Hairy-Rod-Macromolecule type) and processing on the nanoscale making use of the LB-Process.

Examples are a construct having selective membrane properties because of defined spaces length between the backbones of the HRM[11, 13] and a device the function of which is entirely based on the oriented deposition of a precise number of monolayers between two electrodes making use of the LB-technique. This device works as a light emitting diode, the light being polarized along the molecular axis of the constitutive HRM which is a poly (p-phenylene) derivate.[18]

Concluding Remarks

It is worthwile noting that "order", "precision" and "perfection" need to be defined with regard to length and time scales. Again, HRM may serve as an example. The side chains attached to the backbone elements are liquid-like and form a disordered shell around the main chain. Nevertheless, a rather perfect layered assembly is constructed from such objects where "perfection" relates to the sequence of and the distance between indivual layers. However, within a given layer, the correltion between adjacent HRM is of nematic Type[12] and there exists in-plane disorder characterized by disclinations on the length scale of 100-1000 nm.

This is not unusual and is seen more or less well expressed in all forms of supramolecular architectures and even globular proteins can only function in their native state because of segmental dynamics which allows transport of substrate, water and salt to and from the reactive sites.

Thus, the understanding and "design" of molecular dynamics as an important feature in supramolecules will also be the key element in the design of artificial "motors", that is functional nano-scale entities which could serve as transporters for molecules in synthetic molecular scale factories. These few hints may suffice to show how shape persistent macromolecules are essential objects in the context of nanotechnology. They have considerable scope in such fields as microelectronics, cosmetics, pharmaceutical technology and biomedicine. The line of thought leading from the concept of design and engineering in macromolecular dimensions to application for advanced technologies combines synthesis of macromolecular objects with practical concepts of processes which allow to handle and organize macromolecular objects on the nano-scale. The technologies addressed comprise among others sensors and actuators, catalysis, membrane separation, controlled transport and energy conversion.[19]

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