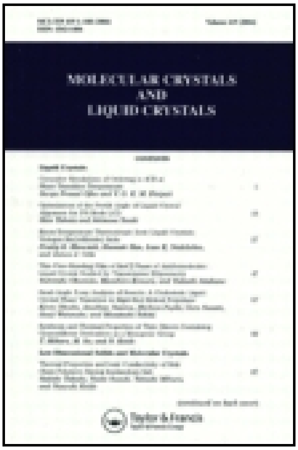

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PHOTOCHEMISTRY AND PHOTOPHYSICS OF NANOCOMPOSITES PREPARED FROM ROD–LIKE MACROMOLECULES BY LB–TECHNIQUE

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Abstract The design of macromolecules described as "hairy rods" proved to be most successful in the attempt to construct layered structures of optimized quality by the Langmuir–Blodgett–technique. Novel types of supramolecular architectures could be realized best described as "molecularly reinforced liquids". First attempts to build prototype devices based on layered assemblies of these non–conventional polymers are reported. The relative orientation of the rod–like macromolecules can be changed deliberately in each layer as well as the chemical nature of the polymer such that true nanocomposites are obtained.

INTRODUCTION

The Langmuir–Blodgett (LB)–technique provides for an unique approach to achieve supramolecular architectures of layered assemblies of suitably designed macromolecules. Originally designed to build–up layered assemblies of simple long chain aliphatic carbocyclic acids and their salts it was later developed into a sophisticated method to produce supramolecular architectures useful to test molecularly controlled processes of energy transfer, charge carrier motion, energy conversion and molecular recognition [1-3]. Unfortunately, most of the transport properties for which the layered assemblies were thought to be useful study objects are strongly influenced if not completely determined by grain boundaries and other packing defects arising from the crystalline nature of the multilayers.

In the light of the shortcomings of the traditional approaches a new type of molecular design was introduced in which the formation of a layered structure at the air–water–interface depends on the form–anisotropic shape of non–amphiphilic entities. Rod–like macromolecules decorated with short and flexible hydrocarbon side chains as to provide the rods with a molecularly defined skin of solvent segments have been designed and tested [4-13]. They are spread from conventional solvents to the LB–trough. They are compressed to a two–dimensional nematic liquid–crystal phase. The latter is transfered to solid planar substrates. A single layer is transfered by each dipping and undipping. Orientation of the rods is observed to occur in the dipping direction, so that anisotropic multilayers are obtained. The multilayers behave as solids with regard to their mechanical properties but as liquids with regard to their optical and other properties [14-16]. In fact, the architecture of these layers is best described as molecularly defined rods embedded in a continous matrix of the liquid–like side–chain segments. The exact description and consequences of this unusual architecture which falls into the category of "molecular composites" is outlined in the following.

DESIGN OF HAIRY–ROD–TYPE POLYMERS

The design principles for the hairy–rod–type polymers are exemplified by Figure 1 with examples of molecular structures which have been investigated in our group. Phthalocyaninatopolysiloxanes substituted with alkoxy chains at the perimeter of the phthalocyanine moiety give high quality LB–layers [7-9]. A further example is provided by copolyglutamates in their helical conformation. Copolymers in which short and long side chains are mixed randomly proved to be highly useful for LB–assembly [6,10,11]. The rod–like character is here achieved by the helical conformation of the macromolecule.

Cellulose is an intrinsically stiff and worm–like macromolecule. If functionalized with alkoxy groups, it proves to be a further example of the hairy–rod structures [12]. Finally, polysilanes can be synthesized which conform with the ideas of a rod–like behavior, if the side groups R are designed to introduce sterical hindrance with regard to bending and to provide flexible groups directed to the outside of the molecule at the same time [13].

THE ARCHITECTURE IN DETAIL

The quality of the layered assemblies and details of their internal architecture can be analyzed by a combination of different methods such as X–ray diffraction, spectroscopic (IR, UV–Vis, Raman) techniques, wave–guide spectroscopies etc.[11]. As an example Figure 2 shows the small–angle–X–ray diffraction obtained from an assembly of 28 polyglutamate layers on a silicon wafer. The insert in Fig. 2 represents a molecular picture of the architecture with only two of the 28 layers drawn. The thickness of an individual layer depends on the choice of the side chains and may vary between 1.5 and 2 nm.

The degree of orientation of the rods within a layered assembly can be characterized by optical spectroscopy, birefringence or diffraction data. The order parameter depends on the flow conditions during the build–up of the assembly and can be improved by annealing of the layered assembly afterwards. It may reach quite high values. "Thick" layers could be constructed suitable to be used as wave guides which consisted of 1000 and more individual layers. Brillouin scattering was recorded from guided waves in such layers and was analyzed to provide the mechanical tensor elements of such molecular composites [14,15]. Another experiment which relies on the wave guiding properties of the LB–assemblies is plasmon spectroscopy [11,17]. The experimental set–up is sketched in Figure 3 together with the results obtained in terms of shifts of the plasmon resonance of a thin silver film on which several monolayers of copolyglutamate had been transfered. Based on such results the construction of an optical memory has been demonstrated [16] based on the fact that small changes in thickness of the layers induced by photoablation give rise to changes in the angular position of the plasmon resonance. Thus information stored as local thickness changes is read out in terms of a change in contrast with regard to the position of the probe beam at constant coupling angle.

This process can be enhanced by doping of the layers with oleophilic dyes. Fairly high amounts of oleophilic dyes can in fact be dissolved in the layers which is a simple consequence of their nature as molecular composites [10]. Further types of molecular composites can be assembled using different types of hairy–rod macromolecules. Alternating layer structures are obtained by successive transfer of either of two compounds. As an example, the molecular architecture of an assembly of alternating double layers of PCPS and copolyglutamate is shown in Figure 4. Not only the chemical structure may alternate or follow any other design principle in terms of the layer–sequence but also the relative direction of the rods in each layer with regard to a frame of reference. The latter follows from the fact that the rod axis direction is related to the dipping direction. Therefore, if the substrate is rotated in–between subsequent dipping cycles the rotation angle will be identified as the angle between subsequent layers in the assembly. The possibilities offered by the assembly technique can be used to device a series of experiments which aim for an understanding of the molecular details of charge carrier motion. The current–voltage characteristics of assemblies of monolayers of PCPS between an ITO and a liquid mercury electrode shows an asymmetric transport behavior. The conductivity is space charge limited. The layers sustain quite large field strength up to $6 \cdot 10^5$ Vcm^{-1}. A room temperature conductivity of $1 \cdot 10^{-7}$ S cm^{-1} can be deduced at small field strength.

The conductivity behavior changes dramatically when a single monolayer of a cellulose derivative as indicated in Figure 1 is inserted in the center of the layered assembly. The conductivity drops by 3–4 orders of magnitude and also the shape of the current–voltage characteristic changes substantially. A further dramatic change is induced by a short annealing step which improves the density of packing of the layers thus removing trapping centers. An excellent rectifying behavior is now verified as expected for PCPS being a hole conductor.

CONCLUSION

Hairy–rod type macromolecules offer a new design principle for layered assemblies in conjunction with the well known LB–procedure. Different types of molecular architectures can be realized which are all characterized by the fact that molecularly defined rod–like entities are embedded in a continuous matrix of side chain elements of essentially liquid character. Thus a novel type of material is at hand, best described as "molecularly reinforced liquid". The same compounds can also be processed by spin–coating from solution or by other shaping processes but their greatest relevance may relate to the LB–technique to obtain extremely well defined layered structures. The optical transparency and their insensitivity to high field strength offers possibilities toward the design of electrooptical, all–optical [11] and field–effect devices [19]. Their potential has been barely exploited since the discovery of the design principle in 1986 [7]. It is, however, sure that these molecules open up a new and exciting chapter in the attempt to build supramolecular structures of materials in a rational way and thus, we will hear and learn a lot more about "hairy–rod" macromolecules in the coming years.

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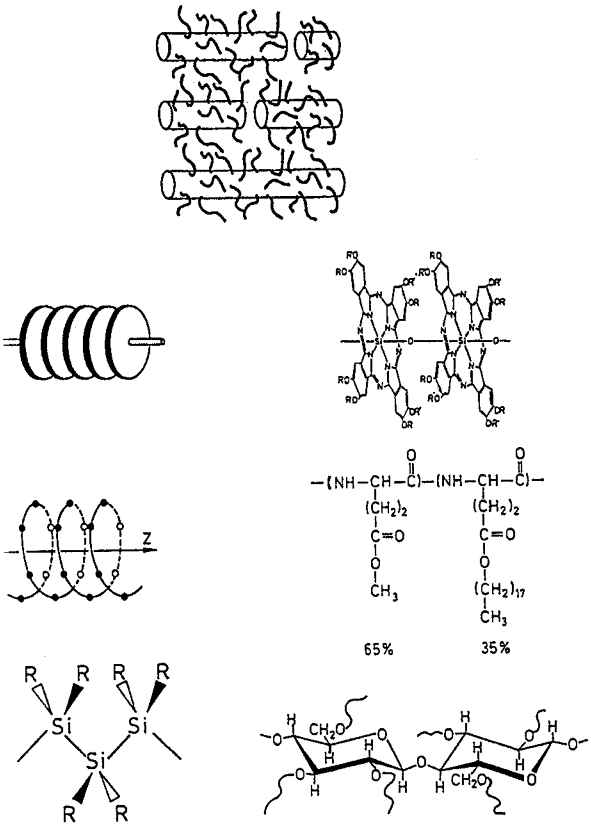
Fig. 1 Examples of hairy rod type polymer structures



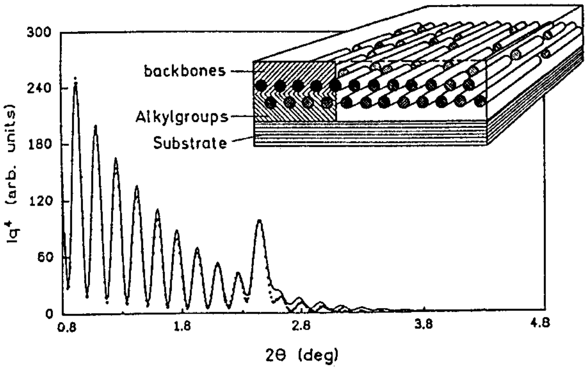


Fig. 2 X-Ray small angle diffraction of 28 monolayers of copolyglutamate on Si-wafer

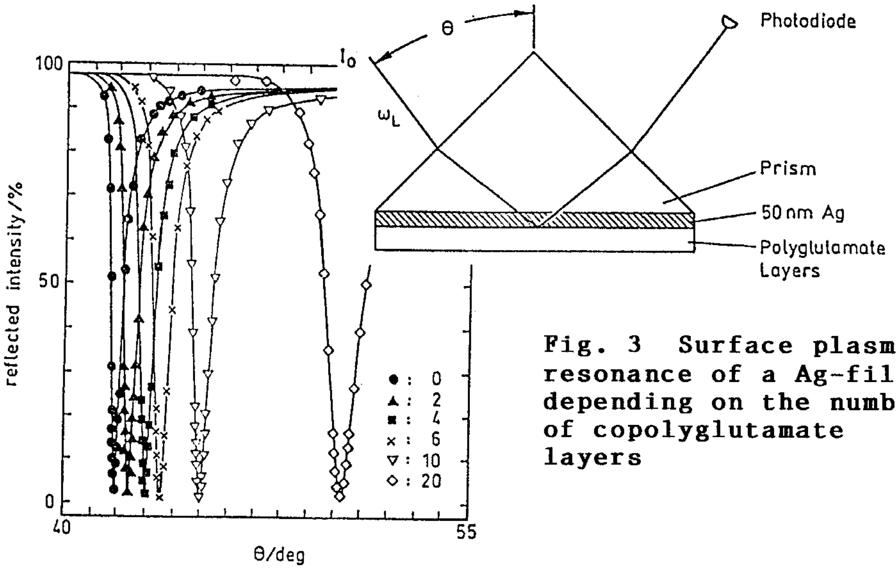


Fig. 3 Surface plasmon resonance of a Ag-film depending on the number of copolyglutamate layers

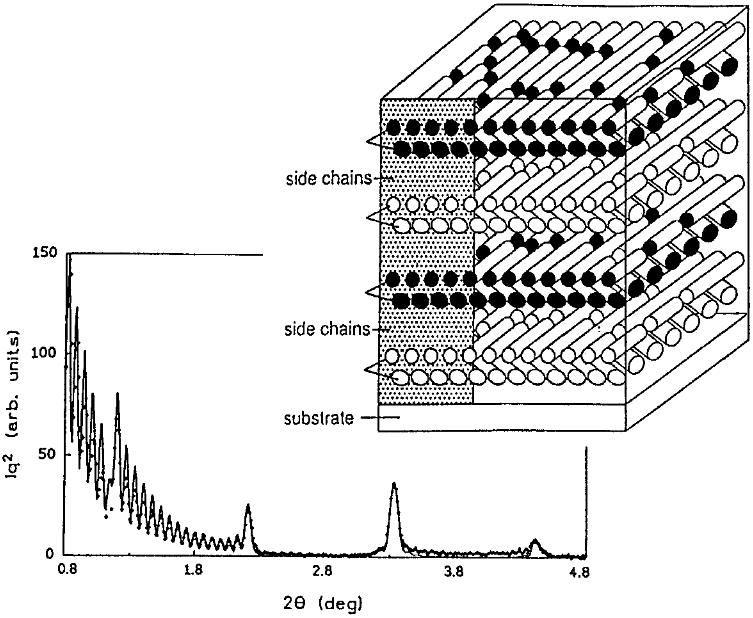


Fig. 4 Nanocomposite of alternating double layers of copolyglutamate and phthalocyanine polymer and corresponding diffractogram