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SUPRAMOLECULAR POLYMER INTERACTIONS USING MELAMINE

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Abstract: Triple-hydrogen bonding between the imide containing polymers **1a-c** and melamine **2** is used to obtain supramolecular interactions between macromolecules. Melamine, known as a compound barely soluble in any organic solvent, is molecularly dissolved in the copolymers **1a-c** by meltprocessing. Maximum concentrations of 1 equivalent amount of melamine per 2.5 equivalent amounts of copolymer are obtained, indicating a 3:1 mol:mol superstructure with physical crosslinking by hydrogen bonding. Crystalline melamine is detected by powder diffraction X-ray analysis at melamine concentrations exceeding the 3:1 imide-melamine mole ratio.

INTRODUCTION

The structure of the supramolecular complex between melamine and cyanuric acid is proposed to be an infinite two-dimensional lattice as is shown in figure 1 (Ref. 1). However, the parent structure is not confirmed by X-ray analysis yet, due to the lack of appropriate crystals. Therefore, only HCl salts have been studied (Ref. 2) and detailed information on the structure-property relationship of the parent complex is obtained by model studies. Recently, fascinating

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Fig. 1. Proposed infinite two-dimensional melamine-cyanuric lattice

results have been reported by Lehn et al. and Whitesides et al. (Ref. 3) in which it is shown that well-defined supramolecular complexes can be obtained by designing appropriate complementary couples based on triple-hydrogen bonding. Despite the importance of macromolecules in natural systems, research in the field of supramolecular chemistry using melamine and melamine-type structures is mainly focused on low molecular weight molecules. The use of secondary interactions in the formation of polymer blends is a well-accepted strategy; donor-acceptor complexes (Ref. 4), ion pairs (Ref. 5) and hydrogen bonding (Ref. 6) represent some successful examples. Self-assembly of macromolecules is investigated in detail for liquid crystallinity, hydrophobic interactions, hydrogen bonding interactions, amphiphilic structures and rotaxanes (Ref. 7). Recently we reported on the results of the supramolecular interactions between the alternating copolymer of styrene and maleimide, **1a**, with melamine, **2**, and of **1a** with the random copolymer of styrene and 2,4-diamino-6-vinyl-1,3,5-triazine (Ref. 8). In this paper we will extend this study with the supramolecular interactions of melamine with the alternating copolymer of 4-methylstyrene and maleimide, **1b**, and of melamine with a random copolymer of styrene and maleimide containing 28 mol% of maleimide, **1c**, aiming at a detailed insight into the structure-property relationship of these molecularly dissolved polymer blends. The interactions between **1a-c** with **2** are based on the concept of triple-hydrogen bonding as is shown in figure 2.

Fig. 2. Triple-hydrogen bonding interactions between 1a-c and 2

RESULTS AND DISCUSSION

In order to study multiple hydrogen bonding of melamine and imide containing polymers, the copolymers 1a-c are synthesized, and commercially available 2 is used. The alternating, atactic copolymers 1a and 1b are obtained by a radical polymerization of styrene, 1a, or 4-methylstyrene, 1b, with maleimide at 60°C, using AIBN as initiator (Ref. 9). DEPT ¹³C-NMR spectroscopy (Ref. 10) as well as elemental analysis of 1a and 1b reveal that alternation over 95% is obtained. Copolymer 1a possesses a glass transition temperature (T_g) of 250°C. The molecular weight (M_n) is 77.10³ g.mol⁻¹ whereas the molecular weight distribution (M_w/M_n) is 2.1 (Ref. 11). Copolymer 1b possesses a T_g of 246°C and a M_n of 3.9.10³ g.mol⁻¹ whereas the molecular weight distribution is 6. Copolymer 1c is prepared by the imidization of the corresponding anhydride copolymer using urea (Ref. 12) and possesses a T_g of 192°C. The M_n is 46.10³ g.mol⁻¹ whereas the molecular weight distribution is 2.2.

Blending the imide copolymers 1a-c with various amounts of 2 is carried out in the melt using an extruder, as previously reported (Ref. 8). The dependence of the T_g on the concentration of melamine is given in figure 3 for the blend of 1a with 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 1a with 2, powder diffraction X-ray analysis of the prepared samples has been performed. Reflections

Fig. 3. Dependence of T_g ($\pm$) and melamine reflection intensity (O) on the concentration of melamine in the blend of **1a** with melamine. Extrapolation of the intensity of reflection to zero results in 20.2%(w/w) melamine.

at 3.41Å (Cu/K α radiation) for crystalline, undissolved, melamine are detected only at melamine concentrations of 23% (w/w) and higher (Ref. 13). Extrapolation of the intensity of reflection to zero (Ref. 14) shows that no melamine crystals are present at a concentration lower than 20.2%(w/w) of melamine, as is shown in figure 3. This corresponds to an imide:melamine ratio of 2.5:1. 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 2.5 : 1. 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.

In order to study the structure-property relationship of this triple-hydrogen bonded interaction of melamine with imide-containing polymers, we have blended **1b** and **1c** with various amounts of **2**. The results are depicted in the figures 4 and 5. From figure 4 it is seen that the results obtained by using **1b** are comparable with the blend of **1a** and melamine. Here too, a dramatic decrease in T_g is observed up to the 3:1 imide-melamine ratio (theoretically 16.3%(w/w)) at which it levels off at around 220°C. Extrapolation of the intensity to zero

Fig. 4. Dependence of T_g (⊕) and melamine reflection intensity (O) on the concentration of melamine in the blend of 1b with melamine. Extrapolation of the intensity of reflection to zero results in 18.6%(w/w) melamine.

Fig. 5. Dependence of T_g (⊕) and melamine reflection intensity (O) on the concentration of melamine in the blend of 1c with melamine. Extrapolation of the intensity of reflection to zero results in 12.0%(w/w) melamine.

shows that no melamine crystals are present at concentrations lower than 18.6%(w/w) of melamine. This value corresponds to an imide melamine mole ratio of 2.5:1, which is in perfect agreement with the blend of **1a** and melamine. Thus, introducing a methyl group on the para position of the styrene unit does not prevent the formation of the proposed 3:1 imide-melamine complex. To investigate the influence of the imide content, copolymer **1c**, which contains 28 mol% maleimide, is used. Blending **1c** with various amounts of melamine results, like the **1a** and **1b** melamine blends, to the proposed 3:1 imide melamine complex as is shown in figure 5. A linear relation between the melamine reflection intensity and the melamine concentration is obtained. Extrapolation of the melamine intensity to zero shows that no melamine crystals are present at concentrations lower than 12.0%(w/w). This value corresponds to an imide melamine mole ratio of 2.5:1. Surprisingly, this is in agreement with the blends of **1a** and **1b** with melamine. Hence, a decrease in imide concentration and an increase in chain flexibility does not lead to an increase in the maximum concentration of molecularly dissolved melamine. Furthermore, no decrease in T_g is observed for this **1c**-melamine blend. Investigations to explain the " T_g behaviour" and the exact nature of the complex are in progress.

The maximum imide-melamine mole ratios of 2.5:1, as found for all three systems studied, are indicative for some kind of supramolecular crosslinking in which three imide units are linked together by one melamine molecule using multiple-hydrogen bonds. Only a cooperative effect is thought to be responsible for dissolving melamine molecularly by the copolymers.

CONCLUSIONS

The characterization of all the blend compositions of **1a-c** with **2** show that multiple hydrogen bonding can give rise to high compatibility. The polymer blends obtained, however, are all amorphous, without showing distinct topologies. Long-range cooperativity is expected as soon as well-defined stereoregular polymers are used. Future research will be focused on material properties and on the supramolecular architecture with more stereoregular polymers.

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