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Miscibility behaviour of sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) copolymers in the blends with poly(styrene-co-maleic anhydride) and with poly(α-methylstyrene-co-maleic anhydride)

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Dedicated to Professor Dragutin Fleš in honor of his 70th birthday

Summary

The miscibility behaviour of sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) of the different degree of sulfonylation blended with poly(styrene-co-maleic anhydride) or poly(α -methylstyrene-co-maleic anhydride) was studied. The critical degree of sulfonylation for phase separation in these blends was found to be 55 mole % and 66 mole %, respectively. The miscibility behaviour was analyzed on the basis of the mean field treatment and studied by DSC.

Introduction

The miscibility behaviour in blends of various types of copolymer systems has been investigated by several authors. The miscibility of the random copolymers containing common segment was studied on the systems: poly(styrene-co-acrylonitrile)/poly(styrene-co-maleic anhydride) (1), poly (styrene-co-methyl methacrylate) with poly(styrene-co-acrylonitrile) and with poly(styrene-co-maleic anhydride), respectively (2). The examples in which both components are copolymers with four distinct repeat units are: poly(butadiene-co-styrene)/ poly(vinyl chloride-co-vinyl acetate) (3) and poly(styrene-co-p(o)-fluorostyrene) with sulfonylated poly(2,6-dimethyl-1,4 phenylene oxide) (SPPO) (4). For these systems the miscibility within a certain range of copolymer composition was found. Recently we have studied the miscibility of the alternating copolymers of α-methylstyrene (αMeSt) with maleimides (MI) in blends with SPPO (5). The miscibility/ /immiscibility behaviour in this system depends on the degree of sulfonylation of SPPO copolymers as well as on the chemical structure of α-MeSt-MI copolymers. The miscibility behaviour was analyzed on the basis of the mean field treatment (6).

In continuation of our studies on the miscibility of alternating copolymers with random copolymers we investigated the miscibility in blends of copolymers of styrene (St) with maleic anhydride (MAn) or poly(αMeS-co-MAn) with copolymers of SPPO with different degree of sulfonylation. The miscibility in this study is based on DSC measurements and on visual observation of film clarity.

Experimental

Materials

Alternating copolymers of St or αMeSt with MAn of high molecular weights were prepared from freshly distilled St or αMeSt and MAn, which had been crystallized from benzene. The copolymerizations were carried out in thermostated 10-ml glass vials sealed under purified nitrogen. Mixtures of these monomers at the equimolar quantities as a 10% w/w solution in toluene or methyl ethyl ketone were polymerized at 60°C in the presence of

2,2' -azobis(isobutyronitrile) (AIBN) as initiator. After the required reaction time, the vial was coold down and the solution of copolymer was precipitated by addition to cold methanol. The precipitated copolymer was filtered off and dried in vacuum at 80°C overnight. The conversion was about 20 wt%.

SPPO copolymers of different degree of sulfonylation were prepared by Friedel-Crafts sulfonylation of PPO (5,7).

Polymer blends were prepared by coprecipitation from equimolar amount of chloroform and dimethylformamide solution (total 5 wt% of polymer in solution) in methanol as nonsolvent. The dried, precipitated blends were used in DSC experiments.

Physicochemical Measurements

The copolymer composition was determined by NMR spectrometry on a Varian EM 390 spectrometer.

Thermogravimetric measurements were made by Perkin-Elmer, TGS-2 thermobalance at a heating rate of 10°C/min with a nitrogen purge.

The glass transition temperatures (T_g's) were measured using a Perkin-Elmer DSC-2 at heating rate of 20°C/min under nitrogen atmosphere. The T_g was taken at the half-height of the corresponding heat capacity jump (second scan).

The average molecular weights were determined by GPC at room temperature in THF (Varian HPGPC model 8500) with PS standards. The poly-(αMeSt-co-MAn) samples were characterized by an average molecular weight of $\bar{M}_w$ 74800 and $\bar{M}_n$ 43300. The average molecular weights of poly(St-co-MAn) samples were $\bar{M}_w$ 119900 and $\bar{M}_n$ 48100.

Results and Discussion

It is known that preparation and thermal history of the samples have a great influence on the glass transition of blends. Glass transition is also influenced by the common solvents and level of miscibility partially depends on the solvent used (8,9). It was also published that annealing temperature and the time have for some blends a great influence on the glass transition temperature (10). During this study this experience was taken into consideration. The thermal stability of the blends studied here was evaluated by thermogravimetric analysis. The samples were first predried at 150°C in the TGA furnace in order to remove the traces of absorbed water and than were heated from 50 to 280°C and the sample weight loss was determined. It was found that the observed weight loss for the blends of poly(St-co-MAn)/SPPO is from 0.5 to 0.8 wt% at 250°C and from 0.6 to 0.8 wt% at 280°C. In the systems poly(αMeS-co-MAn)/SPPO the weight loss from 0.5 to 0.7 wt% at 250°C and from 0.7 to 0.9 wt% at 280°C was observed. The miscibility of the blends was determined by the appereance of a single glass transition in the DSC instrument. All materials were amorphous and the only distinctive features of the thermograms were glass transitions. An initial scan was made to produce a uniform thermal history in all polymers. Therefore, the reported glass transition temperatures are from the second scan. An experiment consisted of heating a sample at fastest available rate to the temperature of 280°C. The sample was then quenched to ambient temperature as rapidly as possible in the instrument. Samples were then reheated at 20°C/min to determine whether one or two phase were present. In this study as a common solvents the mixture of the chloroform and dimethylformamide in equimolar ammount was used.

Alternating Poly(St-co-MAn)/SPPO Blends

Miscibility in this system was studied for the blends containing alternating copolymer and SPPO of the degree of sulfonylation from 11 to 92 mole %. It was found that the blends containing 55 mole % or less of SPPO exhibit two T_g's which are close to that of the pure components. In contrast, the blends with SPPO with 64 to 92 mole % of the degree of sulfonylation show only one T_g and are therefore considered miscible. Figure 1 illustrates DSC thermograms of poly(St-co-MAn)/SPPO of 50/50 wt % blends. It was found that T_g values of the miscible blends depend on the degree of sulfonylation of PPO. This behaviour can be adequately described by the Gordon-Taylor equation (11) with k value of 0.64. From the thermograms, systematic changes also were observed in the widths of the glass transition temperature for miscible blends of increasing SPPO of higher degree of sulfonylation. These transition widths were determined as the temperature interval over which the tangent to the slope of the dQ/dT curve interesected the extrapolation of the baseline before and after T_g. This observed transition width behaviour can be explained on the basis of phase heterogeneity. Such broadening of T_g peaks has been attributed to fluctuation in the interaction of chain segment with its nearest neighbour in excess of the normal thermal fluctuations (12). These changes in the phase separation width during miscibility investigations are a qualitative measure of the approach to phase separation.

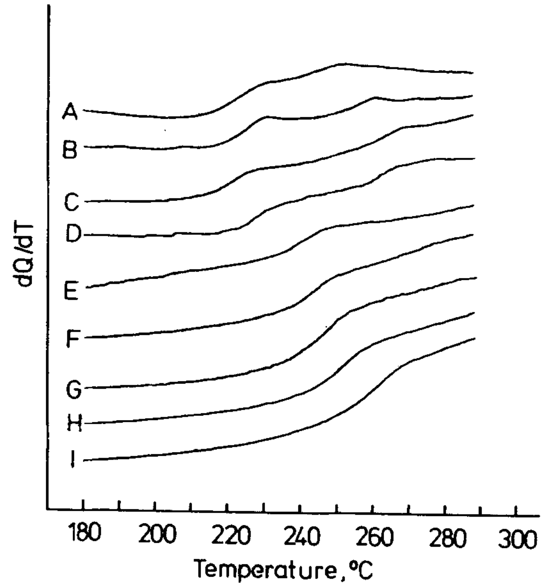

Figure 1. DSC thermograms of 50/50 wt% of the alternating poly (St-co-MAn)/SPPO blends: A,SPPO 11;B,SPPO 27;C,SPPO 47; D,SPPO 55;E,SPPO 64;F,SPPO 68;G,SPPO 75;H,SPPO 87, and I,SPPO 92,respectively.Numbers indicate mole % of SPPO in copolymer.

Further insight into behaviour of these blends was obtained by preparing samples with different blend composition. The samples containing SPPO copolymer of the degree of sulfonylation 37, 55, 64, 66, 75, 84 and 87 mole %, respectively were prepared. It was found that polymer blends containing SPPO of the degree of sulfonylation 35 and 55 mole %, respectively of the different blend compositions exhibited two Tg´s independent on blend composition. Polymer blends containing SPPO of 64, 66, 75, 84 and 87 mole %, respectively of different blend composition exhibited one T_g independent on blend composition. The Tg-composition curves of the miscible blend systems can be fitted by the Gordon-Taylor equation (11).The k values are: 0.54, 0.78, 0.79 and 0.53 and 0.53 for the blends with SPPO 64, SPPO 66, SPPO 75, SPPO 84 and SPPO 87, respectively. Different k values indicate different strenght of intermolecular interaction. For the blends with SPPO of the degree of sulfonylation of 64, 84 and 87 mole %, respectively lower k values were obtained. It is in agreement with the data obtained for the glass transition width, i.e. a possible explanation is that these systems are on the miscibility/immiscibility boundary.

Alternating Poly(α MeSt-co-MAn)/SPPO Blends

The critical degree of sulfonylation for phase separation in these blends was found to be 66 mole %. Polymer blends with 66, 68, 75, 84, 87 and 92 mole % of the degree of sulfonylation exhibited one T_g, what indicates the miscibility. The two distinct T_g´s in the blends with SPPO of the degree of sulfonylation 64, 55, 47 and 39 mole % clearly shows the two-phase nature of these blends. All T_g´s are close to that of the pure components within 10°C. Polymer blends with lower degree of sulfonylation of SPPO, i.e. 27, 19, 11 and 7 were also investigated by DSC. Due to the small difference between T_g of the copolymers, two separated T_g´s were not observed for immiscible blend. The immiscibility was confirmed on the basis of film cloudiness. Polymer blends of these systems, prepared by solution casting from chloroform and dimethylformamide mixture, were cloudy. Again, the T_g values for the miscible poly(α MeSt-co-MAn)/SPPO blends deviate from linear additivity and can be described by the Gordon-Taylor equation with k value of 0.42. Figure 2 shows the DSC curves of several poly(α MeSt-co-MAn)/SPPO blends.

The T_g-composition curve for poly(α MeSt-co-MAn)/SPPO blends deviates from linearity. It was found that T_g-composition curves of the miscible blend of these copolymers can be fitted by the Gordon-Taylor equation using k values of 0.40, 0.41, 0.45 for blends containing SPPO 66, SPPO 75 and SPPO 87, respectively as shown in Figure 3. These k values do not show a dependence on the degree of sulfonylation as observed in poly(St-co-MAn)//SPPO blends. For the copolymers blend with SPPO of the degree of sulfonylation of 55 and 39 mole % two-phase nature was found, with the lower and the upper Tg´s of the blend close to the Tg´s of the pure components.

By using Gordon-Taylor k value and the concavity of T_g-composition curve as a measure of the intensity of polymer-polymer interaction, the present results obtained for poly(St-co-MAn)/SPPO and poly(α MeSt-co-MAn)//SPPO blends indicate that the incorporation of methyl group into styrene molecule has relatively small influence on the interaction with SPPO.

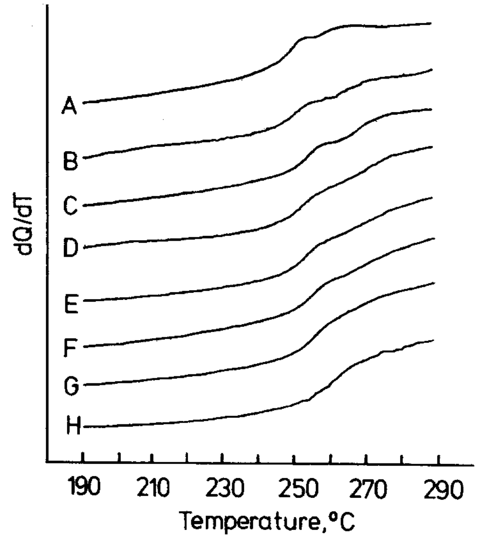

Figure 2. DSC thermograms of 50:50 poly(α MeSt-co-MAn)/SPPO blends: A,SPPO 39;B,SPPO 47;C,SPPO 55;D SPPO 64;E, SPPO 66; F,SPPO 68;G,SPPO 75 and H,SPPO 87. Numbers indicate mole % of SPPO in copolymer.

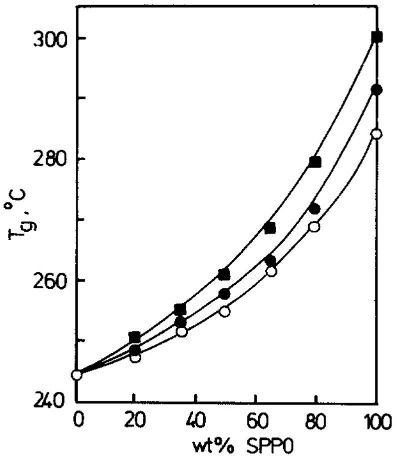

Figure 3. Dependence of the glass transition temperature on the blend composition for the blend (○) poly(α MeSt-co-MAn)/SPPO 66; (●) poly(α MeSt-co-MAn)/SPPO 75; (■) poly (α MeSt-co-MAn)/SPPO 87 blends. Numbers indicate mole % of SPPO in copolymer.

Segmental Interaction Parameters

It is well known that high molar mass polymers are, in general, miscible only if there is a favorable specific interaction between them. However, some blend systems in which at least one of the component is a random copolymer have been found miscible for a particular range of copolymer composition though none of the binary pair or the copolymers is miscible (3,4). These behavior can be explained on the basis of mean field treatment (6) which shows that specific interactions are not always necessary for miscibility. Both systems studied here, i.e. SPPO blends with poly(St-co-MAn) and poly(α MeSt-co-MAn) are of the type$(A_{1-x} B_x)_{n1}/(C_{1-y} D_y)_{n2}$. For this type of blends χ_{blend} is related to six segmental interaction parameters between the different monomer units by:

$$\chi_{blend} = \chi_{AB} x^2 + (\chi_{AC} - \chi_{BC} - \chi_{AD} + \chi_{BD})xy + \chi_{CD} y^2 + (\chi_{BC} - \chi_{AC} - \chi_{AB})x + (\chi_{AD} - \chi_{AC} - \chi_{CD})y + \chi_{AC}$$

In poly(St-co-MAn)SPPO blend system A, B, C and D are St, MAn, PPO and SPPO repeat units, respectively. χ_{AB}, χ_{AC}, χ_{AD} and χ_{CD} were taken from the literature data, and χ_{BC} and χ_{BD} were treated as adjustable parameters to set the best fit to the experimental results. The value of χ_{crit} was calculated from the degrees of polymerisation of the respective blend components as 0.005. Taking from the reference (2) $\chi_{AB} = 0.34$ and from the reference (7) $\chi_{AC} = -0.043$, $\chi_{AD} = 0.2$ and $\chi_{CD} = 0.15$, it was found employing the mean field theory $\chi_{BC} = 0.355$ and $\chi_{BD} = 0.006$. By using so obtained interaction parameters, the boundary of miscibility/immiscibility region was calculated. It was found that calculated domaine of the miscibility is in the range of 55 mole % and 82 mole % sulfonylated PPO. This results are in agreement with experimental data.

In poly(α MeSt-co-MAn)/SPPO blend systen, A, B, C and D are α MeSt, MAn, PPO and SPPO repeat units, respectively. χ_{AC}, χ_{AD} and χ_{CD} were taken from the literature data, while χ_{BC} and λ_{BD} were determined above from the study on the miscibility of poly(St-co-MAn)/SPPO, i.e. $\chi_{BC} = 0.355$ and $\chi_{BD} = 0.006$. Taking from the reference (5) $\chi_{AC} = 0.024$ and $\chi_{AD} = 0.015$, and from reference (7) $\chi_{CD} = 0.15$, calculating χ_{crit} as 0.005, χ_{AB} was determined employing the mean field theory as 0.135. By using this values of χ_{ij} for calculating miscibility/immiscibility region, the boundary line was predicted at 66 mole % of SPPO what is the same value as obtained experimentally.

Acknowledgments

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