ELSEVIER

Polymer 40 (1999) 959–969

polymer

Miscibility enhancement of modified polystyrene blends with a liquid crystalline polymer

Jiasong He*, Jie Liu

State Key Laboratory of Engineering Plastics, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 5 January 1998; accepted 15 April 1998

Abstract

Polystyrene (PS) was completely immiscible with a liquid crystalline polymer (LCP), a copolyester of *p*-hydroxybenzoic acid and poly(ethylene terephthalate). As revealed by differential scanning calorimetry and scanning electron microscopy (SEM), chemically modified PS, sulfonated PS (SPS) and four of its salts, were miscible with the LCP. Each LCP/SPS blend had only one composition-dependent glass transition temperature (T_g), from which and from the T_gs of the SPS compounds, the T_gs of the LCP component were found to be almost the same via the Fox equation. SEM observation showed that LCP/SPS 75/25 blends had a homogeneous texture with no discernible dispersed particles, while LCP/SPS 25/75 blends had dispersed, nanometre-sized particles which were aggregates of SPS anions as confirmed by X-ray photoelectron spectroscopy. Characteristic absorption shifts in the Fourier transform infra-red spectra of LCP/HSPS revealed that miscibility enhancement was caused by specific interactions between the carbonyl groups of LCP and sulfonate groups of the acid form of SPS.

Keywords: Liquid crystalline polymers; Sulfonate ionomers; Miscibility

1. Introduction

Polymer blending is a common and versatile way to develop new materials with a desirable combination of properties. Among these polymer blends, in situ composites containing a thermotropic liquid crystalline polymer (LCP) is one group of particularly attractive materials, owing to their specific rheological and mechanical performance [1–3]. However, because of poor interfacial adhesion resulting from the complete immiscibility between LCPs and most common plastics, it is difficult and impossible (in most cases) to obtain the expected mechanical properties based on the Rule of Mixtures. So, in recent years, several methods have been explored to improve the interfacial adhesion for effective transfer of stress at the interface between the LCP and matrix phases.

Adding ionomers to in situ composites has proved to be an effective way of achieving this purpose [4–7]. Weiss and co-workers [4] reported that the zinc salt of lightly sulfonated polystyrene ionomers (ZnSPS) was an effective compatibilizer for blends of a wholly aromatic liquid crystalline polyester with Nylon 66 and polycarbonate. ZnSPS was miscible with this LCP, a wholly aromatic copolyester of 73% hydroxybenzoate (HBA) and 27% hydroxynaphthanoate (HNA), although Fourier transform infra-red (FTi.r.) spectroscopic analysis of the carbonyl vibration failed to detect a significant interaction between the two polymers. In previous studies we used an ionomer, i.e., lightly sulfonated polystyrene (SPS), for the compatibilization of LCP blends with polysulfone (PSF) [5], polycarbonate (PC) [6] and polyetherimide [7]. Specific interactions led to the compatibilization of SPS in these blends, which was revealed by inward shifts of the glass transition temperatures (T_gs) of the component polymers in differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (d.m.a.) thermograms and by a much finer dispersion of the minor LCP phase in these matrix polymers. As a result, a significant improvement in mechanical properties, with acceptable processability, was achieved by the compatibilization via ionomers in these ternary blends.

In these experiments an interesting phenomenon was observed. Zinc salts of SPS (ZnSPS) were miscible or at least partially miscible with an LCP that was a copolyester of *p*-hydroxybenzoic acid and poly(ethylene terephthalate) (PHB/PET 60/40, mol%), in their melt blends [5–7], although their molecular structures and the rigidity of

* Corresponding author. Tel.: +86-10-6261-3251; Fax: +86-10-6256-9564; e-mail: hejs@infoc3.icas.ac.cn

0032-3861/98/$ - see front matter
PII S0032-3861(98)00299-7

their molecular chains differ greatly from each other. In order to gain insight into these phenomena, an investigation has been conducted on the miscibility of this LCP (a copolyester of PHB/PET), with sulfonated polystyrene and its lithium, sodium, zinc and manganese salts.

Miscibility enhancement via ionic interactions [8,9] is based on incorporating specifically interacting groups into the polymers to be mixed, which results in the formation of ion pairs on the different polymeric chains in the mixture. In such systems, there are specific intermolecular interactions occurring at fixed positions along the polymer chains. The FTi.r. method is becoming one of the most useful techniques to investigate specific interpolymer interactions introduced into immiscible polymer blends for enhancing the miscibility of polymer pairs [10,11]. The information obtained by FTi.r. measurement may give some answers in the fundamental aspects, such as differentiating between miscible and immiscible blends and determining the presence, nature, number and relative strength of specific intermolecular interactions in miscible blends. By means of a spectral subtraction technique, FTi.r. measurements successfully revealed the origin of the miscibility enhanced by ion–dipole interactions between sulfonic acid groups of SPS and polar groups of PC [12].

This paper presents the thermal behaviour of LCP blends with sulfonated polystyrene and its lithium, sodium, zinc and manganese salts, determined by d.s.c., and the morphology and aggregation in these modified blends, determined by scanning electron microscopy (SEM). As an extension, it is concerned with the FTi.r. investigation and spectral manipulation performed upon LCP/SPS blends for revealing the origin of miscibility enhancement.

2. Experimental

2.1. Materials

The starting polystyrene was PS 666D ($M_w = 243\,000$, measured by gel permeation chromatography), obtained from Yanshan Petrochemical Corporation, China. Sulfonated PS (SPS) was prepared by the procedure described by Makowski et al. [13]. This method has relatively little effect on the polymer backbone and the molecular weight, and results in a random placement of sulfonic acid groups at the *para* position on the phenyl ring of polystyrene. The sulfonation level was 6.9 mol%, calculated from the elemental analysis of sulfur. Hereafter the acid form of SPS will be denoted as HSPS. Lithium, sodium, zinc and manganese salts were prepared by neutralizing the SPS with excess lithium hydroxide, sodium hydroxide, zinc acetate and manganese acetate, respectively. They are denoted as LiSPS, NaSPS, ZnSPS and MnSPS, respectively, and commonly as SPS. The thermotropic LCP used was a random copolyester of *p*-hydroxybenzoic acid (PHB)/poly(ethylene terephthalate) (PET) obtained from Chengdu Silicone Research Center, China. Its PHB content was 60 mol% and its melting point was 190°C.

2.2. Blending

Blends of LCP/SPS and LCP/PS were prepared by solution mixing. Before dissolving, all materials were dried at 120°C under vacuum for at least 12 h. SPS was dissolved in a mixture of toluene/methanol (90/10, by weight) and PS in 1,2-dichloroethane. The LCP was dissolved in a 1,1,2,2-tetrachloroethlane/phenol mixture (40/60 by weight) at 70°C for 10 days. Then the LCP solution was added dropwise into a stirred SPS solution to make LCP/SPS 25/75, 50/50 and 75/25 blends (polymer compositions by weight). LCP/PS blends were prepared in the same manner. Stirring of the mixture solutions was continued for 4 days. After evaporating off most the solvent, the blend samples were dried under vacuum at 90°C for 48 h.

2.3. Observation and characterization

D.s.c. measurements were conducted on a Perkin–Elmer DSC-7 instrument under an atmosphere of circulating dry nitrogen. Before performing the d.s.c. measurement with a heating rate of 20°C min^{-1}, all samples were heated to and kept at 300°C for 5 min to eliminate the influence of their different thermal histories, followed by quenching to ambient temperature.

The morphology of the blends was observed with a Hitachi S-530 scanning electron microscope. The fracture surface for the observation was obtained by immersing and breaking the sample in liquid nitrogen, and coating with gold. A Philips EDAX-9100 X-ray photoelectron spectroscope (XPS) equipped with SEM was used to detect elements in different areas of the fracture surface.

Infra-red spectroscopic (i.r.) characterization was performed with a Perkin–Elmer FTIR 2000 spectrophotometer. The specimens for i.r. examination were cast from solutions onto KBr plates. After drying under an infra-red lamp for 20 min, samples were kept under vacuum at 90°C for 6 h to remove completely all traces of solvent. The number of scans per spectrum was 32 in the range of 370 to 4000 cm^{-1}, with a resolution of 1 cm^{-1}. The spectra recorded at elevated temperatures were obtained with a heating chamber and controller mounted in the spectrometer. The heating rate was 1°C every 3 min throughout the whole measurement. Each accumulation of 32 scans took less than 2 min, so that each spectrum could be treated as being taken at a quasi-constant temperature.

3. Results and discussion

3.1. Thermal properties

D.s.c. thermograms of starting materials and their blends are given in Figs 1 and 2 and the glass transition

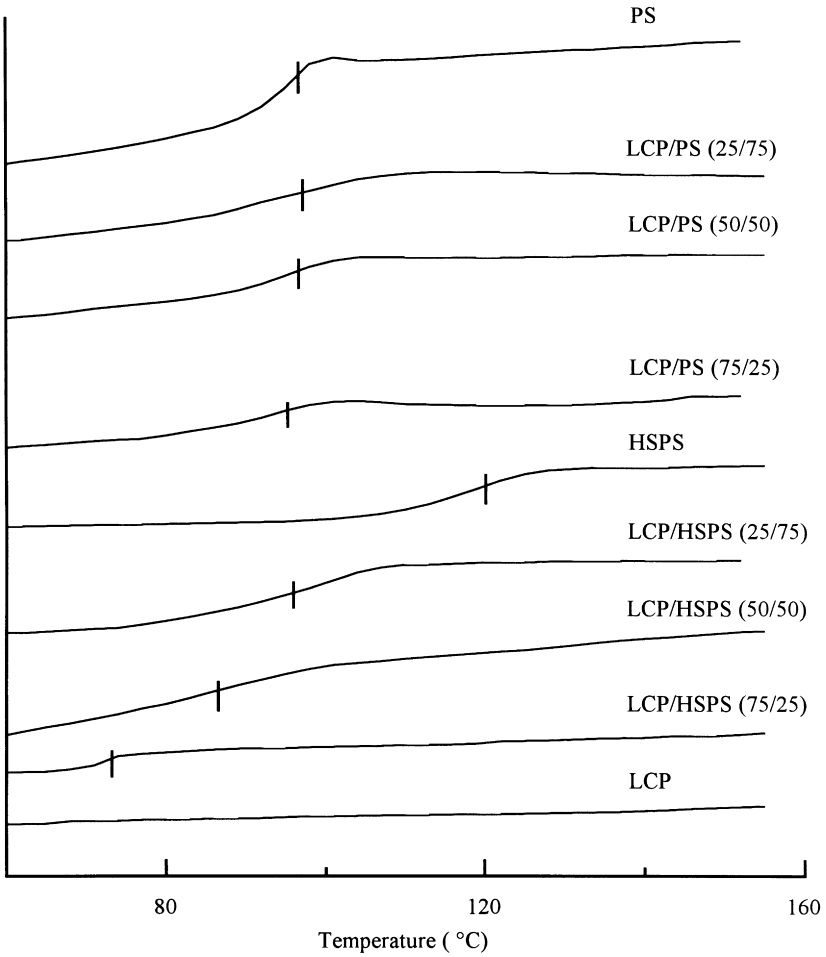

Fig. 1. D.s.c. thermograms of starting materials and of the blends LCP/PS and LCP/HSPS.

temperatures are summarized in Table 1. Because of the rigidity of the LCP chain, we failed to detect its T_g. The T_gs of the three LCP/PS blends show no significant shift compared with that of pure PS at ca. 96°C (Fig. 1). This means that PS and LCP are completely immiscible [14].

On the contrary, it is a surprise to note that all of the LCP/SPS blends exhibit a single T_g which varies with

Table 1
T_gs of ionomers and their blends with LCP, and T_gs of LCP

Ionomer (T_g, °C)	Blend (wt%)		T_g (°C)	T_g of LCP (°C)
PS (96.8)	LCP/PS	75/25	93.7	—
		50/50	94.4	—
		25/75	96.3	—
HSPS (119.3)	LCP/HSPS	75/25	71.2	62.8
		50/50	82.3	62.6
		25/75	94.7	61.4
MnSPS (130.5)	LCP/MnSPS	75/25	71.9	62.5
		50/50	85.5	63.8
		25/75	97.6	59.2
ZnSPS (133.4)	LCP/ZnSPS	75/25	74.2	64.7
		50/50	84.3	61.3
		25/75	101.1	58.4
LiSPS (128.4)	LCP/LiSPS	75/25	72.1	62.9
		50/50	84.4	62.4
		25/75	98.7	58.3
NaSPS (126.6)	LCP/NaSPS	75/25	72.5	63.5
		50/50	84.7	62.8
		25/75	99.2	59.8

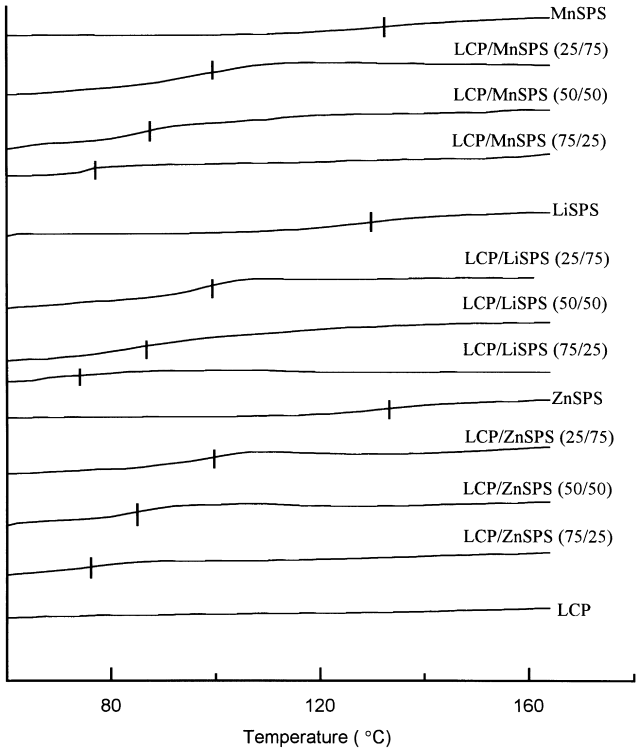

Fig. 2. D.s.c. thermograms of starting materials and of the blends LCP/MnSPS, LCP/LiSPS and LCP/ZnSPS.

composition, and is much lower than those of the pure SPS. HSPS has a T_g at 119.3°C, while the T_gs of the LCP/HSPS 75/25, 50/50 and 25/75 blends are at 71.2°C, 82.3°C and 94.7°C, respectively. Other blends of the LCP with LiSPS, ZnSPS and MnSPS have the same trend (Fig. 2). The composition dependence of the blend T_gs indicates that all of these SPSs are miscible, or at least partially miscible, with the LCP, although their molecular structures differ greatly from each other.

Based on the assumption of random mixing at the segmental level, several theoretical equations have been proposed to correlate T_g with the composition of miscible blends. One of the most common equations is the Fox equation [15]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}}$$

where w_i is the weight fraction of polymer i and T_{g_i} is the glass transition temperature of polymer i. The Fox equation is quite applicable for predicting the T_g of a miscible blend with certain T_gs and weight fractions of component polymers. Inversely, for a miscible blend with certain weight fractions in the blend and known T_gs of one component polymer and the blend, it is possible to use the Fox equation to calculate the T_g of the other component [16]. For this purpose, the postulation that the blend is a completely miscible one should be true. By assuming that all of the LCP/SPS blends were completely miscible, the Fox equation was used to predict the T_g of LCP in the present study. The calculated data are listed in Table 1. It is surprising that the T_gs of LCP calculated from the Fox equation are almost the same, ca. 62°C, with quite small deviations in the case of SPS weight fractions at 25 and 50%. Meanwhile, this T_g of the LCP is consistent with those reported by other researchers [14,17,18] for the copolyester of the same molar composition. This agreement, in turn, proves the validity of the Fox equation for these blends and the fact of complete miscibility in the LCP/SPS blends studied here.

Furthermore, another noticeable feature in d.s.c. thermograms is that the transition for the LCP/SPS 25/75 blends is broadened (Figs 1 and 2) and the T_g values calculated for the LCP component are 3 to 5°C lower than that mentioned above, except for the LCP/HSPS blend. The calculated T_gs for LCP in the LCP/LiSPS, LCP/NaSPS, LCP/ZnSPS and LCP/MnSPS blends are 58.3, 59.8, 58.4 and 59.2°C, respectively (Table 1). Broadening of the glass transition is generally an implication of local fluctuations in the blend composition [19]. The possible explanation for this transition broadening and the negative deviation is that the concentration of interactions decreases with increasing SPS content, presumably due to an increasing amount of competing interpolymer association and aggregation of the SPS ion pairs [4,20].

3.2. Morphology

SEM micrographs of LCP/PS blends at the 75/25 and 25/75 compositions are shown in Fig. 3(a) and Fig. 4(a), respectively. They provide direct evidence for the phase separation in LCP/PS blends. LCP/PS blends have a distinct two-phase morphology, characterized by large globules of the minor phase dispersed in the continuous phase. In the 75/25 LCP/PS blend [Fig. 3(a)], PS spheres having a large variation of diameter are dispersed in the continuous LCP phase. In LCP/PS 25/75 [Fig. 4(a)], large LCP particles with diameters of 1 to 2 μm are scattered within the PS matrix. The poor interfacial adhesion in these blends is evident from undeformed holes left after separation of the dispersed particles from the continuous phase on the fracture surface.

On the other hand, micrographs of all of the LCP/SPS 75/25 blends show a very smooth and homogeneous texture with no discernible dispersed particles [Fig. 3(b–f)]. This dramatic reduction of the domain size, together with the thermal behaviour of these blends, indicate miscibility of the LCP/SPS blends.

It is interesting to note that all LCP/SPS 25/75 blends [Fig. 4(b–f)] have a smooth fracture surface with scattered small particles. Their diameters are smaller than 150 nm, much smaller than those in the LCP/PS 25/75 blend. These particles can be rationally attributed to ionic aggregates of SPS, on the basis of the interpretation of the transition broadening in d.s.c. thermograms and the negative deviation of T_gs estimated by the Fox equation discussed above. For further confirmation, elemental analysis in

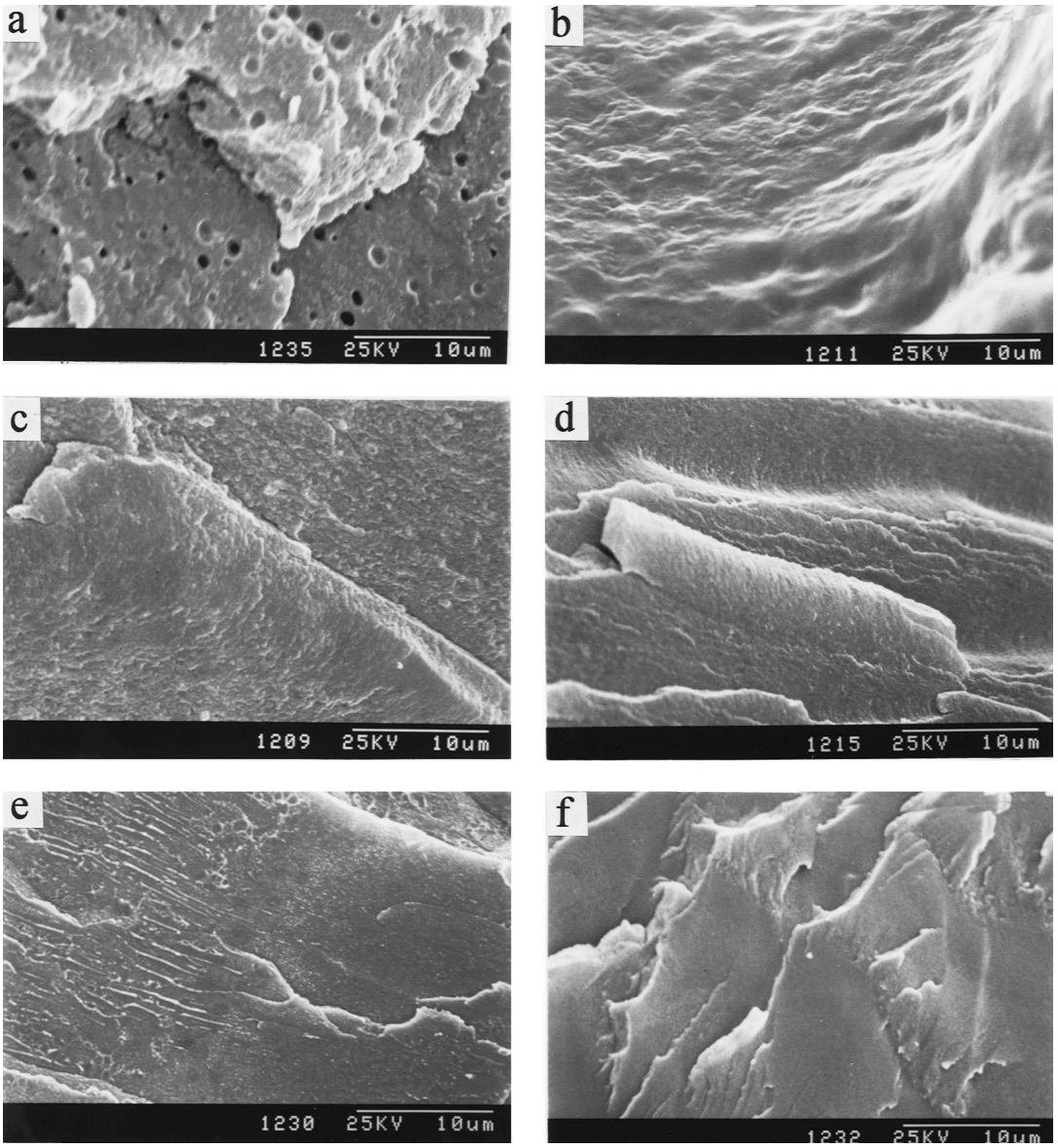

Fig. 3. SEM micrographs of blends at the 75/25 composition: (a) LCP/PS, (b) LCP/HSPS, (c) LCP/MnSPS, (d) LCP/LiSPS, (e) LCP/ZnSPS and (f) LCP/NaSPS.

different fracture areas of the LCP/MnSPS 25/75 and LCP/HSPS 25/75 blend samples was performed by XPS (the results are shown in Table 2). Gold was detected as a consequence of the gold coating for SEM observation. The presence of trace solvent leads to a small amount of chlorine in these samples. In the particle area of LCP/HSPS, the percentage of sulfur atoms is 53.44 at% which is higher than 43.25 at% in the non-particle area. In the particle

Table 2
The elements and their contents at the surfaces, measured by energy dispersion

	Element	Particle area		Non-particle area	
		at%	wt%	at%	wt%
LCP/HSPS	Au	43.21	82.29	50.47	86.07
	S	53.44	16.56	43.25	12.01
	Cl	3.35	1.15	6.28	1.92
LCP/MnSPS	Au	43.36	79.54	70.51	91.21
	S	33.03	9.86	9.41	1.98
	Mn	15.45	7.90	16.68	6.02
	Cl	8.16	2.70	3.4	0.79

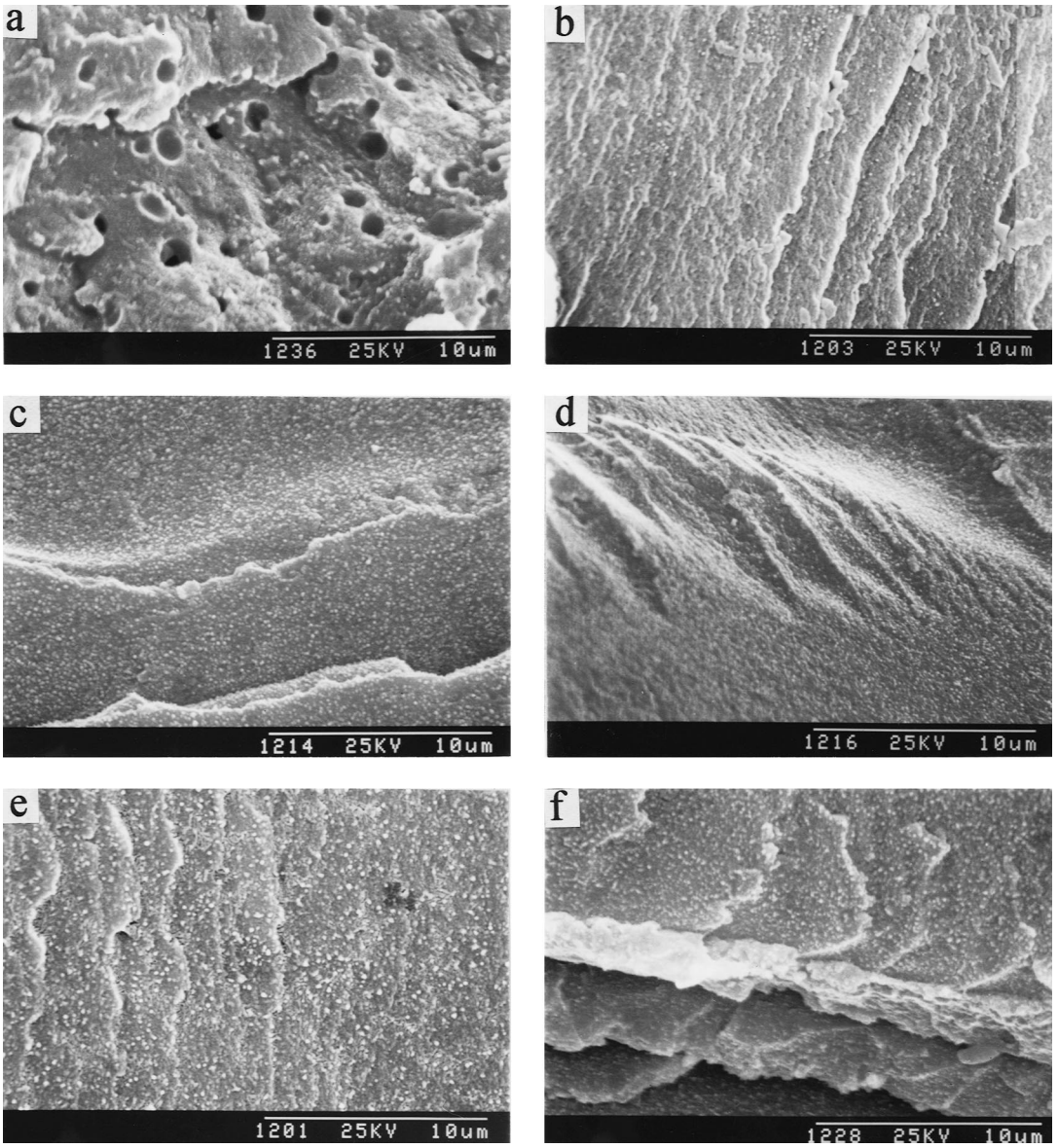

Fig. 4. SEM micrographs of blends at the 25/75 composition: (a) LCP/PS, (b) LCP/HSPS, (c) LCP/MnSPS, (d) LCP/LiSPS, (e) LCP/ZnSPS and (f) LCP/NaSPS.

area, the ratio of sulfur to manganese (at%) is 33.03/15.45 ≈ 2, while in the non-particle area this ratio is only 9.41/16.68 ≈ 0.5. These data indicate that a fraction of the sulfur atoms (in the form of sulfonate) contacts LCP molecules closely to form the ion–dipolar interaction, which appears in the non-particle area, while the surplus fraction of sulfur atoms forms anion aggregates, which are in the form of tiny particles. As for manganese ions, they are dispersed randomly in the miscible LCP/MnSPS phase.

3.3. FTi.r. investigation of miscibility enhancement

Olabisi proposed a concept of 'complementary dissimilarity' in enhancing the miscibility of polymer blends, wherein constituents of individual polymer chains were quite different but the interactions between these groups provided the necessary driving force for mutual miscibility [21]. In the case of the LCP/HSPS blend, the presence of specific interactions is responsible for the improvement of miscibility, according to the FTi.r. results. Two types of interaction are possible: (1) ion–dipole interactions between ionic species in HSPS and polar groups in LCP; and (2) hydrogen bonding between sulfonic acid groups of HSPS and carbonyl groups of LCP, which would result in very intimate mixing of the HSPS with the LCP segments.

It is well known if two polymers are immiscible, i.e., phase-separated in their blend, it is possible to synthesize an infra-red spectrum of the blend which is, at least theoretically, identical to the experimental spectrum of this blend, just by adding up the spectra of the two pure component polymers correlated by appropriate weight fractions. Vice versa, for an immiscible blend, it is possible to obtain an

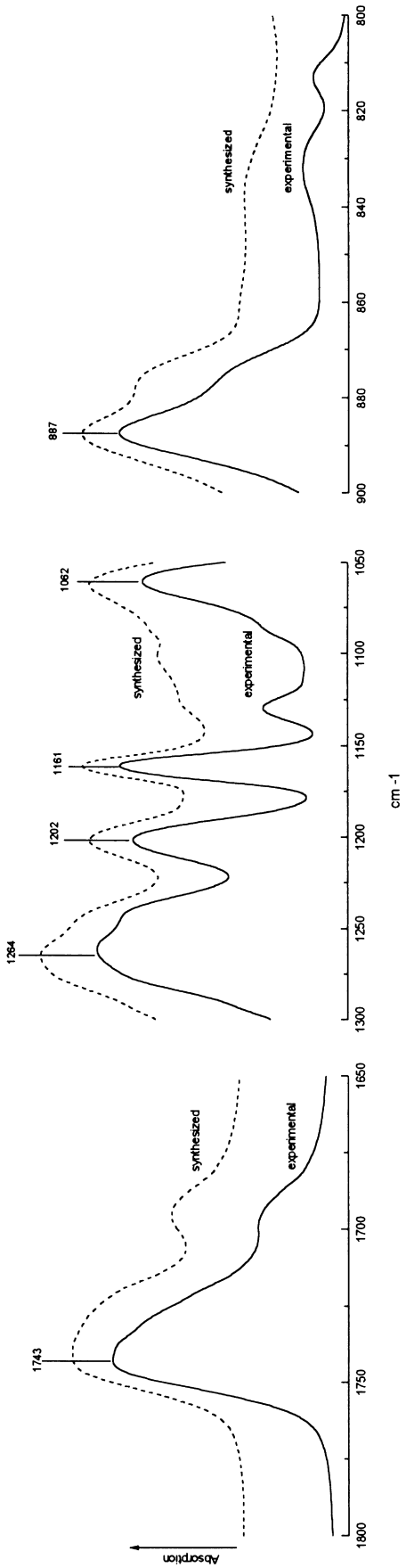

Fig. 5. FTi.r. absorption spectra of the LCP/PS 75/25 blend in different wavenumber regions.

unperturbed spectrum of one component by subtracting the spectrum of the other component from the spectrum of the blend. On the other hand, if polymers are miscible, molecular chains of one component polymer can be mixed closely enough to the other component chains so that the intermolecular interactions will be strong enough to change their molecular environment, which results in i.r. band shifts and broadening. In these cases, considerable differences are generated between the synthesized spectra and experimental ones; or, put in another way, the unchanged spectrum of one component cannot be obtained when the spectrum of the other component is subtracted from the spectrum of the blend. In the present study, the FTi.r. difference spectroscopy technique was used to investigate the miscibility enhancement in LCP/HSPS blends. By comparing synthesized spectra and experimental spectra of blends, the presence of specific interactions can be demonstrated; by subtracting the individual spectra of components from the spectrum of the blend, the changes due to the miscibility effect of the ionic groups can be isolated and characterized.

It was observed that PS is immiscible with LCP by virtue of d.s.c. and SEM in our previous work [5]. Now the conclusion has been confirmed also by FTi.r. results. Fig. 5 shows the spectra of an LCP/PS 75/25 blend recorded in different wavenumber ranges. The spectrum labelled 'synthesized' was obtained by adding up the spectra of pure PS and LCP with corresponding weight fractions (i.e., in this case, 75% for LCP and 25% for PS, respectively). Apparently, the synthesized spectrum is exactly identical to the experimental spectrum obtained from the LCP/PS 75/25 blend. Take the spectra lying in the range 1800 to 1650 cm^{-1}, for example: the synthesized spectrum has a carbonyl absorption at 1743 cm^{-1}, which is the same as that appearing in the experimental spectrum of the blend. Fig. 5 provides more evidence that the characteristic absorption bands remain at the same positions as they appear in the synthesized spectrum.

Fig. 6 gives the spectrum of pure LCP and the difference spectrum of LCP obtained by subtracting the contribution of PS from the spectrum of the LCP/PS 75/25 blend. The difference spectrum therefore represents the sum of the LCP contribution to the blend spectrum and any spectral changes associated with interactions. Compared with the spectrum of pure LCP, the absorption bands characteristic of LCP occur at almost the same position in the difference spectrum of LCP, such as the stretching vibration of carbonyl group at ca. 1743 cm^{-1} and the C–O stretching vibration at 1264 and 1062 cm^{-1}, respectively.

All information described above demonstrates the absence of interactions between LCP and PS molecular chains. In other words, one component keeps its individual properties, especially its molecular environment, unaffected by the presence of the other component in the blend.

Fig. 7 provides experimental and synthesized spectra of the LCP/HSPS 75/25 blend. The double difference spectrum is obtained by subtracting both LCP and HSPS contributions

from the experimental spectrum. The synthesized spectrum is obtained by adding up the spectra of LCP and HSPS to yield an 'immiscible' spectrum of an LCP/HSPS 75/25 blend. In Fig. 7, the synthesized spectrum for LCP/HSPS 75/25 has a carbonyl absorption at 1743 cm^{-1}, whereas the experimental spectrum has its carbonyl absorption shifted to lower frequency, at ca. 1737 cm^{-1}. In the double difference spectrum a carbonyl absorption appears at 1735 cm^{-1}. So it is clear that the carbonyl group is involved in the interactions, as evidenced by the significant band shift. In Fig. 7, considerable differences can be easily detected if the spectra are compared with each other. One distinct difference is that the absorption at 1264 cm^{-1}, associated with the C–O stretching vibration, in the synthesized spectrum shifts to 1259 cm^{-1} in the experimental spectrum and to 1253 cm^{-1} in the double difference spectrum. Considering these band shifts, one has every reason to believe that the C–O groups are also involved in the interactions.

Fig. 8 gives more information about LCP functional groups that may be involved in the interactions. The difference spectrum is obtained by subtracting the HSPS contribution from the spectrum of the LCP/HSPS 75/25 blend. The spectrum remaining here represents the sum of the LCP contribution to the blend spectrum and any spectral changes associated with interactions. Spectral differences are recognized again between the spectrum of pure LCP and the difference spectrum for LCP in several characteristic absorption positions and their appearance. In the difference spectrum a carbonyl absorption appears at 1737 cm^{-1}, whereas in the spectrum of pure LCP it appears at 1743 cm^{-1}, differing from each other by 6 cm^{-1} (Fig. 8). This is consistent with the conclusion reached from Fig. 7 that the carbonyl group is involved in the interactions. In Fig. 8, band shifts are also well documented. Absorption bands associated with the C–O stretching vibration at 1264 and 1062 cm^{-1} shift to lower wavenumber, 1260 and 1060 cm^{-1}, respectively, which agrees well with the conclusion reached from Fig. 7.

The involvement of the sulfonate group in the interactions is confirmed by the change in the absorption bands characteristic of the stretching vibration of the sulfonic acid group (Fig. 9). The difference spectrum of HSPS is obtained by subtracting the LCP contribution from the spectrum of the LCP/HSPS blend. It can be seen that the difference spectrum differs considerably from that of pure HSPS. Of immediate interest is the apparent absorption at 1736 cm^{-1} in the difference spectrum (Fig. 9), resulting from the shift showing the involvement of the carbonyl group in the interactions. It is also noticeable that absorption bands characteristic of HSPS, such as the asymmetric stretching vibration of the sulfonate group at 1245 cm^{-1} and its symmetric stretching vibration at 1058 and 1014 cm^{-1}, shift to lower frequencies: 1224, 1041 and 1011 cm^{-1}, respectively. These shifts to lower frequencies are the consequence of specific interpolymer interactions involving the sulfonic acid group, suggesting a lower polarization of the S–O dipole, due to the increased separation between the sulfonate anion and H^+ [22].

While the results above prove to be attractive and valuable, unfortunately they do not immediately yield information concerning the presence of possible hydrogen bonding, largely because of the relatively low concentration of the bonding and interference of the styrene absorption in the same spectral region. Meanwhile, the complexity of the i.r. spectra of these polymers also hinders qualitative and quantitative assessments. Multipeaked absorption can be observed for each component and blends, resulting from the difficulty in removing the water completely from these

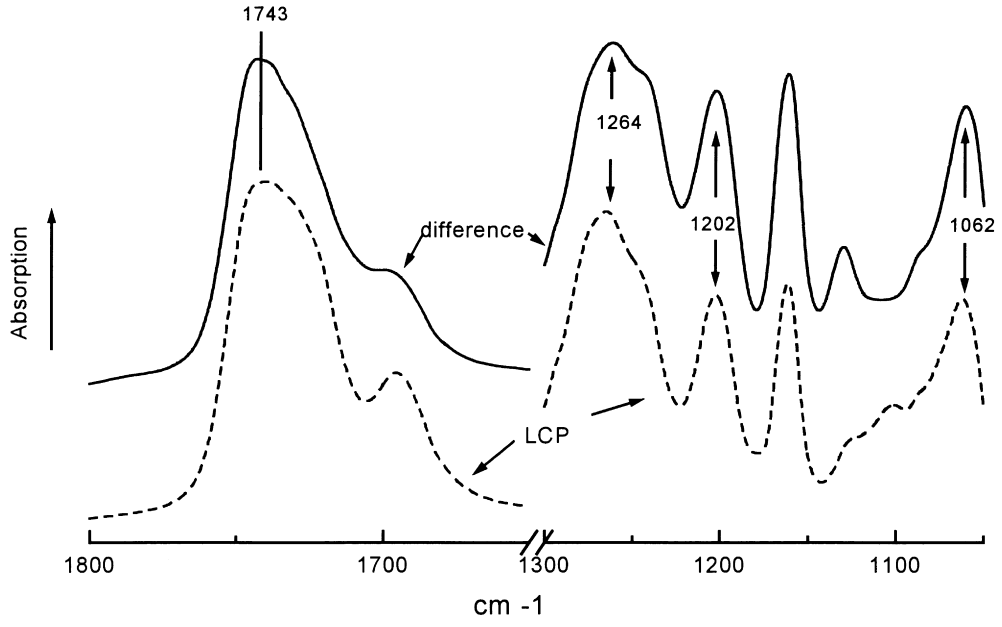

Fig. 6. FTi.r. spectra of pure LCP and difference spectra of LCP obtained by subtracting the contribution of PS from the spectrum of the LCP/PS 75/25 blend.

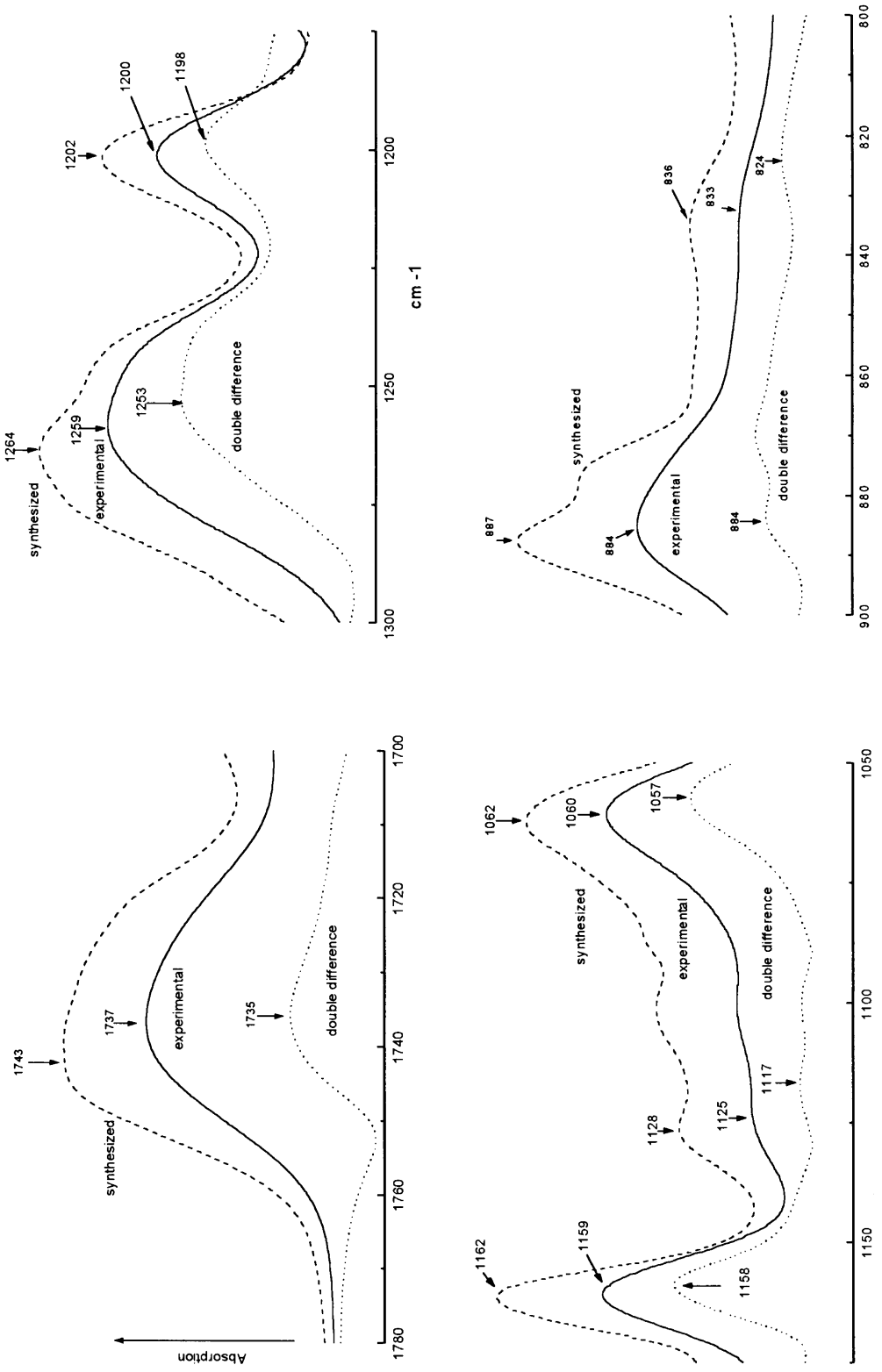

Fig. 7. FTi.r. absorption spectra of the LCP/HSPS 75/25 blend in various regions.

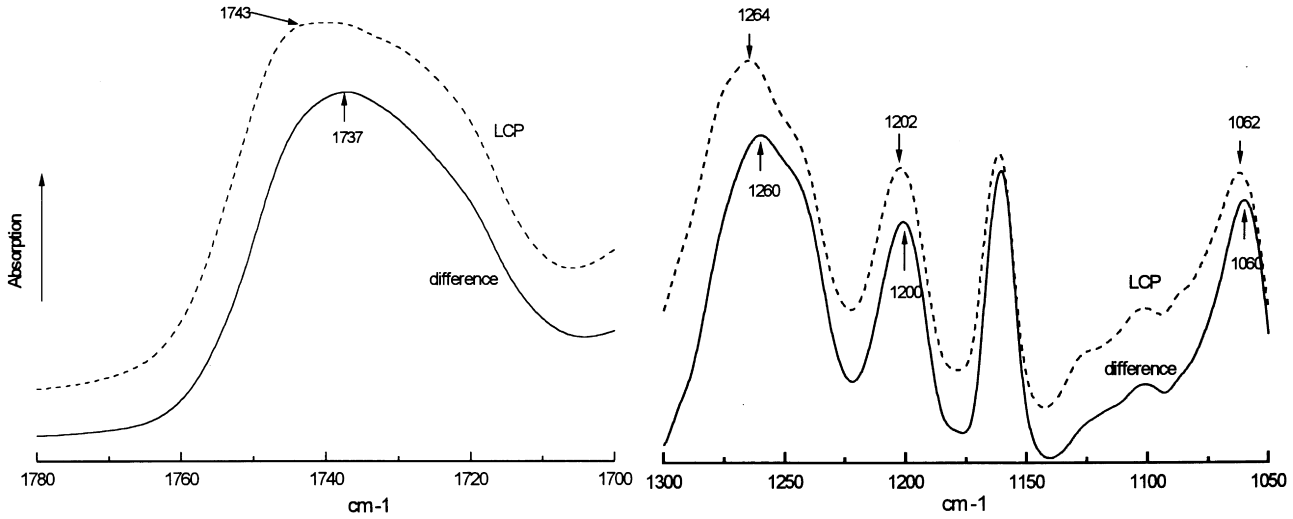

Fig. 8. FTi.r. spectra of pure LCP and difference spectra of LCP obtained by subtracting the contribution of HSPS from the spectrum of the LCP/HSPS 75/25 blend.

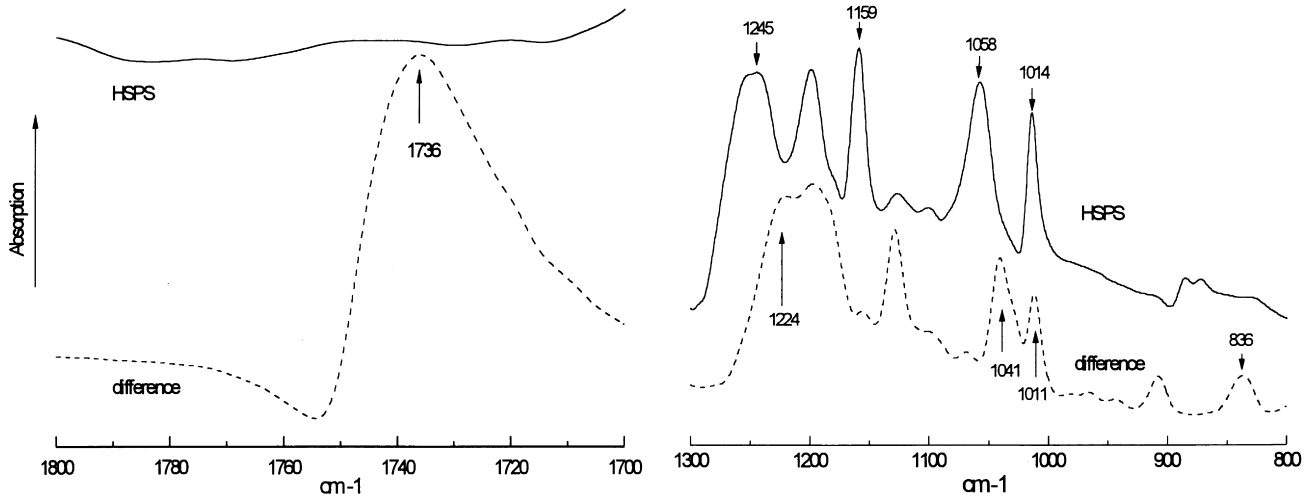

Fig. 9. FTi.r. spectra of pure HSPS and difference spectra of HSPS obtained by subtracting the contribution of LCP from the spectrum of the LCP/HSPS 75/25 blend.

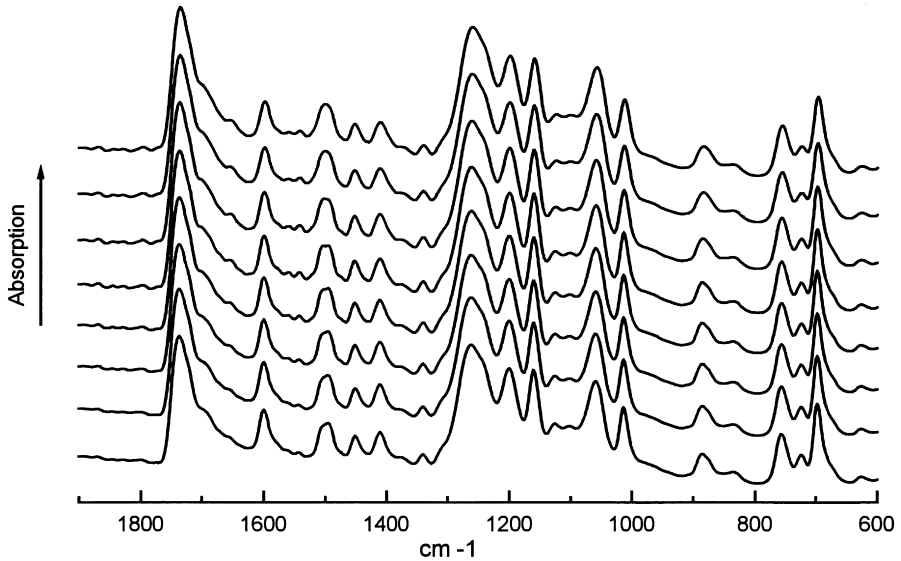

Fig. 10. Spectra of the LCP/HSPS 75/25 blend obtained at different temperatures (from the bottom to the top: 20, 30, 40, 50, 60, 80, 100 and 120°C).

Table 3
The absorption characteristics of the LCP/HSPS 75/25 blend at different temperatures

Temperature (°C)	Absorption position (cm^{-1})				
20	1737	1200	1259	1128	884
30	1737	1200	1260	1127	884
40	1737	1200	1260	1127	884
50	1737	1200	1259	1127	884
60	1738	1200	1259	1127	884
80	1738	1200	1260	1127	883
100	1738	1199	1260	1128	883
120	1738	1199	1259	1127	883

samples. In addition, the aggregation of sulfonic acid groups is well known to occur in the pure ionomer, which is attributed to the effect of hydrogen bonding [23]. Thus the starting HSPS polymer probably already contains a finite concentration of sulfonic acid groups that are hydrogen-bonded with water and other sulfonic acid groups. In the light of these possible factors, especially the presence of ionic aggregation, it is strongly suggested that further FTi.r. studies be undertaken in conjunction with other advanced instrumental analyses.

Finally, another facet of the interactions is worthy of attention. Experiments have been conducted to investigate the effect of temperature on these interactions within the LCP/HSPS 75/25 blend. The experiments were performed under eight intermediate temperatures between 20 and 120°C. The spectra are plotted as a function of temperature in Fig. 10 and the absorption positions of the blend are summarized in Table 3. No apparent changes have taken place in the LCP/HSPS 75/25 blend. The absence of differences within these spectra implies the temperature independence of these interactions, at least within the temperature range from 20 to 120°C.

4. Conclusions

The LCP and PS are completely immiscible. The incorporation of sulfonic acid onto the polystyrene backbone results in single, composition-dependent T_gs and a homogeneous texture of LCP/SPS blends. A complete miscibility of LCP and SPS is reached. FTi.r. studies and spectral manipulations performed on LCP/PS and LCP/HSPS blends show that the driving force for miscibility enhancement lies in the presence of intermolecular interactions involving the carbonyl and C–O groups in LCP chains and the sulfonate group in HSPS. Meanwhile, FTi.r. measurements at stepwise-raised temperatures also indicate that these interactions are temperature-independent.

Acknowledgements

This research was supported by the National Natural Science Foundation of China, Grant No. 59373137.

References

[1] Kiss G. Polym Eng Sci 1987;27:410.
[2] Blizard KG, Baird DG. Polym Eng Sci 1987;27:653.
[3] Isayev AI, Modic M. Polym Compos 1987;8:158.
[4] Dutta D, Weiss RA, He J. Polymer 1996;37:429.
[5] Liu J, He J. Acta Polym Sinica 1996;(4):506.
[6] Liu J, He J. Acta Polym Sinica 1997;(4):496.
[7] He J, Liu J. J Appl Polym Sci 1998;67:2141.
[8] Eisenberg A, Smith P, Zhou Z. Polym Eng Sci 1982;22:1117.
[9] Hara M, Eisenberg A. Macromolecules 1984;17:1335.
[10] Lu X, Weiss RA. Macromolecules 1991;24:4381.
[11] Sullivan MJ, Weiss RA. Polym Eng Sci 1992;32:517.
[12] Liu J, He J. Acta Polym. Sinica 1997;(5):620.
[13] Makowski HS, Lundberg RD, Singhal GH. US Patent 3 870 841, 1975.
[14] Zhuang P, Kyu T, White JL. Polym Eng Sci 1988;28:1095.
[15] Fox TG. Bull Am Phys Soc 1956;1:123.
[16] Koleske JV, Lundberg RD. J Polym Sci, Part A-2 1969;7:795.
[17] Shih HH, Hornberger LE, Siemens RL. J Appl Polym Sci 1986;32:4897.
[18] Gedde UW, Buerger D, Boyd RH Macromolecules 1987;20:988.
[19] Olabisi O, Robeson LM, Shaw MT. Polymer–polymer miscibility. New York: Academic Press, 1979.
[20] Lu X, Weiss RA. Macromolecules 1991;24:4381.
[21] Olabisi O. Macromolecules 1975;8:316.
[22] Lowry SR, Mauritz KA. J Am Chem Soc 1980;102:1665.
[23] Weiss RA, Lefelar JA. Polymer 1986;27:3.