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A High-Resolution Solid-State NMR Study of the Miscibility, Morphology, and Toughening Mechanism of Polystyrene with Poly(2,6-dimethyl-1,4-phenylene oxide) Blends

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ABSTRACT: An extended Goldman–Shen pulse sequence was used to observe indirectly the proton spin diffusion in the blends of polystyrene (PS) with poly(2,6-dimethyl-1,4-phenylene oxides) (PPO). The results indicate that the average distance between PS and PPO is less than 5 Å in the intimately mixed phase, but there are heterogeneous domains on a 100-Å scale. The data of spin relaxation of carbons, T_1(C), for homopolymers and their blends suggest that there is a strong π–π electron conjugation interaction between the aromatic rings of PS and those of PPO, while the aromatic rings of PPO drive the aromatic rings of PS to move cooperatively. It is the cooperative motion that markedly improves the impact strength of PS.

Introduction

Much work has been devoted to study the miscibility, morphology, and toughening mechanism of polystyrene (PS)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blends[1-20] since they were discovered by E. P. Cizek.[21] Different attempts have been made to develop a molecular explanation for the miscibility of PS/PPO. True thermodynamic miscibility of these two polymers in ternary solutions with toluene was discovered.[3] The dynamic mechanical measurements indicated that partial mixing took place between them with two distinct phases, one rich in PS and the other rich in PPO, and existed in all the mixtures studied (PPO, 25, 50, and 75 wt %).[5] A negative heat of mixing and a negative local entropy of mixing were derived from the results of SANS measurements.[7] Kambour et al.,[13] by consideration of the solubility parameters, have estimated that for PS/PPO the interaction parameter is close to zero. A similar conclusion was drawn on the basis of the theory of the glass transition temperatures[11] developed by Kanig.[14] From the results of an IR study, Wellinghoff et al. explained the miscibility by a possible "specific" interaction between the ether linkage of PPO and the phenyl group of PS.[15] It is interesting to point out that according to the results of ^{2}H NMR detection by de Araujo et al.[16] there existed no such specific interaction as suggested by Wellinghoff et al. On the basis of the results of a WAXD study, Mitchell et al.[17] proposed that the PPO chains acted as templates for the PS ones, and the reason for the improved mechanical performance of the PS is that the introduction of PPO into PS disrupts the microsegregation of phenyl groups into stacks.

NMR spectroscopy is one of the most powerful methods available for studying the structure and dynamics of solids.[22-24] Information about localized molecular motions may be inferred from ^{13}C spin relaxation measurements, whereas the spatially averaged information of such motions may be obtained from proton (^{1}H) spin relaxation. Moreover, transfer of magnetization between domains (or different molecules) can be monitored by ^{1}H NMR.[23,25-32] Thus, ^{1}H NMR is a very useful tool for the study of domain structures. The basic idea here is that ^{1}H magnetization associated with different types of domains (or molecules) may have significantly different spin relaxation times. Magnetization M_1 of the relatively more mobile domains (or molecules) will have a longer spin–spin relaxation time T_2 than that of the magnetization M_2 in the rigid domains (or molecules). Magnetization in a particular type of domain (or molecule) can be selectively destroyed by applying NMR pulses while there is still sufficient magnetization remaining in the other type of domain (or molecule). Then the magnetization in the latter is allowed to transfer to the former by a spin diffusion process via the strong ^{1}H dipolar interaction.[33] The spin diffusion rate can be obtained from the recovery of the magnetization associated with the former domain (or molecule) as a function of the transfer time. Therefore, the size and shape of the latter domain, even the average distance between the different molecules, can be roughly estimated from the spin diffusion rate.

In this work, a double resonance extension of the Goldman–Shen pulse sequence[34,35] was used to detect the spin diffusion in PS/PPO blends. The spin–spin relaxation time of protons T_2 was measured indirectly by the pulse sequence devised by Tekely et al.[35] The motions of the main and the side chains were characterized by the spin-lattice relaxation time of carbons. The combination of these independent results leads to in-depth insight into the miscibility, morphology, and toughening mechanism of PPO in PS/PPO blends.

Experimental Section

The polymers used in this study were all commercial products. PS (M_w = 15 000) was obtained from the Yanshan Chemical Factory of Beijing Petro-chemical Co.; PPO (η = 0.05) was obtained from the Shanghai Institute of Synthetic Resin. Solution blending was used in this study, using toluene as solvent, and a solution concentration of 5% (wt/v). Specimens with different compositions were cast from the solution at 60 °C, and then dried under vacuum at 100 °C for 1 week.

Solid-state ^{13}C CPMAS NMR experiments were performed on a Bruker SL-400 NMR spectrometer at 298.0 K. The TOSS

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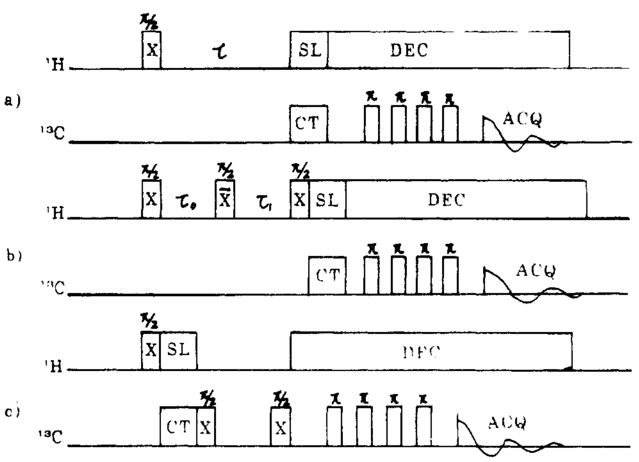


Figure 1. Pulse sequences used for (a) indirect measurements of proton T_2 relaxation times; (b) indirect measurements of proton spin diffusion; and (c) measurements of carbon-13 T_1 relaxation times: SL, spin locking; DEC, decoupling; CT, contact time; ACQ, acquisition time.

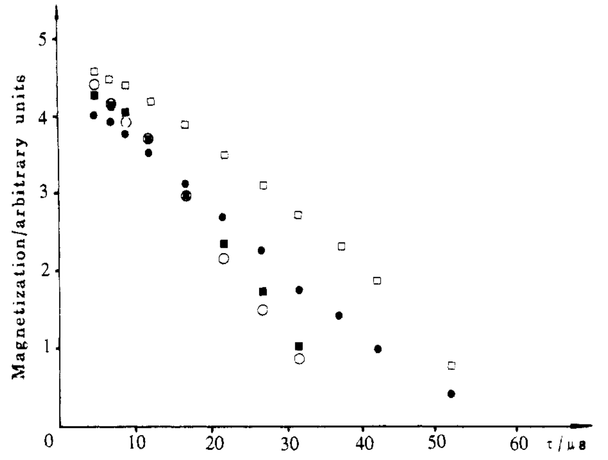


Figure 2. Logarithmic intensity of the ^{13}C cross-polarization spectra versus transverse proton relaxation period τ for methyl carbons of pure PPO (□), aliphatic carbons of pure PS (○), methyl carbons of PPO (●) in the blend, and aliphatic carbons of PS in the blend (■). PS/PPO = 40/60.

method was used for suppressing the spinning side band. The pulse sequences used in this study are shown in Figure 1. The spinning rate was 4.000 kHz. The carbon resonance frequency was 100.63 MHz, and the hydrogen resonance frequency was 400.13 MHz. The Hartmann-Hahn CP matching and dipolar decoupling field was about 49 kHz, while a 5.5-μs 90° pulse for ^{13}C nucleus and a 4.8-μs 90° pulse for ^{1}H were used. The contact time (CT) was 1.0 ms. The delay time was 2 s. Spectra were referred to the chemical shift of the methyl group carbons of hexamethylbenzene, which was 16.9 ppm.

Results and Discussion

1. Indirect Observation of Proton Spin Diffusion. 1.1. Spin–Spin Relaxation Times T_2(H) of PS, PPO, and Their Blends. On the basis of the indirect measurements of proton T_2 relaxation times, using the pulse sequence depicted in Figure 1a, very useful results (see Figure 2) were obtained. First, the proton T_2 relaxation time of PS is about 9 μs; it belongs to the range of proton T_2 relaxation times of the crystalline phase of polymers. Usually the T_2 value of the crystalline phase of polymers is about 8–10 μs.[29,35] This relaxation characterization of PS was supported further by the results of the measurements of the spin–lattice relaxation time of carbons, T_1(C), of PS in this study, which is about 40.0 s. Usually, the T_1(C) values of amorphous phases of semicrystalline polymers or noncrystalline polymers are no more than 20.0 s.[37-44] From the relaxation characteristics of PS, we can conclude that the average distance between the protons in PS is very close and PS has an unusual crystalline-like structure resulting from the microsegregation of phenyl groups. This conclusion is consistent with that of Mitchell.[17,44] Second, mixing has little effect on the spin–spin relaxation times of PS and PPO in the blend which have almost the same T_2 values as pure PS and PPO, respectively. When τ is about 35.0 μs, the magnetization of PS decays to null, but the magnetization of PPO does not vanish until τ reaches 60.0 μs. Even in the blends, the T_2 values of PS are completely different from those of PPO because the magnetization transfer between different kinds of polymers almost cannot occur by means of spin diffusion in such a short time ($\tau < 100$ μs) (according to the equation $X^2 = 4/3Dt$,[34,45] assuming $D = 5.0 \times 10^{-12}$ cm²/s, $t = T_2 = 70$ μs, and the displacement of spin diffusion is about 1 Å).

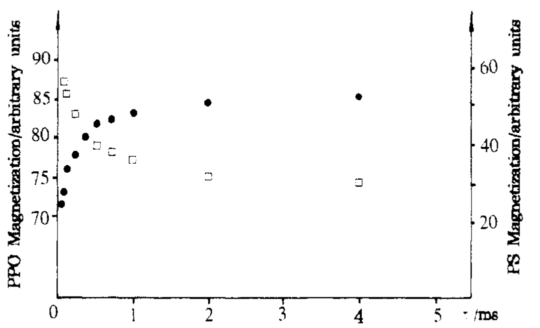


Figure 3. Magnetization changes of PS and PPO as a result of proton spin diffusion from PPO to PS: aliphatic carbons of PS (●), methyl carbons of PPO (□), with τ_0 = 35 μs and 300 scans.

1.2. Indirect Observation of Proton Spin Diffusion. Spin diffusion[33] has been used to observe the spatial inhomogeneity of noncrystalline or semicrystalline polymers in the solid.[22-32] The process of spin diffusion via a dipolar spin–flip interaction is described by the equation.[33]

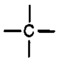
$$\partial M(r,t)/\partial t = D_s(r)\nabla^2 M(r,t) \qquad (1)$$

Where $M(r,t)$ represents the local magnetization concentration and $D_s(r)$ is the spin diffusion coefficient. The assumption of uniform D_s throughout different regions is widely used in polymer systems.[28,45,46] The mean square displacement of spin diffusion during time t is roughly given by[31]

$$\langle X\rangle^2 = 4/3Dt \qquad (2)$$

which permits us to estimate the finite domain sizes or the average distance between different molecules. In this study, as shown in Figure 2, PS molecules are more rigid than PPO molecules. PPO has a longer T_2 value than PS. Using the double resonance of the Goldman–Shen pulse sequence shown in Figure 1b, the magnetization of PS can be destroyed by a suitable τ_0 (=35 μs), but the magnetization of PPO with a sufficiently long T_2 is not destroyed and then can be flipped back to the +Z axis by a second $(\pi/2)_{-x}$ pulse. Thus, spin diffusion is allowed to proceed during a variable time τ_1. Shown in Figure 3 are the changes of magnetization of the methyl groups of PPO and the aliphatic group of PS with the mixing times τ_1. A significant transfer of magnetization from PPO to PS is observed. The magnetization of PS increased with the mixing times τ_1; at the same time, the magnetization of PPO decreased. Obviously, the increase of magnetization of PS is at the expense of the decrease of the magnetization of PPO. The curves in Figure 3 indicate a two-step decay.

Table I
Spin–Lattice Relaxation Times[a] of Individual Carbons of PS, PPO, and Their Blend[b]

polymer	group	T_1(C) (s) homopolymer	T_1(C) (s) blend	ΔT_1(C) (s)
PPO	C_2	10.5	17.3	+6.8
	C_4	9.5	18.2	+8.7
	CH_3	5.8	7.7	+1.9
PS	 $-\overset{|}{\underset{|}{C}}-$	38.5	17.3	−21.2
	CH_3CH	40.8	32.9	−7.9

[a] Estimated error <±10%. [b] PS/PPO = 40/60.

The spin diffusion rate constants R_{SD} can be obtained from a biexponential fit of the curve. They are $R_{SD1} = (246 \pm 10)^{-1}$ μs^{-1} and R_{SD2} $(166 \pm 8)^{-1}/ms^{-1}$. The fast spin diffusion rate can be interpreted as coming from the transfer of magnetization between PS and PPO in the intimately mixed range, and the slow one can be attributed to the spin diffusion between the PS-rich and the PPO-rich phases according to a three-phase model.[32] The average distance between PS and PPO in the intimately mixed phases is less than 5 Å, calculated from eq 2 with an assumption of uniform D_s $(=5.0 \times 10^{-12}$ cm^2/s) throughout different regions. And the average size of the PPO-rich phase is ca. 100 Å. It should be noted that these results are rather rough because there are many factors which affect the spin diffusion rate. For instance, in general the spin lock reduces the spin diffusion rate by a factor of 2,[22] and spin–lattice relaxation has a finite effect on the spin diffusion rate. Therefore, for $\tau_1 \ll T_1(H)$, the effect of spin–lattice relaxation on the spin diffusion rate may be neglected. In this study, $\tau_1 \ll T_1$ ($\approx$1.0 s); hence, the buildup of magnetization in PS is only due to spin diffusion from PPO.

2. Molecular Motions of PS, PPO, and Their Blends. Since spin diffusion between carbon-13 nuclei in natural aboundance is not expected to occur, by combining cross-polarization with proton dipolar decoupling,[46] in principle it is possible to detect the spin–lattice relaxation times of individual carbon-13. The spin–lattice relaxation times in the rotation frame ($T_{1\rho}$) are of particular interest since they are expected to give information about motions in the midkilohertz range.[24,47] The low-frequency motions are capable of dissipating energy as heat to the surroundings, which is the mechanism of avoiding local stress concentration when the polymer is under mechanical stress.[47–50] However, the interpretation of $T_{1\rho}$(C) measurements in terms of molecular motions is hampered, since both spin–lattice and spin–spin processes can contribute to the relaxation, the latter arising from "thermal contact" between the carbon-13 rotating-frame Zeeman reservoir and the proton dipolar reservoir.[51–53] The laboratory-frame carbon-13 spin–lattice relaxation times T_1(C), which are almost not affected by spin diffusion and spin–spin relaxations, can unambiguously reflect the spin–lattice relaxation processes, i.e., molecular motions.

In this study, carbon-13 T_1's of PS, PPO, and their blends were measured by the pulse sequence[54] depicted in Figure 1c. The results are listed in Table I, from which very useful information can be drawn. The motions of the main chains in PS are severely hindered, as its T_1(C) is about 40.0 s, which is near the T_1(C) value (about 60.0 s) of the crystalline phase in poly(vinyl alcohol)[55] and the T_1(C) value (about 40.0 s) of the crystalline phase of some polyethylenes[41] under different crystalline conditions, and is higher than the T_1(C) values of the crystalline phase of polyamide-6 (T_1(cr) = 11 ± 5 s)[40] and poly(oxymethylene) (T_1(cr) = 15 s).[37] At the same time, the T_1(C) of PS is much longer than the T_1(C) values of the main chains of some amorphous polymers, such as PPO (T_1(C) = 9.5 s), PVP (T_1(C) = 13.0 s), PMMA (T_1(C) = 9.5 s), PEMA (T_1(C) = 7.5 s), and PiBMA (T_1(C) = 7.0 s).[43] The crystalline-like structure of PS, obviously, results from the microsegregation or interlocking of aromatic rings. The interlocking of aromatic rings stacks closely and is not easy to move, which hampers the motion of the main chains. It is evident that such a structure will only exhibit poor mechanical stress damping ability and easily result in stress concentration. Therefore, the corollary is that PS's impact strength is very poor.

Interestingly, the situation for PPO is markedly different from that for PS; the spin relaxation time T_1(C) of its aromatic ring is about 5 times faster than that of the aromatic rings of PS. Besides, the T_1(C) value of the methyl carbons of PPO is unusually long as compared with that of the methyl carbons of poly(methyl methacrylate) (PMMA). The former is 5.8 s, and the latter is 0.1 s. In fact, the T_1(C) value of the methyl carbon should be exactly the same as that of the aromatic rings because the methyl carbon has two or three protons more than the aromatic carbons. These protons in excess will hasten the relaxation process of the methyl group. Hence, the methyl carbon rotates synchronously with the aromatic ring. Additionally, we can exclude that there exist interactions between the methyl group and oxygen atom because the chemical shift of the methyl carbon of PPO shifts to higher field compared with that of the methyl carbon of PMMA. The former is 15.9 ppm, and the latter is 17.2 ppm. This means that in comparison with the latter the electronic density of the former increases. Therefore, a reasonable explanation of the greatly hampered motion of the methyl group is that there exists a strong α–π conjugation between the methyl carbon and aromatic ring which hindered the free rotation of the methyl group around the C–C σ bond. This conclusion is in agreement with the results of delocalization of π electrons.[58] In addition, because of the existence of a strong electron-absorbing group, i.e., the oxygen atom, the aromatic ring of PPO, in fact, is an electron-deficient group. At the same time, the aromatic ring of PS is rich in electrons due to the attached electron-donating aliphatic group. Hence, when PPO is mixed with PS, a strong π–π interaction occurs between the aromatic rings of PS and PPO, which is the most direct reason for the miscibility of PS and PPO blends.

This proposed mechanism is supported further by the results of the spin relaxation times of the blend (see Table I). The T_1(C) values of the aromatic rings of pure PPO and pure PS are 9.5 and 38.5 s, respectively. After mixing, the aromatic rings of PPO and PS have almost the same T_1(C) values (T_1(C) = 17.2 s). This means that the aromatic rings of PPO and PS move cooperatively due to the strong π–π conjugation interactions between the different aromatic rings. The effect of this kind of π–π conjugation interaction can compete with that of strong intermolecular hydrogen bonding. It should be pointed out that the change (ΔT_1(C) = −21.2 s) in T_1(C) of aromatic carbons is much larger than that (ΔT_1(C) = −7.9 s) of aliphatic carbons. This indicates again that the interaction occurs between the aromatic rings of PS and PPO.

The equation connecting spin relaxation times T_1(C) with the correlation time τ_c of the motion of individual

Table II
Correlation Times (τ_0) and Activation Energies (E_a) of the Motion of the Aromatic Rings of PS, PPO, and Their Blend

carbon	system	T_1(C) (s)	τ_0 (s)	E_a (kcal/mol)
$-\overset{\vert}{\underset{\vert}{C}}-$ in PS	homopolymer	38.5	1.6×10^{-7}	10.0[a]
	blend	17.3	7.1×10^{-8}	8.0
C_4 in PPO	homopolymer	9.5	4.0×10^{-9}	
	blend	17.3	7.1×10^{-8}	

[a] According to Tonelli,[58] phenyl group rotational barriers are in the order of 10 kcal/mol.

carbon was given by[24,37]

$$1/T_1(\mathrm{C}) = (1/10)\gamma_{\mathrm{H}}^2\gamma_{\mathrm{C}}^2\hbar^2\Sigma r^{-6}[\tau_c/(1 + (\omega_{\mathrm{H}} - \omega_{\mathrm{C}})^2\tau_c^2) + 3\tau_c/(1 + \omega_{\mathrm{C}}^2\tau_c^2) + 6\tau_c/(1 + (\omega_{\mathrm{C}} + \omega_{\mathrm{H}})^2\tau_c^2)] \quad (3)$$

Assuming that the main relaxation mechanism of carbon-13 is proton–carbon dipolar relaxation (this is often true for solid polymers[24,37]) and the average distance between carbon and proton is 1.09 Å, the correlation times τ_c for PS, PPO, and their blend are listed in Table II. At the same time, according to the following equation[24,25]

$$\tau = \tau_0 \exp(E_a/kT) \quad (4)$$

we can obtain the activation energies (E_a) for rotation of the aromatic rings of PS (see Table II).

According to Table II, the correlation time τ_c of PPO is in the order of 10^{-9} s. This means that the aromatic rings rotate with high speed, which is in accordance with the conclusion that PPO's aromatic rings are almost in truly free rotation around the $C_{1,4}$–O bond.[58,59] The nearly truly free rotation nature of PPO was considered to be the source of its substantial impact strength in the glassy state, which is based on the assumption that impact strength is related to the ability of a polymer chain to undergo a rapid, reversible conformational transition without bond rupture.[59] The correlation time of pure PS is about 2 orders slower than that of PPO. This remarkable difference in moving rates between PS and PPO is the basic reason that the impact strength of PS is much poorer than that of PPO. When PS is mixed with PPO, the motion frequency of PS increases nearly 1 order, while its activation energies of motion reduce from 10.0 to 8.0 kcal/mol. The aromatic rings of PPO and PS move with the same frequency. It is the cooperative motion that destroys the microsegregation of aromatic rings of PS, efficiently promoting the ability of PS chains to undergo a rapid, reversible conformational transition without bond rupture; hence, the impact strength of PS is markedly improved.

Conclusion

The extended Goldman–Shen pulse sequence is very useful for detecting indirectly the ^{1}H spin diffusion rate of polymer blends. Our experimental results of PS/PPO blends indicate that the average distance between PS and PPO molecules is less than 5 Å in the intimately mixed phases, but there exist heterogeneous phases rich in PPO on a 100-Å scale. Therefore, this technique can not only characterize the miscibility of blends, but also exhibit the morphology of the blends.

The strong π–π electron conjugation interaction between the aromatic rings of PS and PPO plays a key role in the miscibility of PS and PPO blends. It is this strong interaction that makes the cooperation motion of PS and PPO become possible. This cooperative motion efficiently destroys the microsegregation of the aromatic rings of PS, resulting in the ability of PS chains to undergo a rapid, reversible conformational transition without bond rupture, hence markedly improving the impact strength of PS.

The spin relaxation of carbon, T_1(C), can reflect the characteristics of motion of main and side chains, which may be directly related to the impact strength of amorphous polymers by a mathematical expression. It is a significant subject and deserves further study.

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