Phase behavior and phase separation in blends of a liquid crystalline polymer and an amorphous polymer containing hydrogen-bonding interaction

Wenjie Chen*, Jian Wu, Ming Jiang

Department of Macromolecular Science and the Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China

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SUMMARY: The phase behavior and thermally induced phase separation in blends of poly{styrene-co-[p-(2,2,2-trifluoro-1-hydroxy-1,1,1-trifluoromethyl)ethyl-α-methylstyrene]} (PS(OH)) and a thermotropic liquid crystalline polymer (LCP) were studied by optical microscopy (OM), infrared spectroscopy (IR) and time-resolved light scattering (TRLS). PS(OH) contains strong proton-donating groups $\text{C(CF}_3\text{)}_2\text{OH}$, and the LCP is poly[p-(tert-butyl)phenylene fumarate] (PBPF), which is soluble in common solvents. For blends of PS(OH)/PBPF, the miscible region was found only at high PBPF compositions and low temperature due to intermolecular hydrogen bonding between $-\text{C(CF}_3\text{)}_2\text{OH}$ groups of PS(OH) and the phenolic OH end-groups of PBPF according to IR. The PS(OH)/PBPF blend undergoes phase separation via spinodal decomposition (SD) during isothermal annealing in the two-phase regime of phase diagram. The SD yielded unique Vv and Hv scattering patterns, which can be attributed to regular periodic phase-separated structures composed of an anisotropic phase and an isotropic phase. Preliminary studies on the SD process by TRLS showed that the phase separation spontaneously occurs at a certain time, that might be associated with the presence of the LCP.

Introduction

Polymer blends one of the components being a liquid crystalline polymer (LCP) have been studied recently, because of their technological potential and scientific challenges. LCPs contain inherently rigid units, thereby forming a highly "extended chain" morphology, leading to remarkable mechanical properties and thermal stability. Dispersing LCP in a flexible polymer matrix can thus improve "processibility" and mechanical properties. However, blends of LCP and flexible polymer are usually thermodynamically immiscible due to the strong tendency of the rodlike molecules to aggregate with themselves and the unfavorable entropy of mixing. This problem hinders the applications of LCPs such as to construct "molecular composites", in which the LCP is molecularly dispersed in conventional plastics, and hence the reinforcement takes effect at the molecular level. It has been proved that the incorporation of interaction groups into the polymers can improve the miscibility in binary mixtures of a flexible polymer due to the favorable enthalpic interactions.

It is thus of interest to develop a miscible blend of an LCP with a flexible polymer by introducing hydrogen-bonding interaction. Recent works by Jiang et. al. have shown that poly{styrene-co-[p-(2,2,2-trifluoro-1-hydroxy-1,1,1-trifluoromethyl)ethyl-α-methylstyrene]} (PS(OH)), which contains the strong proton-donating group $-\text{C(CF}_3\text{)}_2\text{OH}$, has the remarkable tendency to form a miscible blend with carbonyl-containing polymers via the formation of intermolecular hydrogen bonding interaction. For instance, for a typical immiscible blend system of polystyrene/poly(methyl methacrylate), only 2 mol-% of the $-\text{C(CF}_3\text{)}_2\text{OH}$ group has rendered the miscibility. It can thereby be expected that miscible blends of PS(OH) with a liquid crystalline polyester may be yielded.

Meanwhile, it is of interest to investigate the thermally induced phase separation process in blends containing an LCP as one component. Mechanism and kinetics of the phase separation of polymer mixtures are the subject of extensive studies in recent years. The studies involve time-resolved analyses of structural evolution from the mixtures in the molten, isotropic liquid state or in a neutrally good solvent, induced by quenching the systems to a thermodynamically metastable or unstable state. Owing to the interests in the academic aspects and the importance in the applications, phase separation in a mixture containing an LCP as one component has received much attention lately. However, the effects of LCP on the dynamics of phase separation have not been completely understood yet, mainly due to the complex process of phase separation in such systems. In the case of polymer mixture with one component being an LCP, phase separation may involve two transitions: isotropic-nematic transition and liquid-liquid transition. The formation of liquid crystallinity may affect the phase separation and the coar-
sening process and hence the phase-separated structure to a certain extent.

In this study, a novel rodlike para-linked aromatic polyester, poly[p-(tert-butyl)phenylene fumarate] (PBPF), was used as an LCP component, which was firstly synthesized from fumaryl chloride and tert-butylhydroquinone by Schmidt et al.\textsuperscript{13} This polymer is a thermotropic nematic liquid crystal above the glass transition temperature and, particularly, is soluble in common solvents and thus avails itself as a candidate for solution blending. Firstly, we studied the phase behavior of PS(OH)/PBPF blends. Secondly, the intermolecular interactions were investigated by Fourier-transform infrared spectroscopy (FTIR) in order to get fundamental insight into the miscibility. Lastly, a preliminary study on the thermally induced phase separation by means of time-resolved light scattering techniques was presented.

**Experimental part**

Poly[styrene-co-p-(2,2,2-trifluoro-1-hydroxy-1-trifluoromethylethyl-α-methylstyrene)] (PS(OH)), was synthesized as previously described\textsuperscript{14}. Two different OH contents of PS(OH), 3.9 mol-% and 8.0 mol-%, respectively, were used in this study, which hereafter are referred to as PS(OH)-4 and PS(OH)-8, respectively. The weight-average molecular weights of PS(OH)-4 and PS(OH)-8 are 4.1 \times 10^4 g \cdot mol\(^{-1}\) and 1.9 \times 10^4 g \cdot mol\(^{-1}\), respectively, measured by gel permeation chromatography (GPC). The glass transition temperature \(T_g\) of PS(OH) was about 90°C determined by differential scanning calorimetry (DSC).

Poly[p-(tert-butyl)phenylene fumarate], PBPF, whose chemical structure is shown in Scheme 1, was synthesized from fumaryl chloride and tert-butylhydroquinone by interfacial polycondensation according to the procedures developed by Schmidt et al.\textsuperscript{13} PBPF was characterized by FTIR, DSC, thermogravimetric analysis (TGA) and GPC, respectively. For PBPF, a 5% weight loss (under nitrogen) was observed at 330°C by TGA, a glass transition temperature \(T_g\) was about 105°C determined by DSC, and the weight-average molecular weight is 1.16 \times 10^5 g \cdot mol\(^{-1}\). No other transitions were observed by DSC examination up to 350°C. However, a typical nematic texture of thermotropic LCP was observed under the polarized optical microscope by annealing the polymer above \(T_g\), indicating that the polymer is thermotropic liquid crystalline. Thermal stability of PBPF was confirmed by FTIR as well. It was found that the spectra before and after annealing the sample at 240°C for 10 h were totally the same. This demonstrates that the polymer is rather stable even though it contains \(\text{C} = \text{C}\) groups, that might owe to the conjugation structure of the fumarate. Hence we are sure that the unsaturated bonds in PBPF would not lead to additional complications during the studies of phase separation.

The film specimens of PS(OH)/PBPF blends for optical microscopy and light scattering observations were obtained as follows: homogeneous 1,2-dichloroethane solutions containing 2.5 wt.-% polymer in total were first prepared, the solvent was evaporated in a cover glass at room temperature followed by further drying at 60°C under vacuum for more than 3 days. The thickness of the film is about 10 \(\mu\)m.

The phase diagrams of the PS(OH)/PBPF mixture were obtained according to the observations with optical microscopy (OM) with and without crossed polarizer and analyzer. After annealing the blend films on the cover glass for 24 h at a given temperature, the nature of the samples whether phase separated or not was tested.

FTIR measurements were performed with a Nicolet Magna-550 model spectrometer on all blends of PS(OH)/PBPF. Thin films were prepared by similar procedure as mentioned above, but casting on an aluminium foil. Infrared spectra were recorded in the reflection mode.

Light-scattering measurements during the isothermal phase separation were conducted on our homemade time-resolved light scattering (TRLS) apparatus, whose detailed setup was described in our previous paper\textsuperscript{15}. The changes in the light scattering patterns and light scattering profiles were recorded at appropriate time intervals during isothermal annealing.

**Results and discussion**

**Phase diagrams of PS(OH)/PBPF blends**

The polystyrene/PBPF blends are totally phase-separated over all composition and temperature ranges of our experiments. However, the incorporation of \(-\text{C}(\text{CF}_3)\text{OH}\) groups into polystyrene leads to the partial miscibility of PS(OH) with PBPF. The as-cast films of 10/90 and 30/70 (wt./wt.) PS(OH)/PBPF after drying at 60°C under vacuum were transparent and homogeneous. Upon annealing at a temperature above \(T_g\), the samples show a faint birefringent behavior under crossed polarizers but no distinct isotropic domains or anisotropic domains can be discerned, characteristic of an anisotropic miscible mixture. Upon annealing at a very high temperature, grossly phase separation took place with formation of an anisotropic phase and an isotropic phase. The typical phase structure yielded by this thermally induced phase separation is shown in Fig. 1, which was obtained by annealing 30/70 (wt./wt.) PS(OH)-4/PBPF mixture at 200°C for 20 min. The micrograph clearly shows the regular two-phase morphology with a periodic distance of about 10 \(\mu\)m and bicontinuous feature, which are the characteristic of spinodal decomposition (SD). This
inversely signifies that a single-phase system at room temperature was indeed formed, otherwise regular and bicontinuous morphology could not be yielded by annealing. From this micrograph, a certain nematic texture of LCP can also be seen within the anisotropic domains.

In contrast to 10/90 and 30/70 PS(OH)/PBPF blends, the as-cast films of PS(OH)/PBPF with larger weight fraction of PS(OH) were translucent. An irregular two-phase structure with anisotropic and isotropic phases was seen distinctly under the polarized microscope. Upon annealing at high temperature above $T_g$, the domains of anisotropic phase and isotropic phase grew in size, and a certain nematic texture of LCP was observed in the anisotropic phase as well. For the blends of PS(OH)/PBPF with 90/10 and 70/30 (wt./wt.) compositions, an isotropy-isotropy two-phase structure was observed under very high temperature, indicating the transition of nematic phase into isotropic behavior with increasing temperature. The results of the observations above were summarized in Fig. 2(a) and (b) for PS(OH)-4/PBPF and PS(OH)-8/PBPF blends, respectively. The phase boundary lines discerning the single-phase and two-phase region were drawn somewhat arbitrarily. Thereby, the type of lower critical solution temperature (LCST) phase diagrams can be seen.

The phase diagrams of PS(OH)-4/PBPF and PS(OH)-8/PBPF blends are qualitatively similar, except the miscible region was enlarged slightly when the OH contents increased from 3.9 mol-% to 8.0 mol-%. We had also investigated the miscibility of PS(OH)/PBPF with very high $-\text{C}$(CF₃)₂OH contents, however, we failed to obtain totally miscible PS(OH)/PBPF blends over the whole composition range. This behavior in the present system is distinguished from the two amorphous polymer blends, i.e., in which the total miscibility can be achieved ultimately with increasing $-\text{C}$(CF₃)₂OH contents. In order to understand the molecular origins of the observed miscibility in the present systems, a FTIR study was undertaken subsequently.

**FTIR investigations**

In the blends of PS(OH)/PBPF, the most likely candidate of specific interaction is hydrogen bonding between the ester carbonyl groups of PBPF and the OH groups of PS(OH), i.e., $-\text{C}$(CF₃)₂OH$\cdots$O=C−. Besides, it is expected that hydrogen bonding also occurs between $-\text{C}$(CF₃)₂OH and $\geq\text{C}$(C₆H₅)OH end-groups of PBPF, $-\text{C}$(CF₃)₂OH and $-\text{C}$(CF₃)₂OH within the pure PS(OH),
A (C₆H₃)OH and A (C₆H₃)OH within the pure PBPF. For the sake of high resolution of infrared spectroscopy, the blends containing PS(OH) with a relatively large content of OH was experimented by FTIR. Fig. 3(A) and (B) shows the FTIR spectra in the OH stretching region, 3650–3000 cm⁻¹, and carbonyl stretching region, 1900–1600 cm⁻¹, for the blends of PS(OH)-8/PBPF with varying blending composition at room temperature, respectively. The spectra were shown separately due to the disparity in absorbance between the extremely strong carbonyl region and the OH region. Pure PBPF is characterized by a band at 3487 cm⁻¹, which is attributed to the OH stretching vibration of self-associated OH end-groups of PBPF (phenolic OH···phenolic OH dimer). As the concentration of PS(OH) increases in the blends, the hydroxyl band at 3487 cm⁻¹ shifted progressively to 3512 cm⁻¹, which is assigned to the OH stretching vibration of the OH···OH dimer within the 1-C(CF₃)₂OH groups. The intermediate compositions exhibit respective peaks intermediate between the pure components. This peak shift instead of the split of the peaks to the corresponding frequency of pure components with the change of composition implies the occurrence of intermolecular hydrogen bonding between OH groups of PS(OH) and phenolic OH end-groups of PBPF. The intermolecular hydrogen bonding interaction may be primarily responsible for the miscibility enhancement in the blends of PS(OH)/PBPF.

Fig. 3(B) shows the FTIR spectra in the carbonyl stretching region, 1900–1650 cm⁻¹, for pure PBPF and the blends with different compositions. The absorption at 1741.2 cm⁻¹ is due to the stretching vibration of the ester carbonyl group. No changes of either the position or the band width of the C=O band were observed for the apparently miscible or immiscible blends compared to that for the pure PBPF. This result affirms that the miscibility observed does not arise from an interaction involving the ester carbonyl group. The absence of hydrogen bonding interaction between the OH groups of PS(OH) and the carbonyl groups of PBPF may be probably due to the steric hindrance of tert-butyl groups in the tert-butyl-hydroquinone unit of PBPF polymer, that prevents carbonyl groups from interaction with OH groups of PS(OH). (Note that there are not any evidences of the bands related to the −COOH groups of PBPF in the OH and carbonyl regions, suggesting that most of the end-groups of PBPF are phenolic OH groups).

Additional evidence to support the present explanation for miscibility was provided by the changes of the absorption region characteristic of the C−OH stretching vibration with blend compositions. Fig. 4(A) and (B) shows the infrared spectra in the region of 1150–1050 cm⁻¹ and 1300–1100 cm⁻¹. To isolate the bands due to the C−OH stretching vibration of phenol OH end-groups of PBPF or OH groups of PS(OH), and to remove any interferences of bands arising from blending, the difference spectra (blend-PBPF or blend-PS(OH)) were calculated and are shown in Fig. 4(A) (blend-PBPF) and Fig. 4(B) (blend-PS(OH)), respectively. Curve a in
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Comparing the spectra of PS(OH)-8 in blends (curve b-f of Fig. 4(A)) to pure PS(OH)-8 (curve a of Fig. 4(A)), it was found that the absorption band at 1104 cm$^{-1}$ of curve a, attributable to the C─O stretching vibration of ─COH groups in PS(OH)-8, shifted progressively to higher frequency with increasing PBPF contents. This could occur when the self-associated OH...OH hydrogen bonding in PS(OH) was replaced by the intermolecular hydrogen bonding (─C(CF$_3$)$_2$OH...OH(C$_6$H$_5$)─). Concurrently, it can be seen from Fig. 4(B) that, by comparing the spectra of PBPF in blends (curve f~b) to pure PBPF, the absorption band at 1210.5 cm$^{-1}$ of curve g, attributable to the C─O stretching vibration of phenolic hydroxyl groups, shifted progressively to low frequency with increasing PS(OH) contents. This could occur when the self-associated (C$_6$H$_5$)OH...HO(C$_6$H$_5$)─hydrogen bonding was replaced by the intermolecular (C$_6$H$_5$)OH...OH(CF$_3$)$_2$C─hydrogen bonding. Hence, the shifts of C─O bands as a function of blend compositions confirm the existence of intermolecular hydrogen bonding interaction, and it, again, leads us to believe that the miscibility between PS(OH) and PBPF arises indeed from intermolecular hydrogen bonding between ─C(CF$_3$)$_2$OH and phenol hydroxyl end-groups.

Looking back on the phase diagram shown in Fig. 2(a) and Fig. 2(b), one can see that the blends cross a phase boundary, separation into two phases from miscible blend, when the weight fraction of PS(OH) increases from 0.3 to 0.5. This result can also be drawn from the infrared spectroscopy investigation. In Fig. 3(A), an additional very broad band centred at 3362 cm$^{-1}$ can be obviously seen in the 50/50, 70/30, 90/10 PS(OH)-8/PBPF blends as well as in pure PS(OH)-8, which is attributable to the C─O stretching vibration of OH...OH multimers within ─C(CF$_3$)$_2$OH groups, while this band did not emerge in the spectra of the single-phase blends (10/90 and 30/70 PS(OH)-8/PBPF blends). The presence of the band at ca. 3362 cm$^{-1}$ signifies strongly that there are grossly aggregations of the PS(OH)-8 component to form a PS(OH)-rich phase in the 50/50, 70/30 and 90/10 PS(OH)-8/PBPF blends. This is in agreement with that as we have apparently obtained in the OM observations. (Note also that some degree of intermolecular hydrogen bonding still exists in a phase-separated mixture. This always happens, because usually there is somewhat partial miscibility in the two coexisting phases even for a phase-separated mixture.)

As a result of the above studies, the intermolecular hydrogen bonding between OH groups of PS(OH) and phenolic OH end-groups of PBPF, which is favorable to the miscibility, has been identified. Meanwhile, self-associating hydrogen bonding within PS(OH) and within PBPF also occurred, which are unfavorable to the miscibility. The miscibility observed in the present system can...
be viewed approximately as a balance between these two large and dominant effects. With the increase of PBPF composition, the intramolecular hydrogen bonds between the phenolic OH end-groups of PBPF and the OH groups of PS(OH) increase, while the self-associating hydrogen bonds within the OH groups of PS(OH) decrease, that results in the single-phase blends emerging at a high PBPF composition. Also, as the degree of intramolecular hydrogen bonding in the present system is dependent mostly on the concentration of phenolic OH end-groups, the further increase in OH contents of PS(OH) might be ineffective for further improvement of miscibility.

**Thermally induced phase separation in PS(OH)/PBPF**

As has been shown in Fig. 1, regular and bicontinuous two-phase morphology can be yielded by thermally induced phase separation, which are the characteristic of spinodal decomposition (SD). Moreover, within the anisotropic domains, a fine liquid crystalline texture can be seen.

The SD in the present system yielded unique Vv and Hv light-scattering patterns, as shown in Fig. 5. Under the Vv scattering condition, a scattering pattern with two-fold symmetry having two strong intensity maxima at the azimuthal angles $\mu = 90^\circ$ and $270^\circ$ was formed (Fig. 5(a)). The scattering pattern obtained under the Hv scattering condition exhibiting two strong intensities on the meridian ($\mu = 0$ and $180^\circ$) is identical to that obtained under the Vv condition only rotated by $90^\circ$.

Under the Hv scattering condition, a four-fold symmetry pattern with intensity maxima at odd multiples of the azimuthal angle ($\mu = 45^\circ$) is observed (Fig. 5(b)). The scattering pattern under Vv in the present system is markedly different from the ring pattern in well-known SD of two amorphous polymer blends. Comparing the two scattering patterns in Fig. 5(a) and (b), it can be found that the scattering angle with the maximum intensity is independent of the orientations of the polarizer and analyzer, i.e. the Hv and Vv scattering pattern give the same scattering angle with the maximum intensity. Moreover, the scattering angle with the maximum intensity was found to shift toward small angle with annealing time.

Similar scattering patterns under Hv and Vv conditions have been also reported by Hashimoto et al. in the system containing poly(ethylene terephthalate) and a copolyester of p-oxybenzoate with ethylene terephthalate$^9$. According to their studies, these unique Hv and Vv scattering patterns can attribute to the contributions of both orientation and concentration fluctuations. The unique Vv and Hv scattering patterns in the present system may be found when the two-phase structure composed of anisotropic phases and isotropic phases exhibits periodicity and more, the contribution of the orientation fluctuation is greater than that of the periodic concentration fluctuation.

The scattering angle ($\theta_{an}$) with maximum scattering intensity is associated with the periodicity ($A_w$) of phase-separated structures, i.e. $A_w = 2\pi/q_m$, and $q_m$ is defined by

$$q_m = 4\pi/\lambda.\sin(\theta_{an}/2)$$

where $q$ is the magnitude of the scattering vector, and $\lambda$ is the wavelength of the incident beam in the medium. The shift toward small angle of $\theta_{an}$ with annealing time is due to the coarsening of the two-phase structure.

Fig. 6 shows the time changes of $q_{m}(t)$ for blends of 30/70 (wt./wt.) PS(OH)-4/PBPF annealing at 200°C. The time evolution behavior of the maximum scattered light intensity $I_m(t)$ during phase separation was plotted similarly. Both $q_{m}(t)$ and $I_m(t)$ were obtained from Vv light scattering. In the earlier time region, $q_m(t)$ doesn’t change.
virtually while the $I_m(t)$ grows up with time, and thus this region could be assigned roughly to the early stage of SD. In the succeeding region, $q_m(t)$ decreases and $I_m(t)$ increases with time, indicating the occurrence of coarsening of the phase-separated structure. The preliminary experimental results show the power law

$$q_m(t) \sim t^{-1}$$

in this region. This is similar to that given by Siggia\textsuperscript{17} for the growth of domains driven by the local instability of percolating networks. Ultimately, $q_m(t)$ and $I_m(t)$ were found to be effectively pinned. Details of the time evolution of $q_m(t)$ and $I_m(t)$ will be reported elsewhere. Here, it is worth noting particularly that the spontaneous pinning of the structure is of importance in structure control. The possibility causing the spontaneous pinning of structure might be illustrated presumably as follows: one possibility is that the pinning may be associated with the structure changing of percolation to cluster, as suggested by Hashimoto et al.\textsuperscript{18} When the percolation structure changes to cluster structure, the coarsening proceeds mainly through the diffusing out from the droplet to the matrix and then condensed into different portion of droplets, this process has to overcome a barrier associated with enthalpy of mixing of polymers as proposed by Hashimoto et al.\textsuperscript{19} or the entropic barrier created for the transport of long chains across sharp interfaces between the phase-separated domains as proposed by Muthukumar\textsuperscript{19}. Such barriers are most likely to be in effect for the present system, due to the anisotropic nature or the wall effect of LCP. Another possibility may be associated with the interaction of PS(OH) and PBPF, i.e. OH group of PS(OH) may react with the ester carbonyl of PBPF to form a grafted polymer at high temperature\textsuperscript{20}, which can act as an interfacial agent to stabilize the structure. Still others are, of course, possible. The detailed studies on the phase separation will be reported in a separate publication.

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{Time changes of $q_m(t)$ and $I_m(t)$ during spinodal decomposition for the 30/70 (wt./wt.) PS(OH)-4/PBPF blend at 200°C.}
\end{figure}

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