ELSEVIER

Polymer 43 (2002) 171–176

polymer

www.elsevier.com/locate/polymer

Solid-state NMR studies on phase behavior and motional mobility in binary blends of polystyrene and poly(cyclohexyl methacrylate)

Ru-Rong Wu[a], Hsien-Ming Kao[b,*], J.-C. Chiang[c], E.M. Woo[c]

[a]*Tainan Regional Instrument Center, National Science Council, Tainan, 701-01, Taiwan*
[b]*Department of Chemistry, National Central University, Chung-Li, 32054, Taiwan*
[c]*Department of Chemical Engineering, National Cheng Kung University, Tainan, 701-01, Taiwan*

Received 19 March 2001; received in revised form 25 July 2001; accepted 31 July 2001

Abstract

The phase behavior and motional mobility in binary blends of polystyrene (PS) and poly(cyclohexyl methacrylate) (PCHMA) have been investigated by solid state ^{13}C NMR techniques. The blend miscibility has been studied by examining the ^{1}H spin-relaxation times in the laboratory frame (T_1^H) and in the rotating frame ($T_{1\rho}^H$) for the PCHMA/PS blends with various compositions and pure components. The $T_{1\rho}^H$ results show that PCHMA and PS are intimately mixed at the molecular level within the blends at all compositions. In addition, according to the results of carbon $T_{1\rho}$ relaxation time measurements, we conclude that mixing is intimate enough to cause a reduction in local chain mobility for PS, but an increase in side chain mobility for PCHMA.

Keywords: Polystyrene; Poly(cyclohexyl methacrylate); Polymer blends

1. Introduction

The lack of any special functional groups in its chain structure makes polystyrene (PS) immiscible with most long-chain thermoplastic polymers. Blends of PS with ester-containing (carbonyl groups) polymers or acrylic polymers are mostly immiscible. A limited number of exceptions do exist. For instance, PS has been known to be miscible with some ether-containing polymers such as poly(1,4-dimethyl-*p*-phenylene oxide) (PPO) [1–3] and poly(vinylmethyl ether) (PVME) [4–6]. On the other hand, blends of PS with acrylic polymers are mostly immiscible, with only one controversial exception: PS and poly(cyclohexyl methacrylate) (PCHMA) are miscible or immiscible depending on molecular weights [7,8], leading to some controversy regarding the true thermodynamic phase structure of PCHMA/PS blend systems. In particular, the proximity of the glass transition temperatures (T_g) of PS and PCHMA makes it especially difficult to resolve the issue of miscibility by using the criteria of thermal behavior. In our previous study [8], composition dependence of phase behavior for the PCHMA/PS blend was examined in detail using differential scanning calorimetry (DSC), optical and scanning electron microscopy, and infrared spectroscopy. DSC results showed that only one T_g value was observed. Since the distance scale for DSC measurements is generally taken to be in the range 20–30 nm, any heterogeneity which may be present on a smaller scale will not be detected by using thermal analysis.

Solid-state NMR is a powerful technique that has been utilized in analyzing miscibility, phase structure or heterogeneity in polymer mixtures on a molecular scale [9–12]. It is especially useful in polymer blend systems containing complex phase structures that may be beyond the resolution limits of conventional microscopic or thermal analysis. The degree to which polymers are mixed in binary blends is often determined via solid-state NMR relaxation methods. In particular, the proton relaxation times in the rotating frame ($T_{1\rho}^H$) and in the laboratory frame (T_1^H) are sensitive to heterogeneity in the blends and may be used to establish upper and lower limits on the length scales of polymer mixing. Stejskal et al. [9] demonstrated an advantage of the use of well-resolved ^{13}C NMR spectra to monitor the ^{1}H relaxation behavior. After that, several examples of the use of T_1^H, $T_{1\rho}^H$, and spin diffusion measurements to characterize polymer/polymer miscibility have been reported [13–21]. Since proton spin-lattice relaxation behavior can reflect the intimate relation of the component polymers through proton spin-diffusion processes, measurements of the proton spin-lattice relaxation times for specific carbons

* Corresponding author. Tel: +886-3-427-5054; fax: +886-3-422-7664.
E-mail address: hmkao@cc.ncu.edu.tw (H.-M. Kao).

0032-3861/02/$ - see front matter
PII: S0032-3861(01)00570-5

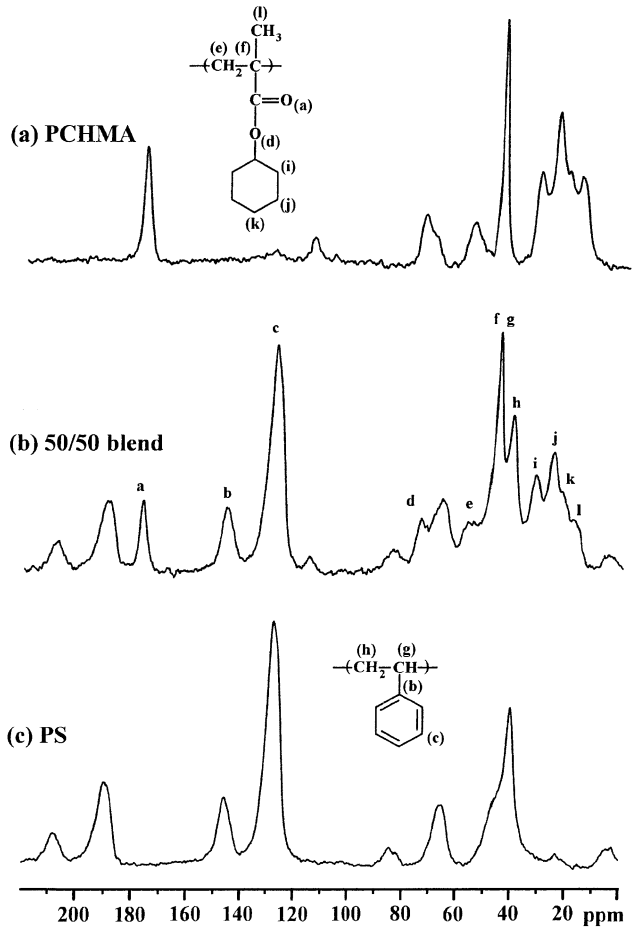

Fig. 1. ^{13}C CP/MAS NMR spectra of (a) PCHMA, (b) their 50/50 blend, acquired at room temperature and at a spinning speed of 6.2 kHz, and (c) PS; peak assignments as indicated in Table 1.

in the blend permit an analysis and characterization of the microheterogenous structures in terms of the differences in their relaxation behavior. Furthermore, the domains with the sizes from a few angstroms to a few tens of nanometers can be evaluated by an approximate approach based on the spin diffusion phenomenon, depending on the use of the relaxation times of either $T_{1\rho}^{H}$ or T_1^{H}. Both $T_{1\rho}^{H}$ and T_1^{H} are powerful measures to the compositional heterogeneity in length scales limited by spin diffusion. The main difference between $T_{1\rho}^{H}$ and T_1^{H} is that they respond to different time scales. The T_1^{H} with a longer time scale (100 ms to a few seconds) characterizes the heterophase domains over larger length scale within a few hundred angstroms, while $T_{1\rho}^{H}$ with a shorter time scale (a few miliseconds), characterizes the size of domains within shorter length scale of ca. 50 Å. These two properties would provide the information about the heterophase domains at two size levels having a difference of one order of magnitude, suitable for the study of polymer blends. Moreover, measurements of carbon spin-lattice relaxation in the rotating frame ($T_{1\rho}^{C}$) could give information on the local mobility of polymer chains at frequencies in the kHz region, and therefore usually are employed to investigate the effect of blending on the local motions in a polymer blend.

We are aware of no previous solid-state NMR studies regarding the miscibility of cyclohexyl methacrylate polymers with PS. Therefore, the aim of the present work is to obtain further evidence regarding both the intimacy and homogeneity of mixing of individual PCHMA and PS chains in PCHMA/PS blends by means of ^{1}H spin-lattice relaxation time measurements. Moreover, the change of local chain mobility upon blending has been investigated with $T_{1\rho}^{C}$ relaxation time measurements at different radio frequency (rf) field strengths. Unlike most miscible polymer blends, the PCHMA/PS blend system has no obvious strong intermolecular interactions between PCHMA and PS. Solid-state NMR studies of PCHMA/PS blends provide an excellent opportunity for examining the role of various factors on polymer/polymer miscibility, and for investigating the relationship between miscibility and molecular motion of the constituent polymers.

2. Experimental

2.1. Materials and sample preparation

Poly(cyclohexyl methacrylate) (PCHMA) was purchased from Scientific Polymers Products, with an approximate $M_w = 32{,}500$ g/mol (Gel Permeation Chromatograph, GPC), polydispersity index (PI) = 4, and a T_g of 110°C. An atactic polystyrene (PS) with a T_g of 85°C, $M_w = 75{,}600$ g/mol, and PI = 2.5–3.1, obtained from Chi-Mei Inc. (Taiwan), was used for blending with PCHMA. The preparation procedure of PCHMA/PS blends with various compositions has been described in detail elsewhere [8].

2.2. ^{13}C CP/MAS NMR measurements

Solid-state ^{13}C cross-polarization (CP)/magic angle spinning (MAS) NMR experiments were performed on a Bruker AVANCE-400 spectrometer, equipped with a Bruker double-tuned 7 mm probe, with resonance frequencies of 100.62 MHz for ^{13}C nuclei and 400.13 MHz for ^{1}H nuclei. The Hartmann–Hahn condition for $^{1}H \rightarrow {}^{13}C$ CP experiments was determined using admantane. ^{13}C CP/MAS NMR spectra were recorded with a CP contact time of 1 ms, a repetition time of 4 s, and a spinning speed of 6.2 kHz. The ^{13}C chemical shifts were externally referenced to tetramethylsilane (TMS).

2.3. Proton relaxation time measurements

T_1^{H} relaxation times were indirectly measured by observing well-resolved ^{13}C resonances after applying the $\pi-\tau-\pi/2$ (inversion-recovery) pulse sequence, followed by CP. For the $T_{1\rho}^{H}$ relaxation time measurements, the spin-locking pulse sequence was applied before CP. The CP contact time

Table 1
Assignments for the ^{13}C chemical shifts in the blend of PCHMA and PS

Peak label	Chemical shift (ppm)	Type of carbon
a	177	Carbonyl (PCHMA)
b	146	Quaternary ring (PS)
c	128	Aromatic CH (PS)
d	74	OCH (ring, PCHMA)
e	56	$-CH_2-$ (PCHMA)
f	46	Quaternary C (PCHMA)
g	46	–CH– (PS)
h	41	$-CH_2-$ (PS)
i	33	$-CH_2-$ (ring, PCHMA)
j	26	$-CH_2-$ (ring, PCHMA)
k	22	$-CH_2-$ (ring, PCHMA)
l	18	α-CH_3 (PCHMA)

was set to be 1 ms and a spin-locking field strength of 45 kHz was used. A proton decoupling field strength of 60 kHz was used in all experiments.

2.4. Carbon $T_{1\rho}$ measurements

$T_{1\rho}^{C}$ data were obtained by using the standard CP experiment with the addition of a ^{13}C spin-lock pulse inserted between the acquisition and CP period. The $T_{1\rho}^{C}$ experiment was used to examine the motional mobility of constituent polymers in the blend.

3. Results and discussion

3.1. ^{13}C chemical shifts

Fig. 1 shows the ^{13}C CP/MAS NMR spectra of PCHMA, PS, and their 50/50 (wt.) blend recorded at room temperature. In general, the resolution of the various polymer carbon signals was quite good, and the interference from spinning sidebands was not a problem under our spectral accumulation conditions. The corresponding resonances are assigned to specified carbons indicated in the inset structures. In addition, the assignments of the resonances are summarized in Table 1. The spectrum of PCHMA consists of resonances at 177 ppm, which arises from carbonyl carbons, at 74 ppm from the OCH group in the cyclohexyl ring, and in the range of 22 to 56 ppm due to the secondary CH_2 groups. In the PS spectrum, the resonances at 146 and 128 ppm are assigned to non-protonated and protonated aromatic carbons, respectively, and the methylene and methine carbon resonances are ascribed to the resonances at 41 and 46 ppm, respectively. The spectrum of the blend is no more than a superposition of the spectra from PCHMA and PS. There is no detectable chemical shift difference or line shape change between the pure polymer and the polymer in the blend, as evidenced in Fig. 1, and thus the ^{13}C chemical shift itself cannot provide direct information about the interaction between PS and PCHMA.

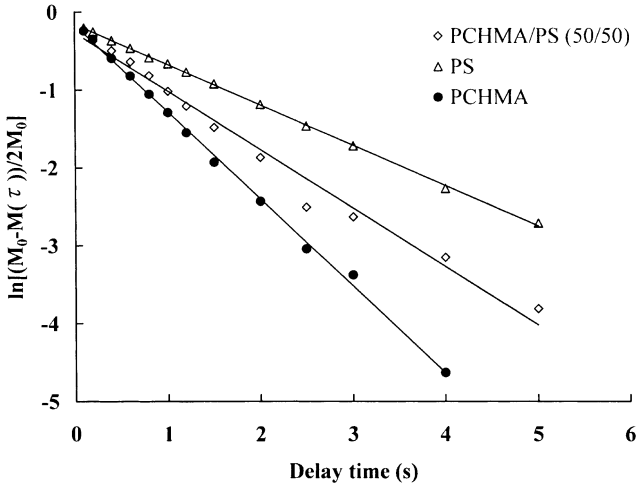

Fig. 2. Logarithmic plots of ^{13}C resonance intensities as a function of delay time τ for PCHMA, PS, and the 50/50 blend at room temperature. The slope yields the proton spin-lattice relaxation time in the laboratory frame, T_1^H.

3.2. Measurements of proton T_1

By determining the proton relaxation times for a blend in comparison to the proton relaxation time values for the pure component polymers, it may be possible under certain circumstances to estimate an upper limit to the scale of heterogeneity present in the blend. If the scale of the phase separation in the blend is sufficiently small to permit rapid diffusion of proton spin energy, a single-component relaxation process will be observed.

In the T_1^H experiments, the inversion-recovery method was used, and the intensities of various carbon resonances of PCHMA, PS, and their blends were measured as functions of delay time. According to the method used, the magnetization of resonances relaxed at single exponential function should obey the following equation:

$$M(\tau) = M_0[1 - 2\exp(-\tau/T_1^H)] \quad (1)$$

where τ is the delay time used in the experiment and $M(\tau)$ is the corresponding resonance intensity; M_0 is the intensity of the resonance at $\tau \geq 5T_1^H$. Taking the natural logarithm of both sides of Eq. (1), Eq. (2) can thus be obtained:

$$\ln[(M_0 - M(\tau))/(2M_0)] = -\tau/T_1^H \quad (2)$$

The slope of the plot of $\ln[(M_0-M(\tau))/(2M_0)]$ against τ yields T_1^H.

Fig. 2 shows a logarithmic plot of the ^{13}C resonance intensities of PCHMA, PS and their 50/50 blend versus delay time τ, where various delay times were introduced between the $\pi/2$ and π pulses, for the measurements of T_1^H. Table 2 gives the experimental T_1^H relaxation times for the pure components and for the blends. They have been measured at 177, 33, and 26 ppm for PCHMA, and at 146, 128 and 41 ppm for PS. A close examination of the experimental T_1^H data shows that the various carbon signals in each pure polymer are characterized by the

Table 2
Observed and calculated T_1^H relaxation times of the studied samples

PCHMA/PS	T_1^H (s)[a]	Calc. (s)[b]
0/100	1.93 ± 0.05	–
30/70	1.39 ± 0.05	1.44
50/50	1.19 ± 0.05	1.16
70/30	1.07 ± 0.03	1.02
100/0	0.89 ± 0.03	–

[a] Experimental data obtained from the peaks at 177 ppm for PCHMA and at 146 ppm for PS. Other carbons give identical or very close values if the experimental error is considered.
[b] Calculation according to Eq. (4).

same T_1^H values (i.e. 0.89 and 1.93 s for PCHMA and PS, respectively), if the experimental error is considered. For the 50/50 blend, for example, the signal decay is best fitted by a single exponential with the T_1^H of 1.19 s within 10% experimental errors, which are identical or very near each other on the various carbons. Although there is not a large difference between the T_1^H values of PCHMA and PS, it is readily apparent that the relaxation processes for the blends are intermediate in value as compared to the pure components. The observation of a single T_1^H indicates that the spin diffusion process is sufficiently fast to equilibrate the relaxation times for all protons among the chemically different constituents, and the studied blends are completely homogeneous on the time scale of T_1^H. The results of T_1^H indicate that the PCHMA/PS blends are intimately mixed on a scale of a few tens of nanometers at all compositions (see below).

3.3. Measurements of proton $T_{1\rho}$

The $T_{1\rho}^H$ values can be determined by monitoring the decay of peak intensities in a series of spectra obtained by varying the spin-lock time (τ). Because of the $T_{1\rho}^H$ relaxation the process follows the exponential function $\ln[M(\tau)/M_0] = -\tau/T_{1\rho}^H$, where M_0 is the maximum magnetization, and the $T_{1\rho}^H$ values can be determined from the slopes in the plots of $\ln[M(\tau)/M_0]$ against τ.

The plots of the $T_{1\rho}^H$ decays for the magnetization of the selected carbons in pure PCHMA, pure PS and 50/50 blend are given in Fig. 3, and the corresponding $T_{1\rho}^H$ values are summarized in Table 3. The $T_{1\rho}^H$ values of the selected carbon resonances for each pure component remain the same as far as experimental error is concerned. These results indicate that a fast spin diffusion process occurs among all protons in both materials, which averages out the whole relaxation process. As seen in Fig. 3, both PCHMA and PS in the blend exhibit single $T_{1\rho}^H$ relaxation behavior. It is found that the $T_{1\rho}^H$ values determined from the selected carbons for PCHMA and PS fractions in each blend are quite close (see Table 3), and can be considered as identical within experimental error. Since these values are intermediate between those of the individual blend components through all the cases of different compositions, they are

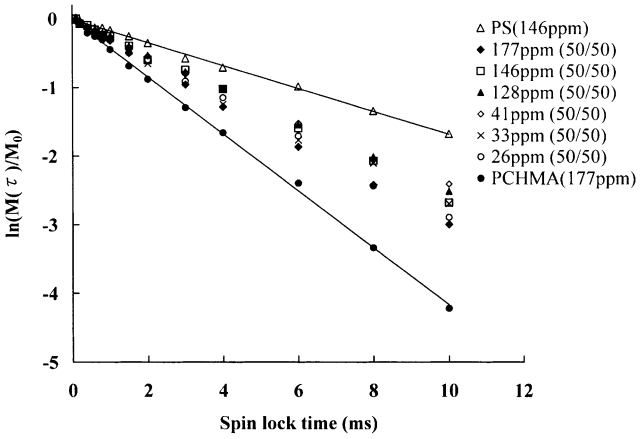

Fig. 3. Logarithmic plots of ^{13}C resonance intensities as a function of spin lock time τ for PCHMA, PS, and the 50/50 blend at room temperature. The slope yields the proton spin-lattice relaxation time in the rotating frame, $T_{1\rho}^H$.

characteristic of miscible phases at the molecular level within the blends at various compositions.

3.4. Domain size determination

If the diffusion length is smaller than the dimension of domains in blends, protons in each component will decay independently of each other and a double exponential decay will be observed. On the contrary, if the diffusion length is much larger than the dimension of the domain in the blend, spin diffusion between both components occurs. T_1^H and $T_{1\rho}^H$ relaxation experiments can provide an estimate of the diffusive path length and hence the sizes of blend heterogeneities. A useful approximate estimation of the upper limit to the domain size can be obtained from [22]:

$$\langle L \rangle \cong (6DT)^{1/2} \tag{3}$$

where $\langle L \rangle$ is the average diffusive path length for the effective spin diffusion, D is the spin diffusion coefficient determined by the average proton–proton distance and the strength of the dipolar interaction; it is of the order of $4–7 \times 10^{-16}$ m^2 s^{-1} in a rigid proton system [22,23] and T is the characteristic time over which the spin diffusion proceeds. Equating T with either T_1^H or $T_{1\rho}^H$ provides a reasonable order of magnitude estimation of the spatial dimensions involved. In our earlier studies of these systems using the traditional DSC techniques, PCHMA/PS blends with all compositions appear to be homogeneous since they displayed a single broad T_g, but this does not necessarily imply homogeneity of the blend on a nanometer scale. In theory, the two polymers, PCHMA and PS, in the blend are from two independent domains where the domain size is smaller than the maximum diffusive path length of proton spin diffusion over T_1^H or $T_{1\rho}^H$ relaxation times. For the spin-diffusion coefficient D a value of 8×10^{-16} m^2 s^{-1} has recently been found in rigid PMMA/polystyrene block copolymers [23]. Using this D value and $T_1^H = 1.19$ s we

Table 3
Observed and calculated $T_{1\rho}^{H}$ relaxation times of the studied samples

PCHMA/PS	PCHMA $T_{1\rho}^{H}$ (ms)[a]				PS $T_{1\rho}^{H}$ (ms)[a]				Calc. (ms)[b]
	177 ppm	33 ppm	26 ppm	$T_{1\rho}^{H}$ (av)[c]	146 ppm	128 ppm	41 ppm	$T_{1\rho}^{H}$ (av)[c]	
0/100	–	–	–	–	6.29	6.42	6.54	6.42	–
30/70	4.11	4.15	4.51	4.26	4.59	4.82	4.94	4.78	3.96
50/50	3.30	3.71	3.42	3.48	3.79	3.97	4.06	3.94	3.27
70/30	2.91	3.00	2.91	2.94	3.55	3.28	2.90	3.24	2.82
100/0	2.40	2.41	2.44	2.42	–	–	–	–	–

[a] The accuracy of the measurements is ±10%.
[b] Calculation according to Eq. (4).
[c] Averaged values.

obtain the upper limit of $\langle L \rangle \approx 70–80$ nm for a 50/50 blend. For PCHMA/PS blends, all $T_{1\rho}^{H}$ values (see Table 3) for various carbon resonances can be considered to be the same within experimental error. Using these observed $T_{1\rho}^{H}$ relaxation times, and taking into account that in the rotating frame the spin-diffusion coefficient D is scaled by a factor of 1/2 [23], the result indicates that a fast spin diffusion process occurs among all protons in a range of 25–35 Å of the blends. Thus, it can be concluded that PCHMA and PS are intimately mixed; no detectable domains on a scale of 25–35 Å are present.

If the complete spin-diffusion occurs during a period less than the ^{1}H relaxation time among all protons of the two polymers, the ^{1}H relaxation rate is averaged as follows [22]:

$$T_{1(av)}^{-1} = (N_A/N) \times T_{1A}^{-1} + (N_B/N) \times T_1^{-1} \quad (4)$$

where $T_{1(av)}$ is the averaged ^{1}H relaxation time, T_{1A} and T_{1B} are the ^{1}H relaxation times for pure components, N_A and N_B are the numbers of protons per mole of the components and N is the total numbers of protons in the blend, i.e. $N = N_A + N_B$. The average T_1^{H} and $T_{1\rho}^{H}$ are calculated on the assumption that T_{1A} and T_{1B} in Eq. (4) are equal to proton spin-lattice relaxation times (in the laboratory and the rotating frames) of respective polymers. The results are listed in Tables 2 and 3, respectively. Good agreement between the observed and calculated T_1^{H} values is obtained, indicating that averaging of T_1^{H} rates due to spin-diffusion really occurs. This also indicates that the blending does not alter the T_1^{H} values of pure polymers; the molecular motions of PCHMA and PS responsible for the T_1^{H} relaxation remain unchanged by mixing. On the other hand, the differences between measured and calculated T_1^{H} values of the PCHMA/PS blends indicate that an implicit assumption of Eq. (4), i.e. that the T_1^{H} values are not changed by blending, is not fulfilled. This might suggest that the molecular motions in the kHz range of PCHMA and PS in the blend are affected by blending, which is in agreement with the observed $T_{1\rho}^{C}$ changes in the blends (discussed below).

Table 4
^{13}C $T_{1\rho}$ results for the blends with various compositions as a function of rf field strength

rf (kHz)	PCHMA/PS	^{13}C $T_{1\rho}$ (ms)[a]	
		177 ppm	146 ppm
28	0/100	–	11.6
	30/70	18.8	10.6
	50/50	17.6	10.6
	70/30	16.8	9.3
	100/0	16.2	–
40	0/100	–	44.7
	30/70	54.4	36.3
	50/50	49.2	32.6
	70/30	42.5	29.7
	100/0	41.5	–
52	0/100	–	86.6
	30/70	89.4	61.8
	50/50	78.2	59.5
	70/30	67.7	55.5
	100/0	66.8	–

[a] The accuracy of the measurements is ±10%

3.5. Measurements of ^{13}C $T_{1\rho}$ relaxation times

Further evidence of a blending effect on the motional state can be obtained from the $T_{1\rho}^{C}$ measurements because the low abundance of ^{13}C eliminates the effect of spin diffusion. If the ^{1}H–^{13}C spin–spin relaxation effects can be neglected, $T_{1\rho}^{C}$ data can be interpreted in terms of the motion of polymer chains, which occurs in a frequency range of 10–100 kHz. $T_{1\rho}^{C}$ relaxation time measurements were performed at different rf field strengths to understand the segmental motion upon blending. A single-exponential decay was adequate for describing the relaxation behavior of the carbonyl carbon (177 ppm) of PCHMA and the quaternary carbon (146 ppm) of PS. The results are listed in Table 4. In most cases the ^{13}C $T_{1\rho}$ decays of the other carbons were clearly best described by a bi-exponential decay.

Both spin–spin and spin-lattice processes can contribute to the measured $T_{1\rho}^{C}$ values. If $T_{1\rho}^{C}$ is determined solely by spin-lattice processes, then $T_{1\rho}^{C}$ would be proportional to the square of the applied spin-locking field strength [24]. On the other hand, if $T_{1\rho}^{C}$ is determined solely by spin–spin processes then $T_{1\rho}^{C}$ would be expected to increase exponentially with

increasing rf field strength [25–27]. The dependence of $T_{1\rho}^{C}$ relaxation times shown in Table 4 on the rf field strength indicates that the $T_{1\rho}^{C}$ relaxation times for PS are determined by spin-lattice processes and can be interpreted in terms of motion.

The $T_{1\rho}^{C}$ values for PCHMA in the blend increase as compared to those of pure PCHMA. In contrast, the $T_{1\rho}^{C}$ values for PS in the blend decrease as compared to those of pure PS. The fact that the $T_{1\rho}^{C}$ relaxation times for pure PS and PS in the blend decrease with decreasing rf field strength, indicating that the correlation time lies on the slow side of the minimum. Therefore a decrease in the $T_{1\rho}^{C}$ relaxation times for PS upon blending can be interpreted in terms of increasing molecular motion of PS in the blend. Consequently, the addition of PCHMA clearly causes a reduction in segmental mobility for PS, as shown by the gradually decreasing relaxation time values for increasing PCHMA concentration. When PCHMA is blended with PS, the $T_{1\rho}^{C}$'s of PCHMA in the blend become longer. These results indicate that the blending hinders the whole segmental motion of the PCHMA side chain. The above observation implies that the blending affects the local motions of the individual polymer side-chains, as these motions are sensitive to the details of the local packing of the polymer chains. Because of overlapping in the aliphatic carbon regions, no detailed information about the changes of the local motions of PCHMA main-chains by mixing can be given.

The ^{13}C NMR technique is sensitive to fluctuating dipolar fields caused predominantly by the motions of C–H dipoles within a few bonds of an isolated ^{13}C nuclei, i.e., on the order of ca. 0.1–0.4 nm. DSC, however, is thought to be sensitive to motions over a scale of hundreds of bonds. A broadening of the T_g transition observed in the DSC of these blends, and which is often reported in the DSC of miscible polymer blends, is due partly to the differences in chain dynamics of the component homopolymers, detected by the $T_{1\rho}^{C}$ relaxation times.

4. Conclusions

The miscibility of the PCHMA/PS blend has been investigated with ^{13}C CP/MAS NMR measurements. T_1^H and $T_{1\rho}^{H}$ results permit the conclusion that the PCHMA and PS are intimately mixed at the molecular level within the blends at all compositions. The various protons in the blends are efficiently communicating spin energy on the time scale of the proton spin-lattice relaxation process in both the laboratory and the rotating frames. This is confirmed by the intermediate single-component T_1^H and $T_{1\rho}^{H}$ relaxation times observed for the blends at various compositions. The bulkier cyclohexyl ester group does not appear to inhibit miscibility with PS. Analysis of $T_{1\rho}^{C}$ data shows that the blending affects the local motions of the individual polymer side-chains due to the changes of the local packing of the polymer chains upon blending.

Acknowledgements

The financial support of this work by the National Science Council of Taiwan is gratefully acknowledged.

References

[1] Stoelting J, Karasz FE, MacKnight WJ. Polym Engng Sci 1970;10:133.
[2] Shultz AR, Beach BM. Macromolecules 1974;7:902.
[3] Prest Jr WM, Porter RS. Polym Sci, Part A-2 1972;10:1639.
[4] Kwei TK, Nishi T, Roberts RF. Macromolecules 1974;7:667.
[5] Bank M, Leffingwell J, Thies C. Macromolecules 1971;4:43.
[6] Bank M, Leffingwell J, Thies C. Polym Sci, Part A-2 1972;10:1097.
[7] Friedrich C, Schwarzwalder C, Riemann RE. Polymer 1996;37:2499.
[8] Jang FH, Woo EM. Polymer 1999;40:2231.
[9] Stejskal EO, Schaefer J, Sefcik MD, McKay RA. Macromolecules 1981;14:275.
[10] Dickinson LC, Yang H, Chu C-W, Stein RS, Chien JC. Macromolecules 1987;20:1757.
[11] Schmidt-Rohr K, Spiess HW. Multidimensional solid-state NMR and polymers. New York: Academic Press, 1994.
[12] Yu T, Guo M. Prog Polym Sci 1990;15:825.
[13] Guo M. Trends Polym Sci 1996;4(7):238.
[14] Asano A, Takegoshi K, Hikichi K. Polymer Journal 1992;24:555.
[15] Asano A, Takegoshi K, Hikichi K. Polymer 1994;35:5630.
[16] Kwak S-Y, Nakajima N. Macromolecules 1996;29:3521.
[17] Kwak S-Y, Kim J-J, Kim UY. Macromolecules 1996;29:3560.
[18] Kwak S-Y, Nakajima N. Macromolecules 1996;29:5446.
[19] Parizel N, Laupretre F, Monnerie L. Polymer 1997;38:3719.
[20] Jack KS, Whittaker AK. Macromolecules 1997;30:3560.
[21] White J, Lohse DJ. Macromolecules 1999;32:958.
[22] McBriety VJ, Douglass DC, Kwei TK. Macromolecules 1978;11:1265.
[23] Clauss J, Schmidt-Rohr K, Spiess HW. Acta Polym 1993;44:1.
[24] Bloembergen N, Purcell EM, Pound RV. Phys Rev 1948;73:679.
[25] Garroway AN, Moinz WB, Resing HA. Faraday Soc. Faraday Soc Symp 1979;13:63.
[26] Garroway AN, Ritchey WM, Moniz WB. Macromolecule 1982;15:1051.
[27] Garroway AN, VanderHart DL, Earl WL. Philos Trans R Soc London, Ser A 1981;299:609.