The effects of hydrogen bonding on the miscibility, complexation and crystallization in blends of crystalline and amorphous components

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SUMMARY:

The miscibility and crystallization of blends of poly{styrene-co-[p-(2,2,2-trifluoro-1-hydroxy-1-trifluoromethyl)ethyl]-a-methylstyrene} (PS(OH)) and polycaprolactone (PCL) have been investigated by viscometry and differential scanning calorimetry. With increasing the hydroxyl content in PS(OH), the transitions from immiscibility to miscibility and then to complexation can be realized. Depending on the states in which the blends exist, a different behavior of PCL crystallization is observed. Crystallization in the immiscible blends, is almost not affected by the presence of PS(OH). In the miscible blends, an apparent depression of crystallization is observed. Particularly, for the blends with a hydroxyl content larger than 8 mol-% in PS(OH), complete depression of PCL crystallization is found, which can be attributed to a complex formed by pairing segments of PCL and PS(OH).

Introduction

In recent years, a progressively increasing interest has been attracted by specific interactions and miscibility of polymer blends1-5. In this field, our previous papers were focused on the effect upon miscibility of introducing hydrogen bonding into otherwise immiscible blends. The blend systems studied were composed of a carbonyl-containing polymer and a polymer with a controllable amount of hydroxyl groups. The proton-donating polymers employed include styrene-based hydroxyl-containing polymers such as poly[styrene-co-(p-vinylphenol)] (STVPh)6,7, poly[styrene-co-(p-1-hydroxyethyl)styrene] (PS(2-OH))8, poly[styrene-co-[p-(2,2,2-trifluoro-1-hydroxy-1-trifluoromethyl)ethyl]-a-methylstyrene] (PS(OH))4 (Scheme 1). Among these, PS(OH) with the strong proton-donating group —C(CF3)2OH shows the most remarkable effect on the miscibility. For instance, for a typical immiscible blend system of polystyrene/poly(methyl methacrylate) (PMMA), only 2 mol-% of —C(CF3)2OH group, has rendered the miscibility. More importantly, complexation between PS(OH) and PMMA has been observed as the hydroxyl content in PS(OH) further increased to 8–10 mol-%.9,10 This means that in the otherwise immiscible blends, transitions from immiscibility to miscibility and then to complexation can be realized by progressively strengthening hydrogen bonding between the components. Besides, our experiments on the blend solutions have found and confirmed that polymer-polymer complexation due to hydrogen-bonding takes place provided the hydroxyl content in PS(OH) reaches a certain level.
Scheme I: Chemical structure of copolymers

This communication is an extension of our long-term research on the miscibility and complexation to the blends composed of crystalline and amorphous components. With respect to the blends containing a crystallizable component, the work in the literature was focused on the thermodynamics, miscibility and phase boundary, etc.\textsuperscript{11-13}. Although the rate of crystallization of the crystallizable component is usually reduced by mixing with the miscible amorphous component as reported for the systems such as polycaprolactone (PCL)/STVPh\textsuperscript{11}, PCL/poly(hydroxy ether of bisphenol A)\textsuperscript{12} and phenoxy/poly(methylene oxide)\textsuperscript{13}, etc., to our knowledge, there was no systematic research on the effect of the specific interactions on the ability of crystallization. In the present work on blends of PS(OH) and PCL, we enjoy the advantage of being able to change the hydroxyl group content in PS(OH) at will. Therefore, we are able to focus on the effects of the density of hydrogen bonding on the miscibility, complexation, and especially, the crystallization behavior of PCL in the blends.

Experimental part

Materials and characterization

\(p\)-[(2,2,2-Trifluoro-1-hydroxy-1-trifluoromethyl)ethyl]-\(\alpha\)-methylstyrene (HFMS) was synthesized as previously described\textsuperscript{1,4}. A series of copolymers with different hydroxyl unit contents was prepared by copolymerization of purified styrene and comonomer HFMS at 60°C in dry benzene using 2,2'-azoisobutyronitrile (AIBN) as initiator. The product was precipitated in petroleum ether (b.p. range 60–90°C) followed by repeated dissolution and precipitation. The content of hydroxyl in the copolymers was measured by means of a fluorine analysis. PS(OH) samples with hydroxyl contents ranging from 1 mol-% to 26 mol-% were used. The sample codes, and the corresponding mole frac-
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tions of hydroxy groups are as follows: PS(OH)-1 (0.97), PS(OH)-3 (2.9), PS(OH)-5 (5.2), PS(OH)-8 (8.1), PS(OH)-17 (16.8) and PS(OH)-26 (25.6).

Poly[styrene-co-(p-vinylphenol)] (STVP) samples with mole fractions of hydroxy groups from 1 to 50% were synthesized via hydrolysis of poly[styrene-co-(4-methoxy-styrene)] according to the procedure developed in our laboratory. STVP-1, 3, 6, 9, 15, 22, 50 refer to the samples with hydroxy contents of 0.98, 3.1, 6.0, 9.1, 15.1, 22.4, 49.8 mol-%, respectively.

Polycaprolactone (PCL, weight-average molecular weight $\bar{M}_w = 33000$) used in this paper was purchased from Scientific Polymer Products, Inc., Ontario, NY 14519, USA.

Preparation of blends

PS(OH)/PCL blends were prepared via solution casting. The respective polymer solutions in toluene (3 g/100 mL) were mixed in the proportion as desired and stirred in a teflon cell with a cover glass for 2 h. After slow evaporation of the solvent at room temperature for 24 h, the products were dried in a vacuum oven at about 60°C for at least three days.

Viscosity measurements

The viscosities of the polymer blend solutions in toluene were measured with an Ubbelohde viscometer (at 30 ± 0.1°C). The original concentration of the individual polymer was 5.0–7.0 × 10⁻² g/mL. Measurements of the apparent reduced viscosities of PS(OH)/PCL blends as a function of the composition were conducted via mixing the solutions of PCL and PS(OH) at 30°C as desired. When the hydroxyl content in PS(OH) was not higher than 5 mol-%, the solution remained clear, but it turned turbid when this content reached 8 mol-%, and precipitation occurred for the blends of PS(OH) having high hydroxyl content ranging from 17 to 26 mol-%. For the last case, the measurements were performed after the precipitate was separated.

Differential scanning calorimetry (DSC)

DSC measurements were conducted with a differential scanning calorimeter (DSC-50, Shimadzu). The heating rate was 10°C/min and samples of about 10 mg in a sealed aluminia cell were measured under a nitrogen gas atmosphere. Two thermal programs were used, i.e. in the quenching program, the sample was heated to and then kept at 130°C for 20 min followed by quenching in liquid nitrogen for several minutes and in the annealing program, the sample was heated to and kept at 130°C for 20 min followed by quickly cooling to and keeping at 40°C for 20 h.

Results and discussion

Miscibility studied by means of differential scanning calorimetry (DSC)

The DSC technique is a simple and effective method to judge miscibility in blends. Generally, a single glass transition temperature $T_g$ observed in a blend will be taken as an indication of miscibility. The DSC curves for our quenched PCL samples present a low $T_g$ transition at about −60°C and a fusion peak at about 60°C. Depending on hydroxyl content and molecular weight, $T_g$s of the PS(OH) samples were found to be in the range from 80 to 120°C. Fig. 1 shows the results for blends of PS(OH)-1/PCL with different compositions. From the inserted figure, which
shows the curves at higher temperature on an enlarged scale, it can be seen that $T_g$ of PS(OH)-1 in the blends does not vary with the blend composition. This indicates that PS(OH)-1/PCL blends are immiscible over all compositions. This immiscibility is obviously attributed to the low density of hydrogen bonding. When the hydroxyl content in PS(OH) reached 3 mol-%, the blends with higher PS(OH) contents, i.e. 60 wt.-% and 80 wt.-%, exhibit miscibility and the others not. However, when the hydroxyl content increases to 5 mol-%, all the PS(OH)-5/PCL blends over the whole composition range show a single $T_g$, which is between the glass transition temperatures of PCL and PS(OH)-5. This indicates that the PS(OH)/PCL blends can realize the immiscibility-miscibility transition by incorporating 5 mol-% of hydroxyl groups into PS. With respect to describing the composition dependence of $T_g$ of a miscible blend, the Fox equation has been widely used, i.e.

$$\frac{1}{T_g} = \frac{W_1}{T_{g,1}} + \frac{W_2}{T_{g,2}}$$

where $W_1$, $W_2$ are mass fractions and $T_{g,1}$, $T_{g,2}$ glass transition temperatures of components 1 and 2, respectively.

However, either negative\(^4\) or positive deviation\(^4\) of the experimental data from the equation are possible, especially for the blends with strong specific interactions. For our present blends of PS(OH) and PCL, the DSC results always present negative deviation. Generally, the negative deviation of $T_g$ decreases as the hydroxyl content in PS(OH) increases. In the blends with high hydroxyl content (17 mol-% and 26 mol-%), over a certain composition range, $T_g$ of the blends becomes very close to or even higher than the values expected from the Fox equation. Related results will be discussed in our forthcoming papers.

**Viscosity behavior and the criterion of complexation**

Viscometry has been successfully applied in monitoring complexation in the blend solutions of PS(OH) and PMMA or other poly(alkyl methacrylate)\(^9,15\). The
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transition from individual polymer coils to complex aggregates can be judged by the profiles of reduced viscosity versus composition. It is remarkable that the results about the complexation and its dependence on hydroxyl content obtained by viscometry are in good agreement with those by non-radiative energy transfer (NRET) fluorospectroscopy and dynamic laser light scattering (LLS). More importantly, the minimum hydroxyl content in PS(OH) required for complexation in inert solvents observed by viscometry is in accordance with that found in the bulk blend cast from the solutions for realizing miscibility-complexation transition. All the related results mean that viscometry can be used as a simple and reliable technique to monitor complexation.

Using viscometry to study complexation in solution is based on the following facts. As composition varies, the viscosity of independent polymer coils follows additivity, while polymer-polymer complexation causes an apparent negative deviation from the additivity, because complexation in solutions always accompanies a contraction or collapse of the component polymer coils. Fig. 2 shows the variation of the reduced viscosities of the PS(OH)/PCL solutions in toluene as a function of the mole fraction of monomeric units, i.e. the ratio of the monomeric units of PS(OH) to those of PCL plus PS(OH). The curves refer to the blend solutions containing PS(OH) components having hydroxyl contents ranging from 3 to 26 mol-%. It can be seen that depending on the hydroxyl content, the solutions show two kinds of a viscosity versus composition relationship. For the mixtures with a hydroxyl content in PS(OH) lower than 5 mol-%, the reduced viscosity varies rather homogeneously with the composition, being close to the weight-average viscosity of the two components. However, for the mixtures with hydroxyl contents equal to and higher than 8 mol-%, a dramatic viscosity decrease appears with the initial addition of the PS(OH) to PCL solution and then reaches a minimum which is much smaller than the viscosity of either pure component. This quite different viscosity behavior as a
function of composition, which is mainly dependent on the hydroxyl content, can be attributed to the difference in the states of the polymer chains in solution. For the former case, with a lower hydrogen-bonding density, the smooth variation of the viscosity indicates no apparent association between the unlike polymer coils. While for the latter case with a hydroxyl content higher than 8 mol-% the apparent viscosity drop indicates the formation of the intermacromolecular complex.

Crystallization and melting behavior of PCL in blends

The crystallization of PCL proceeds quickly around room temperature and a substantial crystallinity often exists even in the quenched samples. In order to study the effect of hydrogen-bonding density and composition on the crystallinity by DSC measuring the heat response during a heating process in crystallization and melting, two groups of samples were used. One was treated by quenching to liquid nitrogen temperature from the melt and the other was annealed after melting and quickly cooling to ensure sufficient crystallization. The conclusion drawn from the two groups is generally in agreement, qualitatively. For simplicity, only the results for those samples being annealed at 40°C for 20 h are discussed.

As in most amorphous/crystalline blends, melting-point depressing in the present blends PS(OH)/PCL was observed. The measurements were conducted for six series of samples containing PS(OH) with different hydroxyl contents and over a broad composition range. For simplicity, only the data for the blend series containing the respective component of PS(OH)-1, PS(OH)-5 and PS(OH)-17 are shown in Fig. 3.

![Fig. 3. Melting point \( T_m \) of PCL versus composition for annealed PS(OH)-x/PCL (x = 1 (\( \blacktriangledown \)), 5 (\( \bullet \)), 17 (\( \blacklozenge \))) blends]

The curves show a different behavior of melting-point depression. In the case of PS(OH)-1/PCL, a very small effect on the melting point of PCL can be detected. This is understandable because the blend is immiscible as judged by \( T_g \) analysis and therefore the crystallization of PCL should proceed in its own phase without interference of PS(OH)-1 except in the area near the interface. However, the blend of PS(OH)-5/PCL presents a different behavior. Except for the blend with 20 wt.-% PS(OH)-5 showing a slight increase of the melting temperature \( T_m \), all the blends
The effects of hydrogen bonding on the miscibility, complexation and show an apparent $T_m$ depression, which increases with the PS(OH)-5 contents. This is a typical behavior of miscible blends containing a crystallizable component. Finally, for the blends of PS(OH)-17/PCL with high hydroxyl content and consequently high density of hydrogen bonding, a much larger $T_m$ depression is observed. For example, the $T_m$ difference between pure PCL and that in the blend with the composition of PS(OH)-17/PCL (mass ratio 50/50) reaches as high as 3.9°C. This remarkable $T_m$ depression is probably associated with the complex state. Although in terms of phase structure, both ordinary miscible blends and complex blends are the same, they are different in terms of chain arrangements. In ordinary miscible blends, unlike chains are believed to be mixed randomly while in a complex the unlike segments are paired. Therefore, it is reasonable to think that this obvious difference will cause a substantial change in crystallinity.

The effect of complexation on crystallization can be seen more clearly from the plot of the crystallinity of PCL versus the hydroxyl content in PS(OH) as shown in Fig. 4, where the blend composition is PS(OH)-x/PCL (mass ratio 60/40), close to

![Fig. 4. Crystallinity $X_c$ of PCL as a function of the hydroxyl content in PS(OH)-x for annealed blends PS(OH)-x/PCL (mass ratio 60/40)](image)

de the composition value giving a minimum reduced viscosity in the curves shown in Fig. 2. In other words, in these blends, the components may form a maximum degree of complexation. The crystallinity of the PCL was calculated according to:

$$X_c = \left[\frac{\Delta H}{\Delta H_0 \phi_n}\right] \times 100$$

where $X_c$ is the crystallinity of PCL in blends, $\Delta H_0$, the heat of melting of 100% crystalline PCL, is 136.08 J/g$^{17}$, $\phi_n$ is the weight fraction of PCL in the blend. As shown in Fig. 4 the crystallinity $X_c$ decreases with increasing the hydroxyl content in PS(OH) substantially, but it does not change evenly. At the beginning, in PS(OH)-1/PCL, a typical immiscible blend, $X_c$ is 0.58, close to that of pure PCL (0.73) obtained at the same annealing conditions. A substantial $X_c$ decrease appears for the blends of PS(OH)-3/PCL and PS(OH)-5/PCL, both of which are miscible as judged by $T_g$ analysis. This kind of crystallinity depression is similar to those for miscible amorphous/crystalline blends reported in the literature$^{12,13}$, although no
quantitative information is available there. The most interesting fact revealed in Fig. 4 is the almost complete depression of crystallization of PCL in the blends with PS(OH) having hydroxyl contents of 8, 17 and 26 mol-%. All these blends are just those to form complex aggregates in solution revealed by viscometry (Fig. 2). Now we found clear evidence of an unusual large depression of crystallization of the crystallizable component in the complex blends.

This conclusion, i.e. that complex blends exhibit extraordinary ability to depress the crystallization of the crystallizable component, has found its support in a system of STVPh/PCL, which has been extensively studied with respect to the miscibility\(^5,11\). Fig. 5 shows \(X_c\) of PCL in blends of STVPh/PCL as a function of hydroxyl content in STVPh over a broad range from 1 mol-% to 50 mol-%. Clearly, depending on the hydroxyl content, \(X_c\) values are at three levels. The large \(X_c\) is associated with the least hydroxyl contents, i.e. 1 and 3 mol-% in STVPh which lead to immiscible blends. A substantial \(X_c\) decrease to about 10 % appears for the miscible blends with hydroxyl contents ranging from 6 mol-% to 15 mol-%. Finally, in the complex blends with the high hydroxyl contents (22 mol-% and 50 mol-%), crystallization is completely depressed.

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