Supramolecular Polymer Interactions Based on the Alternating Copolymer of Styrene and Maleimide

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Biomacromolecules represent one of the most fascinating areas of supramolecular architecture and self-assembly based on multiple-hydrogen bonding, with the DNA double helix as the most prominent example. Despite the importance of macromolecules in natural systems, research in the field of supramolecular chemistry is mainly focused on low molecular weight molecules,[1] while self-assembly of macromolecules is investigated in detail for liquid crystallinity, hydrophobic interactions, amphiphilic structures and rotaxanes.[2] Recently, Lehn et al. introduced the concept of using well-defined secondary interactions based on hydrogen bonding in the synthesis of liquid crystalline polymers, in which the repeating units are linked by triple-hydrogen bonding instead of by covalent bonding.[3] Furthermore, Fréchet et al. studied the liquid-crystalline state obtained by the supramolecular side-chain interactions of polyacrylates with stilbazoles or polysiloxanes,[4] while Stadler reported on supramolecular polymer networks consisting of cooperative hydrogen bonding between (4-carboxyphenyl)urazole units grafted on polybutadiene.[5]

The use of secondary interactions in the formation of polymer blends is a well-accepted strategy; donor–acceptor complexes,[6] ion pairs,[7] and hydrogen bonding[8] represent some successful examples. In this communication, we report on our results of the supramolecular interactions between the alternating copolymer of styrene and maleimide, **1**, with melamine, **2**, and of **1** with the copolymer of styrene and 2,4-diamino-6-vinyl-1,3,5-triazine, **3**. The interactions between **1** and either **2** or **3** are based on the concept of triple-hydrogen bonding as shown in Figure 1.

Results and Discussion. In order to study multiple-hydrogen bonding in polymer blends, we have synthesized the complementary copolymers **1** and **3** and used commercially available **2**. The alternating, atactic copolymer of styrene and maleimide, **1**, is obtained by the radical polymerization of styrene and maleimide in butanone at 60 °C with AIBN as initiator.[9] DEPT-^{13}C-NMR spectroscopy reveals that alternation over 95% is obtained. The atactic, amorphous **1** ($M_n = 77 \times 10^3$, $D = 2.1$, as determined by GPC, Ultrastyragel, THF + 10% CH$_3$COOH and polystyrene as standards) possesses a glass transition temperature (T_g) of 250 °C and starts to decompose at temperatures above 350 °C. Polymer **3** is obtained as a random, atactic copolymer by the radical polymerization of styrene and 2,4-diamino-6-vinyl-1,3,5-triazine in DMSO at 60 °C with AIBN as initiator.[10] The resulting polymer **3** ($M_n = 14 \times 10^3$, $D = 2.8$, as determined with GPC, nucleosil-7-OH, hexafluoro-2-isopropanol + 0.2% CF$_3$COOK and polystyrene as standards) is amorphous and exhibits a T_g of 220 °C, whereas the decomposition temperature is above 360 °C.

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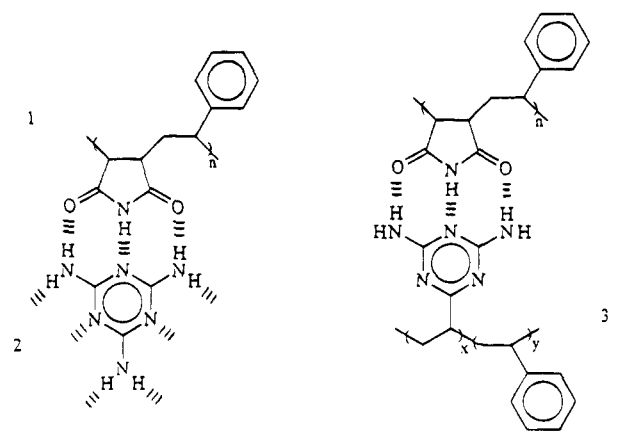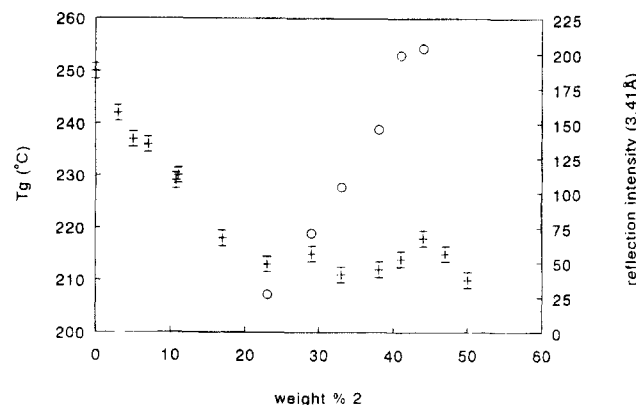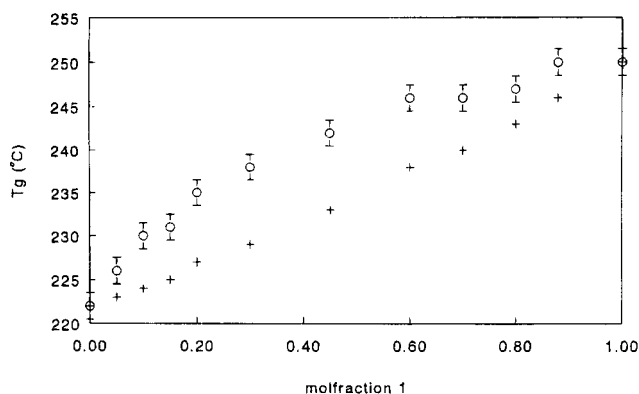
Figure 1.

Figure 2. Dependence of T_g (+) and melamine reflection intensity (○) on the concentration of melamine in the alternating copolymer of styrene and maleimide.

Blending of **1** with various amounts of melamine, **2**, is carried out in the melt, using an extruder, at 320 °C for 2 min. The dependence of T_g on the concentration of melamine is given in Figure 2. Addition of melamine results in a dramatic decrease of the T_g, up to melamine concentrations of 20% (w/w), at which it levels off at around 215 °C. In order to get more insight into the state of mixing of **1** with **2**, powder diffraction X-ray analysis of the prepared samples has been performed. Reflections at 3.41 Å (Cu Kα radiation) for crystalline, undissolved, melamine are detected only at melamine concentrations of 23% (w/w) and higher.[11] Extrapolation of the intensity of reflection to zero shows that no melamine crystals are present at concentrations lower than 19.7% (w/w) of **2**, as is shown in Figure 2. The figure shows, as well, that this point coincides with the onset of T_g stabilization. Therefore, it is concluded that melamine, known as a compound barely soluble in any organic solvent, is molecularly dissolved in **1** up to an imide:melamine ratio of 2.6 :1.[12] Hence, it is proposed that one melamine molecule interacts with three imide units of the polymer, leading to a three-dimensional hydrogen-bonded polymer network, hereby disrupting the imide–imide interaction. Investigations to explain the decrease in T_g and the exact nature of the complex are in progress.

Preliminary model studies of the complexation of **2** with low molecular weight imides have been performed to study these supramolecular polymer structures. X-ray crystal structures of **2** with succinimide and of **2** with glutarimide reveal that a 1:1 sheetlike and a 2:1 herringbone structure are formed, respectively. The

Figure 3. T_g (O experimental, + calculated Flory–Fox) as a function of the composition of the blend of **1** and **3**.

availability of the acceptors and donors for hydrogen bonding is strongly influenced by subtle differences in the molecular structure of the imide. Similar subtle effects are reported for model studies of supramolecular sheets of melamine and cyanuric acid.[13]

In order to extend our approach of multiple-hydrogen bonding to polymer–polymer interactions, we have blended **1** with **3**. The latter polymer with a diaminotriazine unit is complementary to the imide functionalized **1**, as is shown in Figure 1. In this case, the blends are obtained by dissolving **1** and **3** in DMSO, followed by coprecipitation in water. DSC and DMA analyses of the resulting blends show a single T_g for all blend compositions, while the lower critical solution temperature exceeds thermal decomposition. Furthermore, as shown in Figure 3, the T_g's obtained are significantly higher than the calculated ones based on the Flory–Fox equation,[14] indicative of significant intermolecular interactions. In model studies, we have determined a K_{ass} of 10^2 using the ^{1}H-NMR titration technique,[15] while Job plots[16] unambiguously have shown 1:1 complexes for imides and 2,6-diaminopyridine derivatives.[17]

The supramolecular blends prepared are extremely brittle, and therefore, the determination of the ultimate mechanical properties is not feasible, unfortunately. In strong polar solvents, like DMSO, the blends are readily soluble, indicating that the blends are based on secondary interactions. The prominent role of cooperativity of the three hydrogen bonds in the blends of **1** and **3** is demonstrated with the blend of the N-methyl derivative[18] of **1** with **3**. In all compositions studied, a phase-separated blend is observed with two glass transitions at 204 and 220 °C, which correspond to those of the individual components, N-methyl-**1** and **3**, respectively.

Conclusions. The characterization of all the blend compositions of **1** with **2** and **1** with **3**, as well as model studies show, that multiple-hydrogen bonding can give rise to high compatibility. Disturbing the specific interactions by introducing an N-methyl group in the polyimide leads to heterogeneous polymer blends, emphasizing the prominent role of the complementary couples. The polymer blends obtained, however, are all amorphous, without showing distinct topologies. Longe range cooperativity is expected as soon as well-defined stereoregular polymers are used. Future research will be focused on material properties, chain-length dependence of the miscibility, and the supramolecular architecture with more stereoregular polymers.

References and Notes

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MA9412501