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Functional Polymeric Materials: Complexing Amphiphiles as Structure-Inducing Elements

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Summary: Self-assembly of polymeric comb-shaped supramolecules is a powerful tool to prepare functional materials. Enhanced conductivity due to hexagonal self-organization of conducting polyaniline and polarized photoluminance in solid-state films of rodlike poly(2,5-pyridinediyl) obtained by removing hydrogen-bonded side chains from the aligned thermotropic smectic phase are two examples. Hierarchically structured materials are formed when the self-organization of block copolymers is combined with that of comb-shaped supramolecules. These form the basis for tunable nanoporous membranes, nano-objects and materials with anisotropic properties such as tridirectional proton conductivity.

Keywords: amphiphiles; block copolymers; nanotechnology; self-organization; supramolecular

Introduction

In recent years we developed a concept to prepare functional polymeric materials based on the self-organization of comb-shaped supramolecules.[1] An essential element of these comb-shaped supramolecules is a polymeric backbone to which relatively short side chains are attached by physical interactions such as hydrogen bonding, ionic bonding, coordination or a combination thereof. The backbone can be flexible or rigid and may furthermore be connected to another polymer block. Depending on the precise nature of the systems involved, the presence of the side chains serves several purposes such as processability, plasticizing, doping, swelling, hierarchical structures, cleavability, etc.

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Comb-shaped Supramolecules

In general, the presence of the side chains will lead to ordering at a relatively small length scale of ca 3-5nm in bulk materials.[2,3] An explicit example is given by poly(4-vinylpyridine) (P4VP) and pentadecylphenol (PDP) or nonadecylphenol. A comb-shaped architecture arises due to strong hydrogen bonding between the phenol and the pyridine group. At sufficiently low temperatures the nonpolar alkyl tails phase separate from the more polar material. Transmission electron microscopy (TEM)[3] shows that a lamellar structure is formed with a long period of ca. 3.5 nm (see Figure 1). As demonstrated by small angle X-ray scattering (SAXS),[2] in the case of PDP this microphase separated morphology is formed in the melt below ca 60°C. Since P4VP itself has a glass transition (T_g) of 150°C, we observe a huge plasticizing effect. The stoichiometric mixture (i.e. one PDP molecule per pyridine group) has a T_g below room temperature. Even though it is in a microphase separated state, the polar layers remain fluid. Two examples have been constructed where the side chain induced self-organization is actually used to endow functionality.

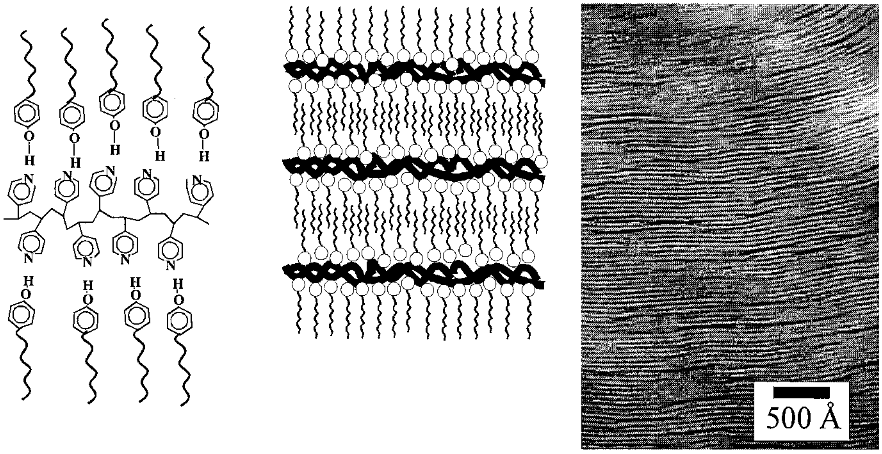

Fig. 1. Comb-shaped supramolecule of pentadecylphenol (PDP) hydrogen bonded to poly(4-vinylpyridine) (P4VP). Cartoon and transmission electron microscopy picture of self-organized lamellar structure.

Hexagonal Assembly of Conducting Nanowires

As a first example we mention polyaniline (PANI) based systems.[4] The iminic nitrogens of PANI are nominally fully doped using camphor sulphonic acid (CSA) to yield PANI(CSA)$_{0.5}$

to which hexylresorcinol (Hres) is further hydrogen bonded which leads to PANI(CSA)$_{0.5}$(Hres)$_y$. The complex nature of the system is clear from the fact that both hydroxyl groups are required to prevent macrophase separation. For a sufficient amount of Hres ($0.5 \leq y \leq 2.0$) self-organization results in a hexagonal array of cylinders, as witnessed by the characteristic $1:\sqrt{3}:2$ SAXS peaks, consisting of PANI(CSA)$_{0.5}$ chains plus the phenolic groups of the Hres molecules. At the critical amount of Hres for structure formation ($y \cong 0.5$), the conductivity increases orders in magnitude. This may be attributed to the more extended chain conformation of the doped PANI compared to the more "compact" coils for small amounts of Hres. Why a hexagonal rather than lamellar structure is formed is not known yet. In this application the particular combination of amphiphiles allows for processability, doping and structure formation with concurrent enhanced conductivity.

Polarized Luminance

This example is similar to the previous one except that also the *cleavability* of the amphiphiles is used: the hydrogen bonded species are removed after self-organization and processing by simple evaporation after the chains have been aligned by shear flow. This leads to a highly ordered solid state film of rigid rod polymers (Figure 2).

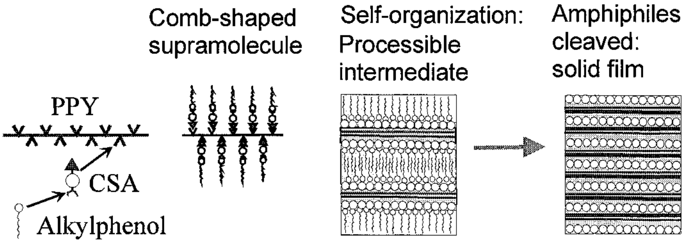

Fig. 2. Illustration of procedure to produce ordered solid state films of rigid rod polymers via comb-shaped supramolecule intermediates.

The system is poly(2,5-pyridinediyl) (PPY) consisting of para-coupled pyridyl rings. PPY is a very stiff polymer, approaching a rigid rod. In contrast to most other schemes to provide charges into the chain, protonation with CSA does not significantly reduce the photoluminescence quantum yield.[5] Further hydrogen bonding with octylgallate (OG) leads to comb-shaped supramolecules that can easily processed and self-organize in the form of a layered structure. The rodlike entities can be oriented by simple shear. SAXS demonstrates that a highly ordered structure is formed. After evaporation of OG the corresponding highly ordered solid film is obtained exhibiting polarized luminescence.[6] Here processability is combined with structure formation and cleavability.

Hierarchical Structures

If, instead of homopolymers, suitable block copolymers are used as starting materials, characteristic two length scale hierarchical structures are formed upon complexation with amphiphiles.[7,9] The best-studied example involves a diblock copolymer of polystyrene (PS) and poly(4-vinyl pyridine) (P4VP) where pentadecylphenol (PDP) or nonadecylphenol (NDP) is hydrogen bonded to the P4VP block: PS-b-P4VP(PDP). Usually, a microphase separated morphology consisting of PS and P4VP(PDP) domains is present throughout the experimental temperature range (0-250°C) with a characteristic length scale in the order of 10-20nm. Below ca. 60°C the short length scale structure due to the comb-shaped nature of the P4VP(PDP) blocks is formed inside the P4VP(PDP) domains. Lamellar-*within*-lamellar, lamellar-*within*-cylinders and lamellar-*within*-spheres, as well as the complementary structures have all been demonstrated and imaged by TEM.[9]

Tridirectional Protonic Conductivity

An interesting example where the presence of *hierarchical* structures is explicitly used, involves proton conductivity, important for fuel cell applications. Complexation of P4VP with a strong acid, such as toluene sulfonic acid (TSA), creates a proton conducting material. If a stoichiometric complexation is used and subsequently combined with the hydrogen bonding PDP amphiphiles, self-organization leads to a layered structure below ca. 135°C, where the polar layers are proton conducting. If instead of homopolymer P4VP, the P4VP-*b*-PS block copolymer is used, a hierarchically ordered *lamellar*-within-*lamellar* material is obtained. After applying an appropriate oscillatory shear protocol to such a PS-*b*-P4VP(TSA)(PDP) sample, the macroscopic ordering is improved, although far from perfect. In this material, the proton conducting one-dimensional slabs have a preferred orientation with concurrent tridirectional proton conductivity.[10] This application uses the hierarchical structure formation, but also the plasticization. Without the latter, macroscopic ordering via large oscillatory shear would have been impossible.

Dielectric Stacks

Self-organization in block copolymer systems leads to well-ordered structures that are potentially interesting also for photonic crystals applications.[11] There are, however, several important problems to be solved before this potential can be fully realized. One of this is the large periodicity required (order of $\lambda/4$, where λ is the wavelength of the electromagnetic radiation used). A large periodicity requires high molecular weight block copolymers, which are notoriously difficult to prepare in a single crystal-like state. Here our concept may be of some use as well. Apart from inducing hierarchical structures in the case of block copolymers, the supramolecular side chains also act as very efficient *swelling agents*. In the example studied so far, P4VP-*b*-PS was used in combination with an excess of Dodecyl Benzene Sulfonic Acid (DBSA). Here, the excess DBSA hydrogen bonds to the DBSA that is stoichiometrically complexed to P4VP, thus combining again ionic bonding and hydrogen bonding. When the amount of DBSA is large, the P4VP domains are extremely swollen (the P4VP backbone is all but extended). For a molar ratio of 2.0 between DBSA and the pyridine groups of P4VP, a structure with a long period of ca. 140nm is obtained as demonstrated by TEM and SAXS. The transmission spectrum suggests that a photonic band-gap opens due to the dielectric stack.[12] Swelling of block copolymers with the corresponding homopolymers have been used by other groups to obtain similar results.[11] However, we believe that our concept may have an additional advantage due to the strong *plasticizing* effect allowing improved ordering and due to the enforced stretching of the P4VP backbone leading to large periodicities.[13]

Functional Membranes

The cleavability of the supramolecular side chains makes our materials ideally suited to prepare nanoporous materials. A most simple example concerns the preparation of membranes containing hollow self-organized cylinders with polymer brushes at the wall (Figure 3).[14]

By a proper selection of the PS-*b*-P4VP block molecular weights a cylindrical morphology of the PS-*b*-P4VP(PDP) can be obtained where the supramolecular side chains are inside the cylinders. Thus self-organization may be used to prepare hexagonally ordered films, where the order extends over macroscopic distances after the application of suitable external fields. The supramolecular side chains, accounting for no less than 75% of the material inside the cylinders, can easily be dissolved afterwards, leaving a porous membrane. Interesting possibilities arise if instead of the PS-block a low T_g block such as polybutadiene or polyisoprene is taken. After crosslinking the matrix (e.g. polybutadiene) and subsequent removal of the complexing additive by simple dissolution, a stretchable nanoporous template may be obtained. Using biaxial stretching relatively large nanopores may be obtained to which e.g. appropriate monomers and chemical oxidizing agents can be added. Subsequent partial stress relief results in a porous membrane with cylindrical pores of a controlled diameter, filled with an appropriate solution. In this way for instance conducting polymer fibres confined to nanocylinders of a controlled diameter may be prepared.

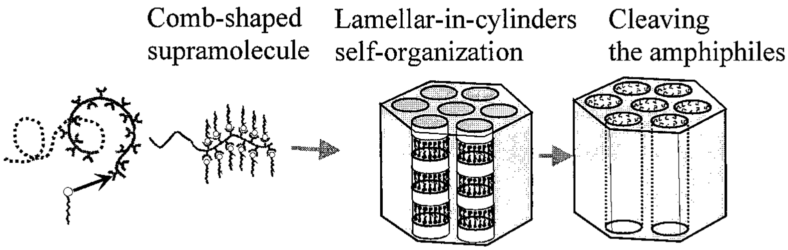

Fig. 3. Functionalizable nanoporous materials are obtained by cleaving side chains from lamellar-*within*-cylinders structure of comb-shaped supramolecules obtained by connecting amphiphiles to one of the blocks of a diblock copolymer.

Nano Objects

In the opposite case where the supramolecular comb-shaped material forms the majority phase and a hexagonal cylindrical morphology with PS-cylinders is used, the dissolution of the side chains will lead to "hairy rods".[15] Other nano objects, potentially even more interesting, may be obtained from lamellar-*within*-cylindrical hierarchical morphologies. Here, crosslinking of the P4VP slices inside the cylinders with 1,4-dibromobutane or 1,4-diiodibutane leaves the microphase separated morphology intact and results in discotic objects of P4VP disks with long PS hairs after dissolution of the side chains (e.g. PDP).[16]

Conclusion

The examples discussed in this review demonstrate that self-assembly of comb-shaped supramolecules is a fruitful way to achieve nanostructured materials with controllable functions.

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