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This microphase-separated morphology may be significant for a number of theoretical and practical reasons. First, the dynamics of these copolymers is much faster than that of corresponding homopolymers. Second, this morphology may provide a novel approach to host–guest systems. This two-phase system can selectively dissolve anisotropic and isotropic guests in its different phases.[13] Therefore, we can easily envision systems that can be thermally regulated to capture and release these guests. Third, as we can observe in Chart I, this system provides a unique technique to molecular engineer the thickness, a, of a flexible random-coil backbone at will. Combined systems based on more than one immiscible flexible polymer backbone and identical side groups are also of interest.

At least for these reasons it is important to further elucidate the mechanisms by which these microphase-separated systems function, as well as their capabilities for some practical applications which can be considered from the above discussion. Research on these lines is in progress in our laboratory.

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New Multiphase Architecture from Statistical Copolymers by Cooperative Hydrogen Bond Formation

It is well-known that hydrogen bonds stabilize supramolecular structures in biopolymer systems.[1] Typical structures are helices or β sheets. It is a common feature for these complex biological systems that supramolecular structures are formed by cooperative self-organization. In most biological systems each repeating unit is capable of contributing to the three-dimensional structure. The configuration of the covalent backbone has a strong influence on the nature of the supramolecular ordering stabilized by the secondary valence interactions. However, no covalent backbone is necessary to observe a "polymer-like" association and structure formation via hydrogen bonding. Recently Wuest et al. have reported on the crystal structure of a polymer-like association structure of a low molecular weight molecule based on a bipyridone.[2]

We have previously reported on thermoreversible polymer networks based on binary hydrogen bond complexes in an unpolar polymer matrix.[3-5] Temporary junctions between highly polar phenylurazole groups (**1**) attached to polybutadiene chains served as a model system (Figure 1).

In the simple system the complexes are dispersed homogeneously in the unpolar polymer matrix, without indication of cluster formation like in ionomers.

For the formation of a three-dimensional structure it is necessary that each group has two sites for hydrogen bond association. In the case of the phenylurazole groups (**1**), one hydrogen bond donating group (>NH) and two hydrogen bond acceptors (>C=O) are available for complexation. If the phenyl group is substituted by a 4-hydroxy group (**2**), an additional hydrogen bond donor becomes available. In this case the viscoelastic properties indicate the formation of a three-dimensional hydrogen bond network.[7]

In this paper we report on the first successful approach to synthesize a multiphase material by the combination of flexible covalent polymer chains to which an association-type polymer based on hydrogen bonding is connected. Again polybutadiene is used as the base polymer, and the polar groups are introduced by a polymer-analogous reaction using a triazolinedione having two potential sites for hydrogen bonding. This bifunctionality is necessary to form a linear association polymer. It is realized by using the 4′-carboxy derivate of 4-phenylurazole (**3**). Details on the synthesis of the modifying agent and the polymers are reported elsewhere.[9]

In addition to the strong urazole–urazole complexes, dimeric carboxyl hydrogen bond complexes can be formed. Alternatively, urazole–acid H bonds could form the basic units of the association polymer. In Figure 2a the structure of the block-type polymer formed from flexible PB chains and H-bonded complexes is shown schematically.

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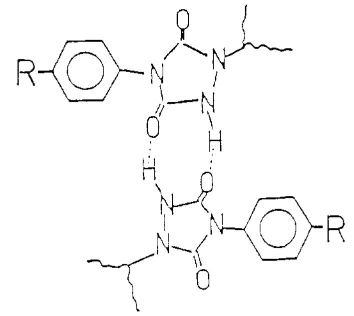

Figure 1. Urazole–urazole hydrogen bond complex. For each compound, R equals the following: 1, -H; 2, -OH; 3, -COOH; 4, -$COOC_2H_5$.

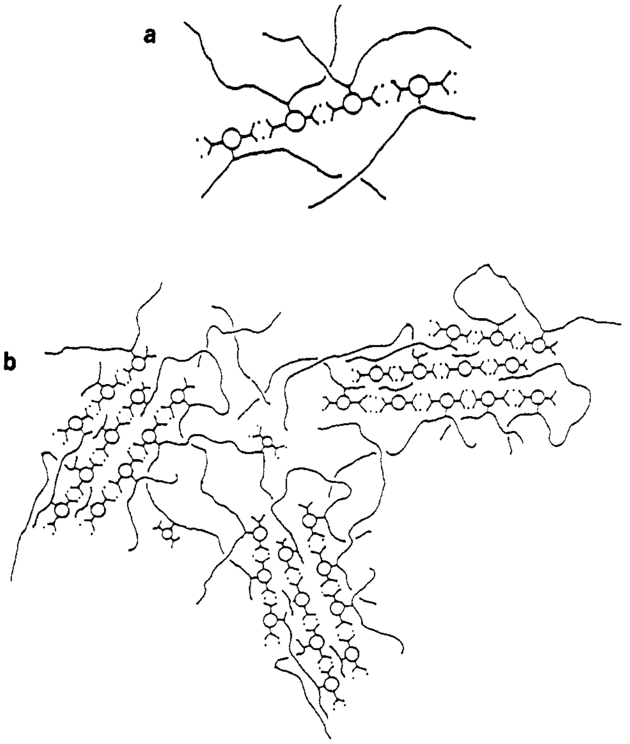

Figure 2. (a) Association polymer of difunctional polar groups (">-O-<") in a matrix of a covalent polymer (schematically). (b) Phase separation between bundles of association chains and covalent polymer chains (schematically).

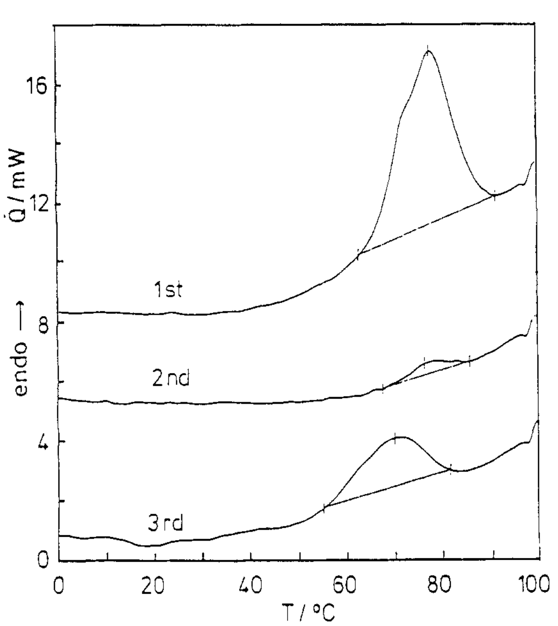

Figure 3. Differential scanning calorimetry (DSC). Trace of polybutadiene modified with 4 mol % **3**: heating rate, 40 K/min. Upper trace: 1st heating. Middle trace: heating after rapid cooling to −100 °C. Lower trace: heating after annealing at 25 °C for 1 h.

The properties of a material containing such isolated association polymer chains would be very similar to that of isolated complexes because of the high complex dynamics.

However, the material behaves like a covalently cross-linked network up to 80 °C for a degree of modification of 4 mol %. Upon further heating a change in the viscoelastic properties is observed within a temperature range of 10–15° from solidlike to viscouslike behavior. This behavior is explained by phase separation between covalent and association polymer chains in the temperature range below this transition (Figure 2b). Direct evidence for the existence of such a phase-separated supramolecular structure based on cooperative complex formation can be obtained from calorimetric measurements.

In Figure 3 the DSC traces of the polybutadiene (polymerized anionically in cyclohexane, M_n = 30 000), carrying 4 mol % of **3** obtained at a heating rate of 40 K/min, are shown. The upper trace corresponds to the first heating. A distinct endotherm is observed with a heat of "melting" on the order of 6 J/g. In the second trace, which was obtained after rapid cooling down to temperatures below the glass transition temperature at −90 °C, only a very small bump in the base line is observed. Upon annealing at room temperature for about 1 h the third trace is obtained. The melting is observed again, though the transition is much broader than in the first heating cycle. The heat of transition is on the order of 2.2 J/g, increasing with longer annealing times. It has to be emphasized that none of the polybutadienes carrying any of the other functional groups (**1**, **2**, **4**) show any calorimetric transition above their respective glass transition.

The observation of a melting endotherm peak at the same temperature where the viscoelastic and spectroscopic behavior changes abruptly indicates a "first-order transition" in the material. Visual observation of the transition is obtained by light microscopy: A film prepared by pressing the precipitated polymer at room temperature is highly birefringent. This birefringence does not relax within several weeks. Upon heating to 80 °C, i.e., above the melting endotherm, the birefringence disappears. Similar to the melting endotherm, the birefringence reappears upon annealing at room temperature. From the experimental data currently available, the molecular origin of the birefringence is not understood.

Additional experimental support for a phase-separated structure is obtained from SAXS. In Figure 4 (left) the scattering pattern observed with a pinhole Kratky camera at room temperature is shown. A distinct scattering maximum is found at low angles indicating the phase separation between the PB and the association polymer. Similar to the situation in ionomers, it is not clear whether the scattering maximum results from inter- or intraparticle interferences.[8] No wide-angle reflections are observed. Upon uniaxial deformation the SAXS maximum is only observed in the horizontal position perpendicular to the stretching direction [Figure 4 (right)]. This finding shows that the scattering units become anisotropic in stretching direction.

Until now no temperature-dependent X-ray investigations have been performed, which should show whether the scattering maximum at low angles disappears upon heating above the transition temperature and reappears upon annealing as the DSC endotherm.

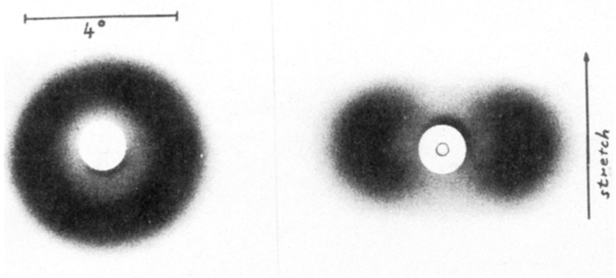

Figure 4. SAXS pattern of a technical grade polybutadiene (CB10 by Chemische Werke Hüls) carrying 10 mol % of **3** (distance sample film, 388 mm; Cu Kα radiation; exposure time, 4 h): left, unstrained; right, strained (about 400%).

The experiments reported in this paper show that a multiphase architecture is realized by cooperative structure formation of the polar comonomer units.

This molecular arrangement resembles somehow multiblock copolymers where phase separation occurs between hard and soft segments. This analogy becomes even more striking if the stress–strain behavior of this new material is analyzed.[9]

Presently, no information about the molecular organization of the functional groups into the three-dimensional structure is available. Urazole–urazole and acid–acid interactions might be the basic structural elements, but urazole–acid complexes could also be present. On the basis of molecular models, both a bundlelike and a helical structure formed by **3** are possible. More detailed information about the supramolecular structure is needed to understand in detail the properties of this interesting new class of multiphase materials.

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Surface Modification of PMDA–ODA Polyimide: Surface Structure–Adhesion Relationship

This paper reports on preliminary results of a polyimide surface modification, the characterization of modified polyimide surfaces, and the surface structure–adhesion relationship. The average thickness of the modified layers was studied using a nondestructive measurement technique. It is possible to modify polymer surfaces to obtain the desired surface properties without altering the bulk properties.[1] One of the most desired properties in the electronic industry is adhesion between polymers and other materials such as polymers, metals, and ceramics.[2] There are many techniques for polymer surface modification, but they can be divided into two major categories. One is a dry process in which the polymers are modified with vapor-phase reactive species that are often plasma enhanced.[3] The other is a wet process in which the polymers are modified in chemical solutions.[4,5] In this work we are interested in a wet-process surface modification of polyimides that are employed as insulating layers in the fabrication of chips and chip carriers.[6] It is known that the imide ring can be opened with a base such as an amine or a hydroxide.[7] As shown in Scheme I, a polyimide such as poly(pyromellitic dianhydride–oxydianiline) (PMDA–ODA) reacts with KOH or NaOH to give a polyamate (potassium or sodium salt of polyamic acid), which is subsequently protonated with acid to give the corresponding polyamic acid.[8] Upon curing at 230 °C or higher, the polyamic acid is converted back to polyimide. This reaction can be confined to the film surface by adjusting the reaction conditions and the solvent. It is important to understand the relationship between polymer surface structure and adhesion property and to *nondestructively* measure the thicknesses of the modified layers.

Surface Modification of PMDA–ODA with KOH. PMDA–ODA samples[9] were treated with 1 M KOH aqueous solution at 22 °C for 1–90 min to give the corresponding potassium polyamate. The excess of KOH was removed by washing with water (2 × 3 min). These samples without further washing and drying were used for the protonation reaction (discussed below). To analyze the modified surface by X-ray photoelectron spectroscopy (XPS) and external reflectance infrared (ERIR) spectroscopy, the samples were further washed with isopropyl alcohol (2 × 3 min) and dried under vacuum at ambient temperature for 12 h. The XPS survey spectrum displays a new peak due to potassium. Figure 1 shows the XPS C 1s regions of polyimide and the modified surfaces. The absolute binding energies are shifted due to charging and have not been corrected. We are interested in changes of the characteristic line shapes. There is only one carbonyl carbon peak (highest binding energy peak) of polyimide starting material (Figure 1a) since the polyimide carbonyls have the similar nuclear environments. But the spectrum (Figure 1b) corresponding to potassium polyamate surface exhibits two carbonyl carbon peaks since the binding energies of carboxylate carbon and amide carbon are different. Changes in the O 1s spectra are consistent with the changes in the C 1s region.

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