Study of miscibility enhancement in poly(styrene-co-4-vinylphenol)/poly(ethylene oxide) blends by the spin labelling method

Li Tan, Shiming Chen, Zhenghua Ping and Yimin Shen

Abstract: The electron spin resonance (ESR) spectra of end-group spin labelled poly(ethylene oxide) (SLPEO) using 2,2,6,6-tetramethyl-piperdine-1-oxyl nitroxide and its blends with poly(styrene-co-4-vinylphenol) (STVPhs) of different hydroxyl contents were recorded over a wide temperature range. For a blend of SLPEO and pure polystyrene (PS), the ESR spectrum was composed of a single motion component, indicating that PS was immiscible with PEO. For blends composed of SLPEO and different-hydroxyl-content STVPhs, two spectral components with different motion rates were observed over a certain temperature range. The difference between the motion rates should be attributed to microheterogeneity in the blends, with the faster rate corresponding to a nitroxide radical motion trapped in the PEO-rich domain and the slower rate corresponding to a nitroxide radical motion trapped in the STVPPh-rich domain. Variations in the values of a number of the ESR parameters (T_a, T_d and T_50G) and the apparent activation energy (E_a) with hydroxyl content in the blends indicated that the miscibility of the blends increased with increasing hydrogen-bonding density due to specific interactions between the hydroxyl groups in STVPPh and the ether oxygens in PEO.

INTRODUCTION

In recent years, polymer blending has proved to be a simple and efficient means of developing new high-performance polymer materials. Unfortunately, most polymer pairs are immiscible, giving rise to two-phase morphologies which are unusable in practice. Many experiment results have proved that the presence of specific interactions in a blend, such as hydrogen bonding, ion–ion pairing, etc. favor a mixing decreased enthalpy and improves the miscibility of polymers. This has not only provided a practical guideline for producing miscible blends from existing polymers but has also opened up a new area that aims to enhance miscibility in polymer blends by chemical modification or copolymerization which incorporates various chemical groups capable of creating specific interactions into one or both of the immiscible component polymers. Among all of the interactions examined, hydrogen bonding seems to be the most attractive one, since it quite efficiently improves miscibility without the accompaniment of many changes in properties of the component polymers. This is why the progressive elucidation on the effect of hydrogen-bonding interactions in the miscibility of polymer blends has been one of the most noticeable achievements in this area over the last two decades. Many authors have studied blends of modified polystyrene comprising hydroxyl-containing units with a counter-hydroxyl accepting polymer by many different techniques, such as transmission electron microscopy (TEM), Fourier-transform infrared (FTIR) spectroscopy, nonradiative energy transfer fluorescence (NRET), differential scanning calonmetry (DSC) and nuclear magnetic resonance (NMR) spectroscopy. However, studies uncoloring electron spin resonance (ESR) spectroscopy have been less commonly reported.

It is well known that ESR spectroscopy is a simple and effective way to determine molecular mobility. This technique provides information on motional processes and phase transitions in polymers. Various paramagnetic species, commonly stable nitroxide radicals, are widely used as indicators. These may be dispersed in the polymer blend ('spin probe' method) or covalently attached to a polymer matrix ('spin label' method). The latter approach is extensively adopted for polymer solutions, copolymers, polymer blends and interpenetrating networks, according to the ESR signal shapes and their intensities. The spectral shape of the spin label depends on environment heterogeneity in a given sample,

Keywords: ESR; spin label; miscibility; hydrogen bonding
result of different intermolecular interactions between the polymer chains. This spectroscopic technique allows a close look into structural heterogeneities in multi-component polymer systems, on a length scale of <50 Å, which is too small to be observed by other techniques such as DSC, dynamical mechanical analysis (DMA) or electron microscopy.13

In this paper, we present a study on the miscibility of a blend consisting of spin labelled poly(ethylene oxide) (SLPEO) and poly(styrene-co-4-vinylphenol) (STVPhs) by the spin label method. Because there is a strong hydrogen-bonding interaction between the hydroxyl groups of the STVPhs and the ether oxygens in PEO, these two polymers become partially miscible. By increasing the hydroxyl content in the STVPh copolymers, we can expect an improvement in the miscibility, detected by corresponding changes in the ESR spectra. In addition, this present study will explore the phase structures of the blends on a molecular level, as a function of the hydroxyl contents in the STVPh copolymers.

**EXPERIMENTAL**

**Materials**

Spin labelled poly(ethylene oxide) 2,2,6,6-Tetramethyl-piperidine-1-oxyl end-group spin labelled PEO (SLPEO) was prepared according to the method described in our previous paper (Fig 1).14 The weight-average molecular weight ($M_w$) of the SLPEO was 10 000 g mol$^{-1}$.

**STVPh copolymer synthesis**

Poly(styrene-co-4-vinylphenol) (STVPh) with various hydroxyl contents was prepared by copolymerization of styrene and 4-methoxystyrene, followed by a demethylation reaction.15 The number-average molecular weight ($M_n$) and polydispersity index ($M_w/M_n$) of these polymers were determined by size exclusion chromatography (SEC). SEC was performed using a Waters Model 510 pump, an ERMA ERC-7512 refractive index detector and a set of columns from Polymer Standard Service. All samples were run in HPLC-grade THF at ambient temperature with a flow rate of 1.0 mL/min. Monodisperse polystyrenes were used as standard samples for calibration. The compositions of the poly(styrene-co-4-methoxystyrene)s were evaluated by $^1$H NMR spectroscopy from the ratio of the integral methoxy peak to that of the aromatic protons. Characterization data for the STVPh-X copolymers are given in Table 1. (The styrene–vinyl phenol copolymers are abbreviated as STVPh-X, where X is the hydroxyl group mole content in the copolymer.)

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>OH content (mol%)</th>
<th>$M_w$ (10$^3$ g mol$^{-1}$)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>STVPh-2</td>
<td>2.1</td>
<td>150.4</td>
<td>1.48</td>
</tr>
<tr>
<td>STVPh-6</td>
<td>6.0</td>
<td>318.2</td>
<td>2.03</td>
</tr>
<tr>
<td>STVPh-17</td>
<td>17.2</td>
<td>294.7</td>
<td>2.18</td>
</tr>
<tr>
<td>STVPh-26</td>
<td>26.4</td>
<td>124.7</td>
<td>2.45</td>
</tr>
<tr>
<td>STVPh-48</td>
<td>48.4</td>
<td>107.8</td>
<td>1.95</td>
</tr>
</tbody>
</table>

**Preparation of blends**

Blends of SLPEO and STVPh-X with different hydroxyl contents, in a ratio of 1:3 (by weight), were prepared by mixing 3% solutions in benzene, evaporating in Teflon containers at ambient temperature for 24 h and drying in vacuum at 323 K for 72 h. The dried blends were stored in a desiccator before use. (We have abbreviated the STVPh-X/SLPEO blends to SP-X where X represents the hydroxyl group mole content in the copolymer.)

**ESR measurements**

Blend samples (SP-0–SP-48) were stacked in ESR sample tubes and evacuated to 10$^{-5}$ mmHg. The ESR spectra were measured at the $X$-band by using a Bruker 200D-SRC spectrometer. An Aspect 3000 computer, with software EPR3002, controlled the data acquisition. The spectra as a function of temperature were measured with a Bruker variable temperature unit ER4111VT. All of the samples were measured over the temperature range 100–440 K, at intervals of 10 K or less, and were allowed to equilibrate for at least 5 min after approaching the corresponding temperatures. The operating parameters for spectra acquisition were as follows: microwave power, 20 mW; microwave frequency, 9.67 GHz; modulation amplitude, 1.0 G; modulation frequency, 100 kHz. All of the parameters were adjusted well below saturation and distortion of the spectra.

**RESULTS AND DISCUSSION**

**ESR spectra of SLPEO**

ESR spectra of SLPEO over the temperature range 100–400 K were measured, and the results obtained are shown in Fig 2. From this figure, we can see that in the PEO homopolymer the spin labelled polymer chain was located in a homogeneous environment, and the spectrum shape, related to the polymer chain motion at given temperature, is characteristic of its
Figure 2. ESR spectra of SLPEO over the temperature range 100–400 K: (a) 400 K; (b) 360 K; (c) 320 K; (d) 305 K; (e) 300 K; (f) 290 K; (g) 270 K; (h) 230 K; (i) 160 K; (j) 120 K; (k) 100 K.

At lower temperatures, the spectra were broad, corresponding to a slow rotation rate of the nitroxide radical with rotational correlation times \( \tau_c \) in the range \( 10^{-7} – 10^{-9} \) s. At higher temperatures, the spectra became narrow, corresponding to a high rotation rate, with \( \tau_c \) in the range \( 10^{-9} – 10^{-11} \) s. We can also qualitatively represent the spin label rotation rate by the extreme separation between the two outer peaks of the spectrum \( 2A_{zz} \). The larger the extreme separation, then the lower the rotation rate. At 100 K, the ESR spectrum of SLPEO approached the rigid limit, with \( 2A_{zz} \approx 70 \) G. With increasing temperature, the spectral lines narrowed and the outer peaks shift inwards, with the spectra eventually becoming a similar narrowed form, with \( 2A_{zz} \approx 30 \) G at 400 K. Such changes in the extreme separation with temperature were typical of a nitroxide spin labelled polymer, which are illustrated in Fig 3. In this figure, \( T_{50G} \) is defined as the temperature at which \( 2A_{zz} \) of the ESR spectrum = 50 G. This temperature depended on the nitroxide spin motion, which reflects the thermally activated segmental mobility of the polymer chains. From Fig 3, a value of 296 K was estimated.

Furthermore, such a temperature could be related to the glass transition temperature \( (T_g) \) of the polymer, although its value should be higher than the \( T_g \) because of the higher measuring frequency of \( T_{50G} \) (about \( 10^7 – 10^8 \) times higher than the DSC measuring frequency). Kusumoto et al proposed a simple formula (see Equation (1) below) to quantify the label size effect according to \( T_{50G} \) and \( T_g \). This relationship assumed that the spin label was part of the polymer segment whose motion was activated at the \( T_g \) and thus the label explored a space which was roughly equal to this polymer segment.

\[
T_{50G} - T_g = 52[2.9f(1 - \ln f) - 1] \tag{1}
\]

Where \( f \) is the ratio of the activation volume of a label to the activation volume of a polymer segment undergoing relaxation. For SLPEO, \( T_g = 208 \) K and \( T_{50G} = 296 \) K; thus, a value of \( f = 0.65 \) was obtained, with the volume of the motional segment being 260 Å\(^3\), knowing that the volume of the label was 170 Å\(^3\). We have deduced that about seven monomer units were involved in the segmental motion above the \( T_g \) if the volume of one PEO monomer unit is 36.8 Å\(^3\). A refinement of the Kusumoto approach leads to the following relationship:

\[
\ln \tau_c = \ln \tau_0 + f[2.3C_1C_2g/(T - T_g + C_2g)] \tag{2}
\]

where \( C_{1g} \) and \( C_{2g} \) are the Williams–Landel–Ferry (WLF)\(^24\) universal parameters, equal to 17.44 and 51.6, respectively. A plot of \( \ln \tau_c \) versus \( 2.3C_1C_2g/(T - T_g + C_2g) \) gave a slope of \( f = 0.52 \) (Fig 4). This result implied that segmental motion above the \( T_g \) comprised about nine monomer units. These two approaches therefore suggested that the
region explored by the label was of the order of 7–9 PEO monomeric units.

**Phase separation in SP-0**

ESR spectra of the SP-0 blend (SLPEO with pure PS), in the temperature range 100–400 K, are illustrated in Fig 5. It was found that the spectral shapes and their variations with temperature in this blend were obviously similar to the pure SLPEO homopolymer. At a given temperature, the spectrum of the SLPEO in the SP-0 blend was uniform, being composed of a single motion component: slow motion between 100 and 300 K, fast motion between 300 and 400 K. This indicated that the spin label in the SP-0 blend was located in a single or homogeneous environment uniquely containing PEO, in which no PS chains had penetrated. In other words, there was no other penetration of SLPEO chains into the PS domain, no matter what the temperature was. The SP-0 blend could thus be considered as an immiscible polymer blend. DSC studies have produced an analogous result,9 with this polymer pair blend showing two widely differing $T_g$ values ($T_g$ for PS of 373 K and for PEO of 208 K). However, in spite of the similar change with temperature of the SLPEO and SP-0 spectra, their $T_{50G}$ values were little different, with the former being 296 K and the latter 306 K (see Table 3 below). The apparent activation energies ($E_a$), calculated from a plot of $\ln \tau_c$ as a function of $1/T$ for the fast-motion regime, were 4.2 and 5.0 kJ mol$^{-1}$ in the case of SLPEO and SP-0, respectively. This indicated the influence of PS in the SP-0 blend on the PEO chain mobility. In other words, motion of the PEO segments in the SP-0 blend was more difficult than in pure PEO because of the stiffening effect of the glassy PS component around them. Weber
and Helfand and Cameron and co-workers have proposed a theoretical prediction for the structure and composition of the interphase region in an immiscible blend. According to this, the ends of the SLPEO chain tended to aggregate themselves in the interphase between the two polymers, as a result of a thermodynamic driving force. Such effects were derived from the mutual interaction of the chain segments, particularly these of the chain ends, in the interphase. Consequently, the free volume concentration decreases and the mobility of the SLPEO in the SP-0 blend should be lower than that in pure PEO matrices.

**Micro-heterogeneity existence and miscibility enhancement in SP-X blends**

Figures 6 to 10 show the ESR spectra of blends with different hydroxyl contents, ie SP-2, SP-6, SP-17, SP-26 and SP-48 over the temperature range 100–440 K. Some of these spectra were simultaneously composed of two motion components over a certain temperature range: a slow motion and a fast motion, marked by 's' and 'f', in the spectra, respectively. This indicated that parts of the SLPEO chains are dispersed into two different environments with different mobilities. At lower temperatures, the ESR spectra were predominantly composed of slow-motion components. With increasing temperature, the fast-motion components appeared and their intensities increased at the expense of the slow-motion components, until at a specific temperature a particular spectrum appeared to consist almost entirely of the motional-narrowed form. Observations of the slow and fast motions indicated that the SLPEO segments exist in two dynamically different molecular environments due to the local heterogeneities in the blends: a PEO-rich micro-domain and an STVPh-rich micro-domain. In the PEO-rich domain, the environment was more flexible and the polymer segmental motion was faster, while in the STVPh-rich domain the environment was more rigid and the polymer segmental motion was lower. The appearance of two motion components in the ESR spectra showed that the above blends were partially miscible, with the two kinds of polymer chains penetrating each other due to the hydrogen-bonding interactions between the hydroxyl groups in STVPh and the ether oxygens in PEO. We observed no macro-phase separation, as in the case of SP-0, while micro-phase separation was observed in the cases of the SP-2, SP-6, SP-17, SP-26 and SP-48 blends. The miscibility was improved from SP-2 to SP-48 due to the hydrogen-bonding density enhancement. According to the variation of spectral shape with temperature, we have defined two specific temperatures: $T_a$ represents the temperature corresponding to the appearance of a noticeable
fast-motion component, while $T_d$ is the temperature corresponding to the disappearance of the slow-motion component, in the spectra. The $T_s$ and $T_d$ values for the blends with different hydroxyl contents are listed in Table 2. From this table, it can be seen that the values of $T_s$ and $T_d$ both increased with increasing hydroxyl contents in the STVPh-X copolymer and that $T_s$ is lower than $T_d$ in each polymer blend. Whether in either a PEO-rich micro-domain or an STVPh-rich micro-domain, the hydrogen-bonding density simultaneously increased with increasing hydroxyl content in the polymer blends. This means that the penetration of one type of polymer chain into the other polymer domain becomes more and more profound with increasing hydroxyl content and, accordingly, the miscibility is raised. Decreasing mesh size of the physical network induced by an increase in the hydrogen-bonding density is expected to restrict the SLPEO mobility because of the physical cross-linking enhancement. The higher $T_s$ and $T_d$ values for higher-hydroxyl-content SP-X blends suggests that the reduced dynamics of the polymer matrix hinder the formation of concentration fluctuation and higher

Table 2. $T_s$ and $T_d$ data (K) for SLPEO and SP-X blends

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SLPEO</th>
<th>SP-0</th>
<th>SP-2</th>
<th>SP-6</th>
<th>SP-17</th>
<th>SP-26</th>
<th>SP-48</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_s$</td>
<td>—</td>
<td>—</td>
<td>270</td>
<td>275</td>
<td>290</td>
<td>300</td>
<td>310</td>
</tr>
<tr>
<td>$T_d$</td>
<td>305</td>
<td>310</td>
<td>325</td>
<td>330</td>
<td>350</td>
<td>380</td>
<td>400</td>
</tr>
</tbody>
</table>

temperatures are therefore needed in order to obtain the concentration heterogeneity necessary to observe composite mobility components in the ESR spectra. The outer extreme separations of the SP-17, SP-26 and SP-48 blends as a function of temperature are plotted in Fig 11, with their corresponding $T_{50G}$ values being listed in Table 3. The results showed that the
$T_{50G}$ increased with increasing hydroxyl content in the STVPh-X copolymers. The $T_{50G}$ of SLPEO in the SP-48 blend was about 100 K higher than in its homopolymer. On the other hand, the characteristic ESR spectrum of fast tumbling nitroxyl radicals consists of three narrow lines. With an assumption of isotropic Brownian motion, relatively precise values of $\tau_c$ in the range $10^{-11} - 10^{-9}$ s can be estimated by using the following formula based on Kivelson’s theory:  

$$
\tau_c = 8.7 \times 10^{-10} \times [(h_0/h_{-1})^{1/2} - (h_0/h_{+1})^{1/2}] \Delta H_{sp}
$$

where $h_0$, and $h_{-1}$ and $h_{+1}$ are the measured central, and high and low peak-to-peak amplitudes, respectively, of the three lines of the ESR spectrum of the nitroxide radical, and $\Delta H_{sp}$ is the width of the central peak (in gauss (G)). Arrhenius plots of $\ln \tau_c$ as a function of $1/T$ over the entire fast-motion range, measured for blends of SP-2, SP-6, SP-17, SP-26 and SP-48, are shown in Fig 12. From this figure, values of the apparent activation energies ($E_a$) were calculated and these are shown in Table 4. The dependence of the mobility of the PEO chain on the hydrogen-bonding density in the SP-X blends can also be deduced from the variation of $\tau_c$, as shown in Fig 12. The fact that both $\tau_c$ and $E_a$ increased with increasing hydroxyl content indicated that the mobility of SLPEO was hindered more severely and much more energy was needed to overcome the obstacle that SLPEO encountered. We can also deduce from the increasing $T_{50G}$ values that the miscibilities of the polymer blends increase with increases in the hydrogen-bonding density. Pearce et al have obtained similar results in similar blend systems from DSC measurements.  

**CONCLUSIONS**

By studying the ESR spectra of SLPEO over the temperature range 100–400 K, we obtained a value of $T_{50G}$ equal to 296 K. It was found that the spatial resolution of the label was of the order of 7–9 PEO monomer units. This meant that the SLPEO was sensitive to the local structure change over this order. In addition, the miscibilities of various SP-X blends with different hydroxyl contents and the effects of hydrogen bonding were investigated by ESR spectroscopy according to their spectral shapes. The ESR spectra of the SP-0 blends showed a single component, this indicating the immiscibility of these blends. The ESR spectra of other blends showed composite spectra, hence indicating the miscibilities of the blends. Increases in the $T_a$, $T_d$, $T_{50G}$ and $E_a$ values, with increasing hydroxyl contents in the blends, indicated an enhancement in the miscibility due to the increased hydrogen-bonding interactions.

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**REFERENCES**

23 Bullock AT, Cameron GG and Miles IS, Polymer 23:1536 (1982).