

Rigid-rod molecular composites via ionic interactions

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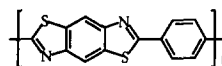
The first example of ionic molecular composites, i.e. the formation of rigid-rod molecular composites via ionic interactions between the polyelectrolyte host and the reinforcing rigid-rod polymer, was provided by the physical blend of poly(2-acrylamido-2-methylpropanesulphonic acid) (HAMPS homopolymer) and poly(*p*-phenylene benzobisthiazole) (PBZT). HAMPS homopolymer was formed *in situ* from its sodium salt form (NaAMPS), which is commercially available. A 52/48 (w/w) PBZT/HAMPS homopolymer blend was prepared by co-dissolving the components in methanesulphonic acid. Upon precipitation in cold water, the molecular composite was obtained as an orange-yellow fibre, which became red when it was dry. This solid-state chromatic variability is reversible and was observed when the blend (polymer pulp or coagulated film) was immersed in a variety of organic solvents. In addition, coagulated film showed relatively little lateral shrinkage after vacuum drying at 110°C overnight and no phase-separated morphology was detected by scanning electron microscopy within 500 Å resolution.

(Keywords: molecular composites; ionic interactions; poly(sodium 2-acrylamido-2-methylpropanesulphonate); poly(*p*-phenylene benzobisthiazole))

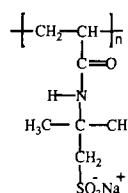
INTRODUCTION

In the field of polymer blends, a variety of chemical binding forces are invoked to enhance the miscibility of the component coil-like polymers. Among these intermolecular forces (hydrogen bonding, charge-transfer complexation, etc.), ionic interactions (cation/anion formation arising from proton transfer from one component to the other) are found to be the strongest^{1,2}. Thermodynamically, the enthalpy of mixing plays the most important role in causing polymer-polymer miscibility, since the entropy gain in a polymer blend is almost non-existent³. The critical nature of the enthalpy factor in rigid-rod molecular composite (RRMC) systems is even more so because of the greater propensity of rod-like macromolecules to aggregate. It was thought that a strong specific interaction of acid-base nature may contribute sufficient enthalpy to RRMC systems⁴ to overcome the overwhelming phase-separation proclivity inherent in these systems^{5,6}.

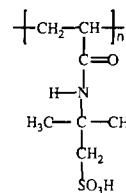
This communication will describe our efforts to obtain such an RRMC system comprising the rigid-rod polymer, poly(*p*-phenylene benzobisthiazole) (PBZT), and the high-molecular-weight, coil polymer, poly(2-acrylamido-2-methylpropanesulphonic acid) (HAMPS homopolymer). The molecular structures of PBZT, NaAMPS and HAMPS homopolymers are shown below:



poly (*p*-phenylene benzobisthiazole)
PBZT



poly (sodium 2-acrylamido-2-methyl-propanesulfonate)
(NaAMPS-homopolymer)



poly (2-acrylamido-2-methyl-propanesulfonic acid)
(HAMPS-homopolymer)

EXPERIMENTAL

Extraction of poly(sodium-2-acrylamido-2-methyl-propanesulphonate) (NaAMPS homopolymer)

Solid NaAMPS homopolymer ($FW = 229.23$) was isolated from its aqueous solution marketed under the tradename 'Lubrizol 2420'. Lubrizol 2420 is a milky white, viscous liquid; upon prolonged standing at room temperature, two phases appeared as the partially dissolved NaAMPS homopolymer settled down at the bottom. However, homogenization can be achieved by vigorously shaking the container.

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About 120 ml of Lubrizol 2420 was poured slowly into a magnetically stirred solution of toluene (200 ml) and methanol (1000 ml). The white, wax-like polymer that precipitated was collected by filtration (without suction) using a coarse fritted filter funnel and washed with toluene/methanol (v/v 5:1, 2 × 200 ml). It was then dried *in vacuo* at 70–80°C for 48 h. About 15 g of NaAMPS homopolymer was obtained. Analysis calculated for $\text{NaC}_7\text{H}_{12}\text{O}_4\text{NS}$: C, 36.67%; H, 5.28%; N, 6.11%; S, 13.98%. Found: C, 38.67%; H, 5.98%; N, 5.05%; S, 9.75%.

Stability of NaAMPS homopolymer in methanesulphonic acid

First 0.23 g of NaAMPS homopolymer and 25 ml of redistilled methanesulphonic acid (MSA) were placed in a 50 ml ground-joint Erlenmeyer flask with a glass stopper. The mixture was then mechanically shaken for about 2 days. The resultant homogeneous solution, which was amber and very viscous, was filtered through a coarse fritted filter funnel. No residue was observed. The filtrate was then transferred to a Cannon–Ubbelohde viscometer (capillary size 150), with which the flow time of redistilled MSA had previously been determined. The flow time of NaAMPS homopolymer/MSA solution was determined daily over a period of 21 days. The reduced viscosities are plotted in Figure 1.

Preparation of 52/48 (w/w) PBZT/HAMPS homopolymer

First, 1.953 g of NaAMPS homopolymer (equivalent to $1.953 \text{ g} \times 207.24/229.23 = 1.766 \text{ g}$ of HAMPS homopolymer) was placed in a 150 ml polymerization vessel, followed by addition of 50 ml of freshly distilled MSA via a volumetric pipette. The resultant mixture was then mechanically stirred with a multi-blade stirrer overnight under a steady stream of nitrogen. A very viscous (climbing up the stirring rod when the solution was

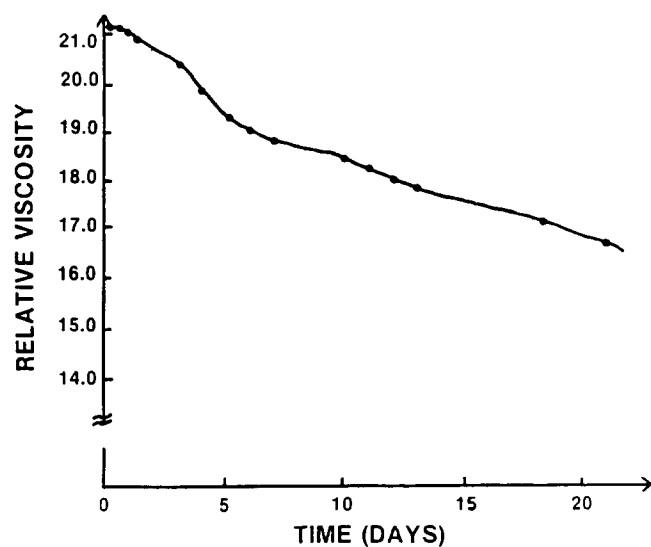


Figure 1 Stability of NaAMPS homopolymer in methanesulphonic acid at 30°C

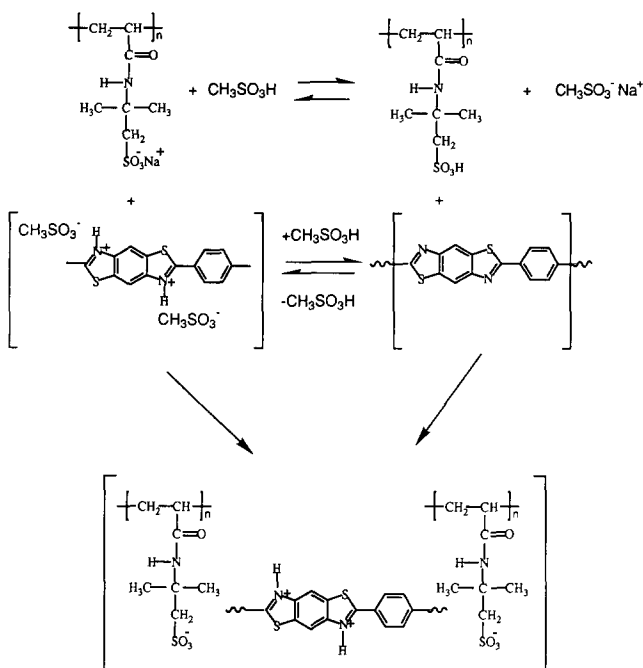
rapidly stirred) amber solution was formed. To this solution was added in small portions 1.950 g of PBZT polymer (intrinsic viscosity in MSA at 30°C was 21.4 dl g^{-1}). The resultant mixture was then agitated for another 21 days. (Stirring became increasingly difficult after the addition of PBZT due to the tremendous bulk viscosity and could be allowed only intermittently in order to prevent the motor from overheating.) The final dark-green blend was poured into a 4 l beaker containing about 2 l of ice/water. Immediately the mixture changed colour from dark green to orange-red. The remaining blend in the vessel was treated with ice/water and the coagulated blend was poured into the beaker, which was allowed to stand overnight. The precipitated blend was chopped into fine fibres in a blender and washed with a copious amount of water until the filtrate was almost colourless and neutral to a wet litmus paper. The wet yellow fibres were suction-dried overnight. The fibres, which had become red, were subjected to Soxhlet extraction with methanol for about 20 h, followed by drying *in vacuo* at about 50°C for 24 h. Some 3.35 g of PBZT/HAMPS homopolymer was obtained, tantamount to 90% of the theoretical yield.

RESULTS AND DISCUSSION

Previous RRMC systems, with one exception⁷, contained commercial thermoplastics such as nylons^{8,9}, poly(ether ether ketone) (PEEK)¹⁰ and other experimental linear polymers such as poly(2,5(6)-benzimidazole) (ABPBI)^{4,11} and poly(*p*-phenylene quinoxaline) (PPQ)¹². The interactions between PBZT and coil matrix macromolecules are limited to physical entanglement and relatively weak intermolecular bonding (van der Waals or dispersion forces and hydrogen bonding). These types of binding forces are easily disrupted by an input of thermal energy into the systems, resulting in phase separation of the components. The aforementioned exception⁷ entailed PBZT polymer and benzocyclobutene-terminated aromatic imide oligomers, which spontaneously formed a highly crosslinked polymer when heated to about 200°C. This thermoset RRMC system undergoes phase separation during the precipitation/coagulation of the blend in non-solvents (H_2O and isopropanol) from its MSA solution, owing to the vast difference in the molecular weights of the components. However, upon curing, the system displayed very little additional degree of phase separation, implying that the formation of network matrix had effectively prevented the rod molecules from further assembling.

A dilute MSA solution of PBZT, i.e. an isotropic solution, can be used to represent the idealized molecular dispersion of protonated rod macromolecules among the counterions (CH_3SO_3^-) and the solvent molecules ($\text{CH}_3\text{SO}_3\text{H}$). If the counterions were to be connected covalently to form long, linear macromolecules having sulphonate ($-\text{SO}_3^-$) pendants, then the consequence would be a solution of molecular composite, which would stand a better chance of sustaining such a state of dispersion during coagulation and perhaps also during consolidation. Such a 'polymeric sulphonate' could be found in NaAMPS homopolymer. The following scheme showing the chemistry for the preparation of PBZT/HAMPS homopolymer molecular composites, depicts

our concept of an ionic-interaction-enhanced RRMC system:



Before we investigated the PBZT/HAMPS homopolymer system, we first examined the protonation capability of such an alkanesulphonic acid group since the monomer 2-acrylamido-2-methylpropanesulphonic acid (AMPSA) is also available commercially as a white crystalline solid. We found that AMPSA was able to solubilize PBZT and PBO (poly(*p*-phenylene benzobisoxazole)) as soon as it melted, as evidenced by the formation of orange-yellow solutions as some of the polymers dissolved at about 180–200°C, followed immediately by the decomposition of AMPSA.

NaAMPS homopolymer readily dissolved in MSA (3–4% by weight) and formed a very viscous amber solution, which showed little or no hydrolysis during the first 24 h at 30°C. However, prolonged standing without extra measures to prevent atmospheric moisture from contacting the solution showed a slow but steady reduction in the relative viscosity (see Figure 1).

A sample of 50/50 (w/w) PBZT/NaAMPS homopolymer blend (which corresponds to 52/48 PBZT/HAMPS homopolymer) was prepared by dissolving the components consecutively (NaAMPS homopolymer first) in MSA at room temperature under an atmosphere of dry nitrogen, followed by precipitation of the solution in cold water. The crude blend was washed with copious amounts of water and then subjected to Soxhlet extraction with methanol. (Both HAMPS and NaAMPS homopolymers are very soluble in both water and methanol.) About 90% of the theoretical yield was obtained.

The foregoing blend was redissolved in MSA under dry N_2 atmosphere to form a 2.5% solution. This concentration is below the critical concentration at which the rod molecules would aggregate in solution, and is a requirement to minimize phase separation during processing. The solution was extruded through a coat-hanger die onto the surface of a rotating stainless-steel drum which was half-submerged in a deionized water bath. As the drum rotates, a thin layer of extruded solution was

coagulated into wet film. The details of film extrusion have been described previously¹³. The coagulated film was washed free of MSA, and wound without overlapping on a 6 inch (~15 cm) diameter plastic pipe with both ends taped down. It was then dried in a vacuum oven at 110°C overnight.

The dried film was 6–10 μm thick and showed much less shrinkage width-wise than any of the molecular composite films we had ever processed. The shrinkage was only 10–15%, whereas other similar molecular composite films with the same composition and using thermoplastic matrix such as nylon-6,6 showed 40–50% shrinkage. Such dimensional stability on drying is quite unusual, and could be due to the well dispersed nature of the rod molecules. The film was orange-red in colour when dry, and turned yellow on contact with water. The colour change was reversible.

The processed film was coated with C/Pt and was examined for possible phase separation using a Jeol 840SM scanning electron microscope. The film appeared homogeneous and there was no detectable phase-separated morphology within 500 Å resolution. It was among the most homogeneous molecular composite films that we had obtained. However, wide-angle X-ray diffraction using a flat-film Statton camera showed two weak diffraction rings with 3.5 and 12.5 Å *d*-spacings, which were attributed to PBZT. Thus, the molecular composite did show a small degree of aggregation of the rod molecules without any evidence of gross phase separation.

It is interesting to note that PBZT/HAMPS homopolymer blend adopted a variety of colours when it was immersed in non-solvents. The blend was red in methylene chloride, orange-red in dry methanol, yellow in dimethylsulphoxide and brown in triethylamine. Furthermore, when it is wet with water, it is deep red and becomes orange-yellow as soon as water was eliminated. Such chromatic variability was always reversible and can be explained in terms of an acid–base equilibrium. In the PBZT/HAMPS homopolymer blend, PBZT polymer exists as a protonated species whose charges are counterbalanced by the sulphonate anions attached to the HAMPS homopolymer. The red colour of the blend in the dry state is most probably due to the mixture of protonated and unprotonated PBZT. Completely protonated PBZT, as in the case of PBZT/MSA solution, is yellow-green. In an aqueous medium, the protons are immediately transferred from protonated benzobisthiazole units to water, to form the hydronium (H_3O^+) ions. The resultant orange-yellow colour is due to the neutral PBZT polymer. Thus, in a relatively less basic environment (CH_2Cl_2 and MeOH), the equilibrium is shifted towards protonated PBZT polymer, and towards neutral PBZT polymer when the blend is in an organic base such as triethylamine. The colour of the blend changes accordingly.

CONCLUSIONS

We have prepared a prototype of a new class of rigid-rod molecular composites, which invokes a specific interaction of ionic nature between the matrix and the reinforcement at the molecular level. As such, it is expected that the solution behaviour with respect to the critical concentration effect will depart from the predictions based on Flory's theory¹³, which considered only

athermal systems, in which there is no interaction between the rod and coil solutes. The present system will provide an opportunity to study the solution behaviour of molecular composites under thermal conditions, in comparison with the known athermal systems, which have been shown experimentally to be in good agreement^{9,12} with Flory's theory. Also, since strong chain entanglement between the coil and the rod polymers can impede phase separation during coagulation and since NaAMPS homopolymer has a molecular weight of about $(3-4) \times 10^6$ (ref. 14), adequate for effective entanglement, it is reasonable to assume that chain entanglement should also play an important role in this system. However, its significance relative to ionic interaction is yet to be determined. Nevertheless, we are inclined to believe that both effects should be synergistic and the latter should be predominant, based upon an energetics consideration. These issues will be addressed in our future studies.

ACKNOWLEDGEMENT

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