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Novel Architectures of Macromolecular Systems*

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An important thrust in modern macromolecular chemistry is to construct complex architectures either directly from monomer units, or to design macromolecules capable of forming a desired superstructure by self-organization. Chain-rigidity is an example of a structural principle leading to self organization depending on the aspect ratio of the molecular objects and their mutual interactions. These molecularly defined objects serve as the building blocks of systems for which ultrathin layers composed of hairy rod macromolecules (HRM) are an example. Depending on architectural details layered architectures of HRM are models for molecular nanocomposites, exhibit interesting optical, electrochemical, dielectric or barrier properties. They are also designed to be used in devices the performance of which depends on molecular interactions. Thus, the design of novel macromolecules comprises the design of supramolecular architectures and functions based on architectural principles from the very beginning. A systems approach is emphasized as part of the synthetic strategy.

Design Principles of Nanocomposites

Rational Design of Supramolecular Materials

The target of research is the rational step-by-step construction of molecular solids useful for a variety of advanced technologies in which control of the molecular and supramolecular architecture is a prerequisite to function. The philosophy and strategy is outlined in scheme I. Molecularly defined objects of the same or different kind are assembled in a controlled manner. Supramolecular architectures of materials arise which have specific functions by design. The targets are materials for micro (and nano-) mechanics, membranes, catalytic systems, photonic devices, LC-displays etc.

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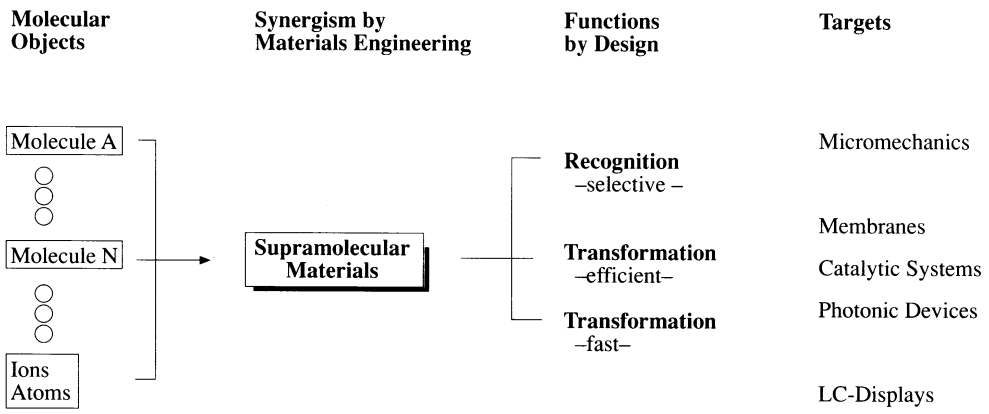


Hairy-Rod Macromolecules (HRM) and the Assembly Process

Our approach to the problem starts by definition and design of shape persistent macromolecules, Fig. 1[1–8]. They serve as objects to be assembled in a first step as monolayers at the air-water-interface of a Langmuir-trough as shown in Fig. 2[9–11]. These are transferred to solid substrates by a dipping process. Flow alignment of the rod-like element occurs in the course of the transfer which has been shown to work as a two-dimensional analogue of an extrusion[9].

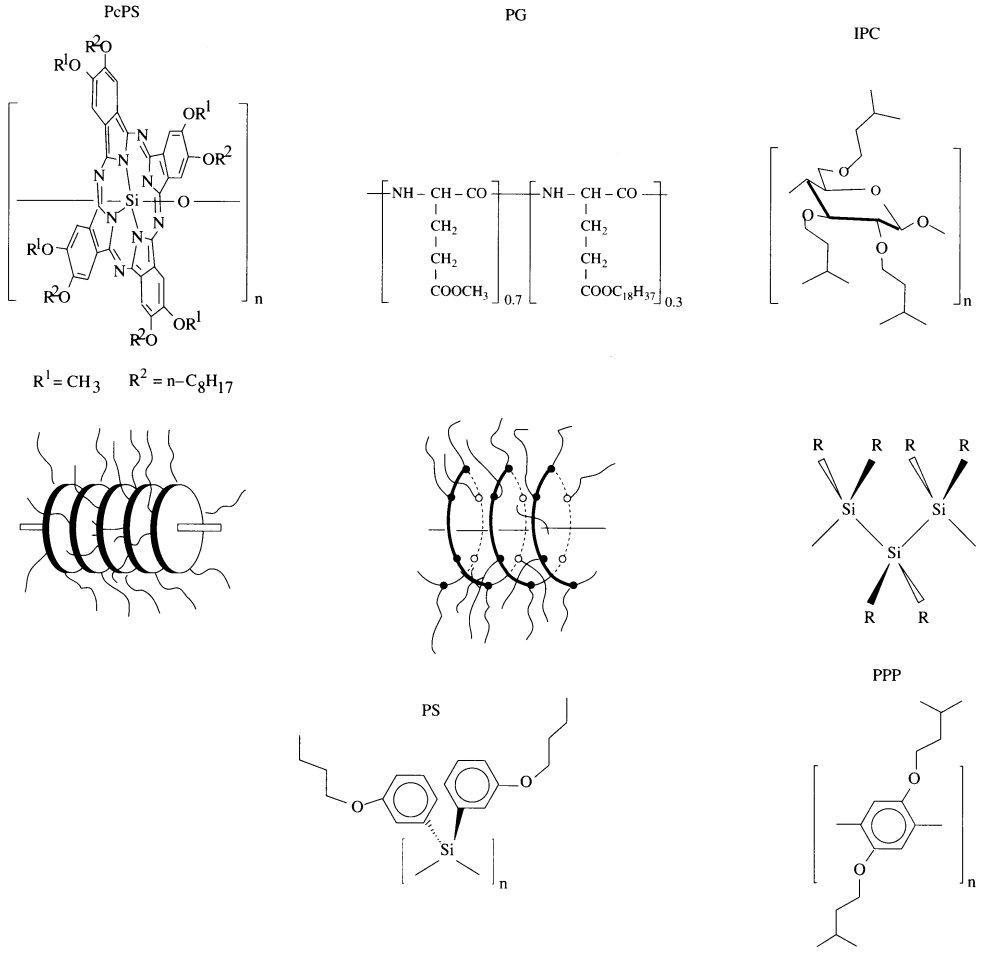


Figure 1. Typical hairy rod molecules
PsPS = phthalocyaniato-(poly)siloxanes; PG = polyglutamate; IPC = Isopentyl cellulose; PPP = poly (*p*-phenylene)

Rod-like macromolecules with their backbones decorated by numerous short and flexible hydrophobic side chains (see Fig. 1) have been thus designed for construction of layered films by this technique[1-9]. The shape persistent backbones are surrounded by a liquid-like skin of side chains. The layered films are best described as molecularly reinforced liquids where the backbone elements are embedded in a continuous matrix of interdigitating side chains. The build-up process results in a homogeneous orientation of all backbone elements within a given layered assembly[9,10]. In general, the layered assemblies of these hairy-rod macromolecules (HRM) have a liquid-crystalline texture and are without any pinholes at all[11,12]. When rods of different chemical composition are used, a series of different architectures is achieved, e.g. nanocomposites composed of layers alternating in chemical structure and direction of the rods. Such systems show interesting optical, electrochemical and electrical properties when properly composed. Furthermore, guest molecules can be placed ('doped') into the matrix of the side chains in which the rod backbones are embedded. Thus, when ionophores are chosen as guests, ion sensitive membranes and ion sensitive FET-devices can be achieved[1-3,15].

Nanocomposites and Their Properties

The excellent mechanical and optical properties of such composites are demonstrated by Fig. 3. Here the architecture (simplified) of a multilayer film of copolyglutamates is shown together with the components of the mechanical tensor determined from a layered assembly of total thickness of ca. 1 μm (500 layers) by a light scattering technique (Brillouin spectroscopy). The anisotropic character of the composite is thus proven[13].

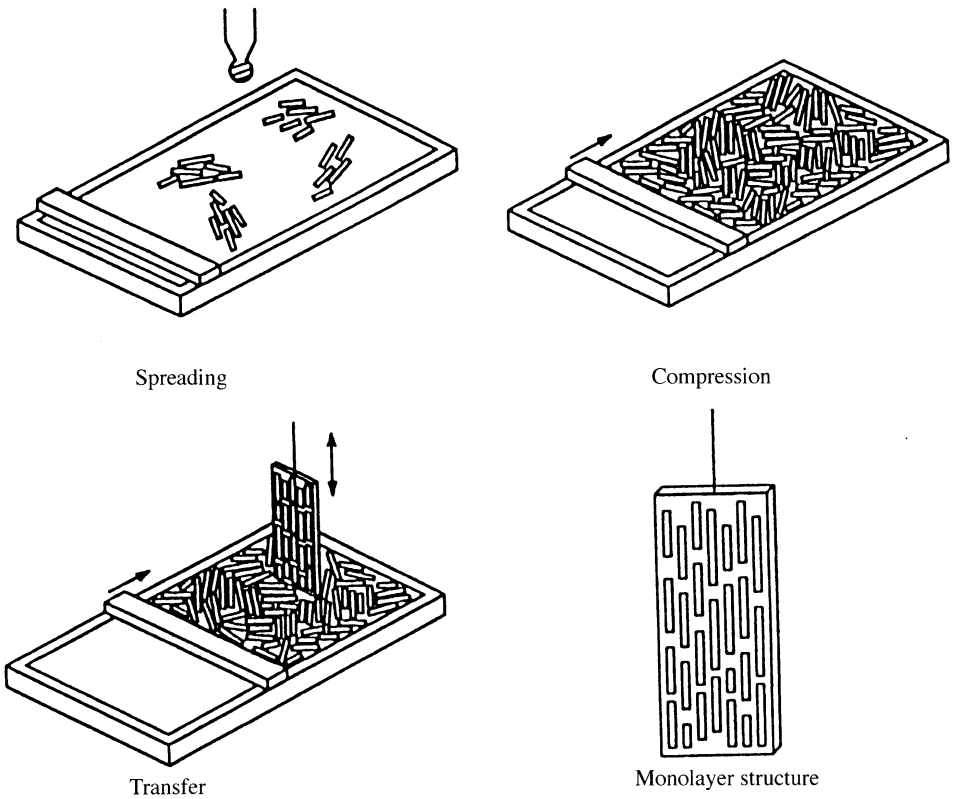
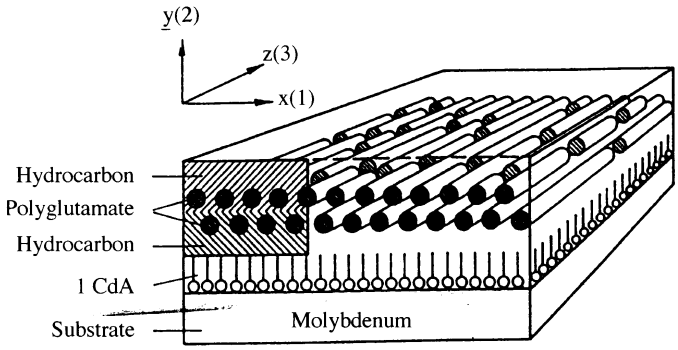


Figure 2. Construction of monolayers[1-4]



d Angstroms	c_{11}	c_{13}	c_{33}	c_{55}	c_{12}	c_{66}
			GPa			
16.5	5.66	4.20	12.22	1.26	3.45	1.10

Figure 3. Mechanical modulus of a multilayer assembly of copolyglutamate

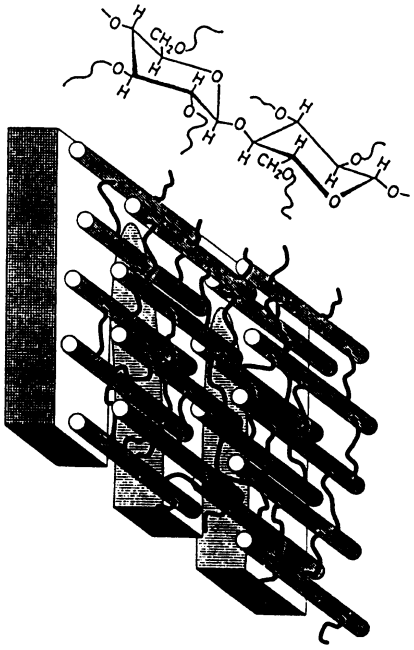


Figure 4a. Crosslinked multilayer of cellulose derivatives on top of porous substrate

The fact that multilayers of photocrosslinkable HRM are readily formed and that the introduction of crosslinks gives rise to solvent swellable stable ultrathin films supports the idea to use these systems as liquid separation and/or transport membranes. HRM based on cellulose alkylethers or coply(glutamate)s can be used to construct membranes if transferred by the LB technique to a porous Celgard 2400 ® film as the substrate[5].

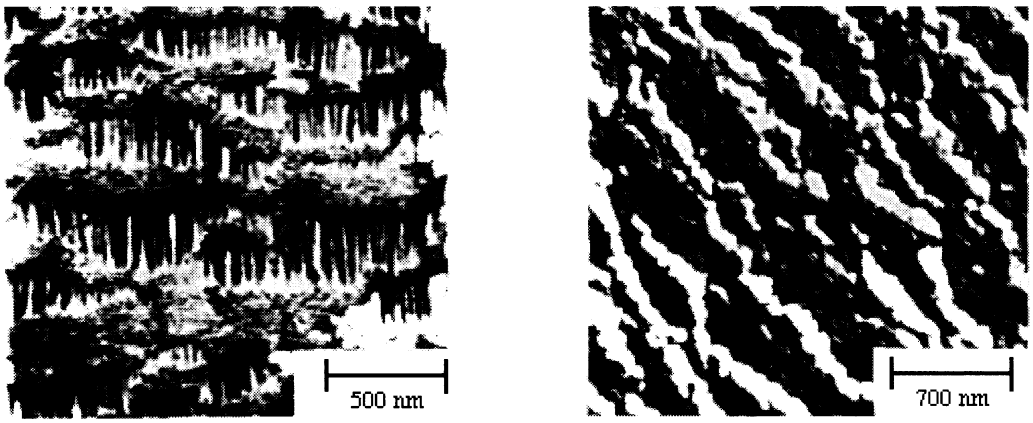


Figure 4b. Celgard 2400 film before and after coverage by 40 ML of crosslinked cellulose derivative (TEM-replica)

Because of the small layer thickness of less than 10Å for each individual layer[6] and the possibility to introduce functional groups, cellulose ethers are most promising for the design of membranes. The ability to undergo crosslinking is achieved by attaching a few cinnamoyl residues to the cellulose backbone; all residual OH-groups are alkylated by isopentyl residues. Fig. 4a shows schematically the architecture of such a crosslinked multilayer assembly on top of a porous substrate. Fig. 4b shows the actual porous Celgard 2400 ® -film before and after coverage. These membranes serve as size exclusive separation devices or osmotic membranes, since they are constructed like a sieve: only molecules of smaller diameter as the distance between the bars can penetrate[5].

Design of Polarized Light Emitters

Another application is demonstrated by Figs. 5a, b. Here HRM's based on poly-p-phenylene substituted with alkoxy side chains are used to construct an electroluminiscent device which emits polarized light in the visible region of the spectrum. LED's based on polymers have been pioneered by the Cambridge group in the recent years and have become a rapidly growing field of research. The device shown here is the first rational approach to create polarized light as is necessary for background illumination of LCD-devices and computer screens.

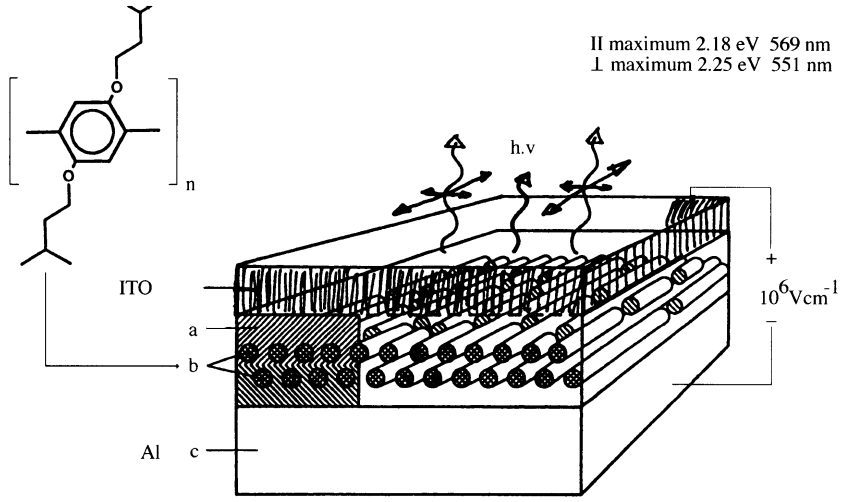


Figure 5a. Light emitting device (LED) (see ref. 14)

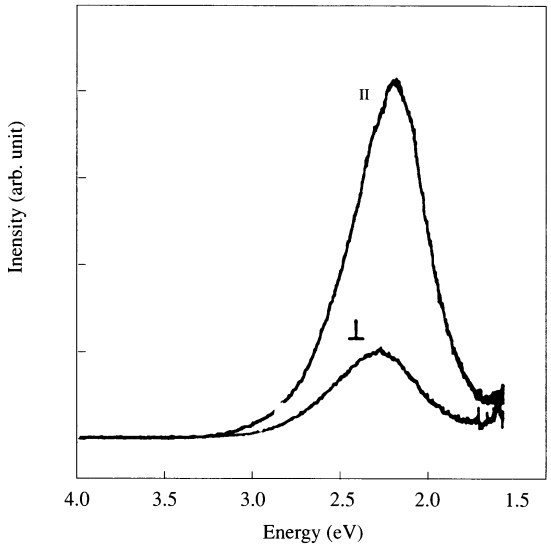


Figure 5b. Polarized light emission from the device shown in Fig. 5a (100 ML, ext. quantum eff. 4×10^{-3})

Other phenomena related to charge carrier transport have been described, among other the construction of spatially and electronically defined tunneling barriers consisting of a single monolayer of an insulating HRM (cellulose derivative) placed in the middle of a multilayer assembly of semiconducting phthalocyanine polymers (PCPs, see Fig. 1)[16]. Furthermore, the same polymers (PCPs) have been evaluated for their electrochemical properties. Thin films of 1-100 ML show facile eletron and ion transport in electrochemical oxidation and reduction in aqueous and non-aqueous media[11].

Construction of CHEMFET

A final example is given in Fig. 6 describing the set-up of a field effect based ion sensor (CHEMFET) for monitoring the ion concentration in electrolytes. This set-up was developed[15] to measure the Na or Ca-ion concentration in aqueous media and relies on the presence of multilayer arrangement of ionophore doped HRM's on top of the MOS-FET which is in contact with the electrolyte. The time and environmental stabilities of such devices is excellent and compares well with conventional glass electrodes. As explained in Fig. 6 the acronym ELBOS device was used to describe the special composition. The quantity to be measured is the change in capacitance which in turn is controlled by the interfacial potential between electrolyte and LB-membrane and MOS-surface respectively The LB-membrane itself consists of 10-30 ML of a copolyglutamate doped with an ionophore with selectivity for the ion in the aqueous electrolyte to be monitored. In order to prevent loss of the ionophore to the electrolyte the layered structure is covered by a few (ca. 2-6) ML of PCPs which works as a diffusion barrier for the ionophore but not for the ions to be detected.

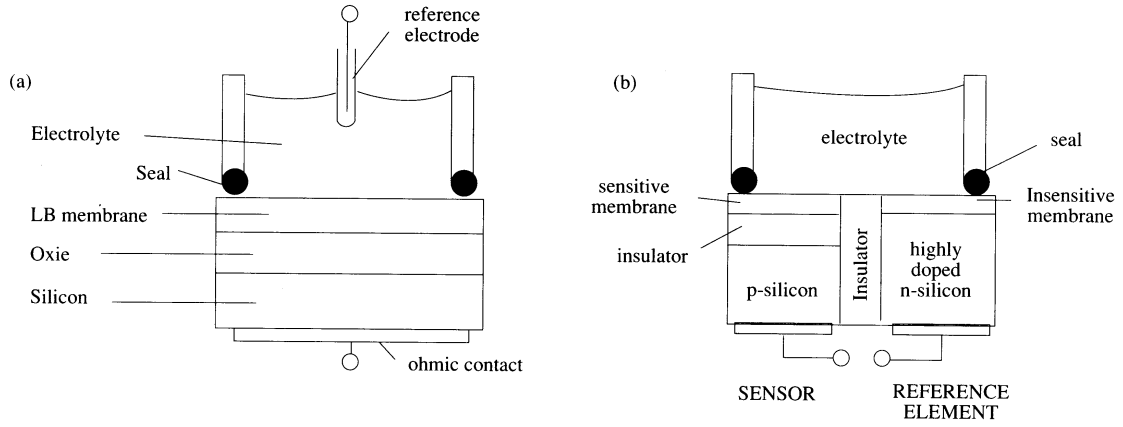


Figure 6. ELBOS-CHEMFET to monitor ion concentration in aqueous electrolytes[15] a) principle of the set-up; b) complete device layout

Fig. 7 shows the exceptionally fast response of the ELBOS device to instantaneous changes of the ion concentration. This is of course due to the fact that the sensitive layer which controls the surface potential is only a few nm thick.

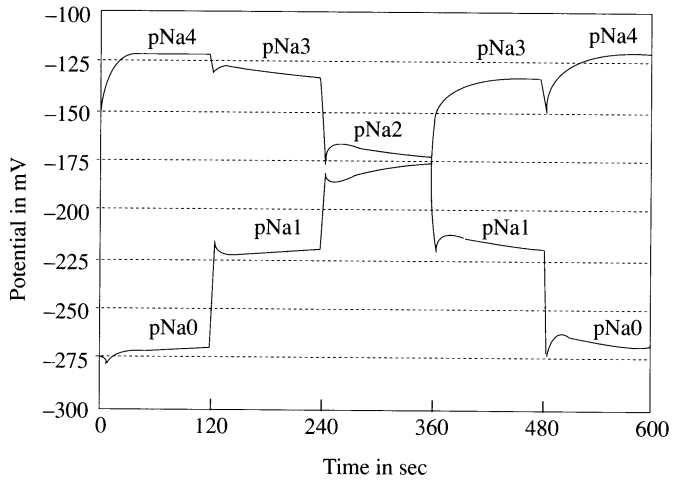


Figure 7. Time dependent response of the ELBOS device in Fig. 6b (the LB-layer was doped by a Na-ionophore) to instantaneous change in Na-ion concentration.

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