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Structure and Properties of Naphthalene-Containing Polyesters. 2. Miscibility Studies of Poly(ethylene naphthalene-2,6-dicarboxylate) with Poly(butylene terephthalate) by ^{13}C CP/MAS NMR and DSC

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ABSTRACT: The miscibility of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) with poly(butylene terephthalate) (PBT) has been studied by ^{13}C CP/MAS NMR complemented with DSC measurements. The blends were prepared by a solution precipitation method. The DSC examination shows that the T_g of the blends is between the T_g of the two homopolymers. The crystalline enthalpy of PEN decreases continuously when the amount of PEN decreases. The T_m and ΔH_m of PBT were lowered continuously as the PEN ratio was increased, while that of PEN was lowered as the PBT ratios were increased. These results imply that PEN is compatible with PBT. $^{H}T_{1}\rho$ values for the blend 50 PEN/50 PBT and pure components have been measured. Since single-component NMR relaxation behavior was observed, miscibility was demonstrated for the blend. Intermolecular cross polarization from the protons in PBT to carbons in deuterated PEN was examined by measuring the full decoupling, no decoupling, and delayed decoupling ^{13}C CP/MAS spectra of the blends of deuterated PEN with different compositions of PBT. The results from such independent measures of effective mixing of chains within the deuterated PEN and PBT blends lead to the conclusion that the PEN/PBT blends with weight ratios 80/20, 50/50, and 20/80 are miscible in the molecular level.

Introduction

Poly(butylene terephthalate) (PBT) is a fast crystallizing thermoplastic polyester with a high melting point (226 °C) and an excellent solvent resistance, but its low T_g induces a noticeable decrease in some mechanical properties, such as tensile and flexural modules.[1,2] Poly(ethylene naphthalene-2,6-dicarboxylate) (PEN), which is stiffer than poly(ethylene terephthalate) (PET), is a relatively well-known polymer used for engineering and packaging purposes[3−7] because of its photochemical properties,[8,9] electrical properties,[10] excellent mechanical and gas barrier properties, and its ability to form liquid crystalline polymers when polymerized with suitable comonomers,[11] such as 4-hydroxybenzoic acid.[12,13] PEN has a glass transition temperature (T_g) of 118 °C (ca. 45 deg higher than the T_g of its chemical relative, PET). Blending both PBT and PEN together, it is possible to find new materials which can combine the properties of the component polymer. The aim of the present work has been to obtain evidence for miscibility in PEN/PBT blends by means of different solid-state ^{13}C CP/MAS NMR methods, complementing DSC measurements.

Cross polarization (CP)/magic angle spinning (MAS) dipolar decoupling (DD)^{13}C NMR has been established as a valuable tool for the determination of polymer−polymer miscibility on a molecular scale.[14−17] The most used ^{13}C CP/MAS/DD NMR methods to study polymer−polymer miscibility are (1) investigation of the perturbation of the isotropic chemical shift[18−20] (a strong interaction between blends such as hydrogen bonding,[18] molecular complexes[19] and charge-transfer interactions[20] should cause changes in the ^{13}C chemical shifts of those resonances involved in the interaction), (2) examination of intermolecular CP in a mixture of deuterated and protonated materials[21] (this method is based on the short effective range of the dipolar interaction between carbons and protons), and (3) determination of the proton relaxation times, $^{H}T_1$ and $^{H}T_{1\rho}$, through analysis of the decay rates of all carbon atoms, for the components of the blend.[22] Several solid state 2D NMR techniques have also been used to study the miscibility of polymer blends.[16,23]

In the case of some polymer blends, e.g. blends of PEN and PET, the chemical shifts and even the proton relaxation times of the components are the same. It is difficult to use the above mentioned three methods to study the miscibility of the systems. Other methods,[21] namely delay decoupling and no decoupling ^{13}C CP/MAS NMR, can be utilized to obtain information about the miscibility of such blends.

In the present studies, four different CP/MAS NMR methods are used to investigate the miscibility of PEN/PBT blends.

Experimental Section

PBT is a commercial BASF product (Ultradur B4500) with a molecular weight $M_n = 30\,200$, as determined by intrinsic viscosity measurements at 25 °C in phenol/tetrachlorethane solvent.[24] PEN was synthesized from dimethyl naphthalene-2,6-dicarboxylate and ethylene glycol using $Mn(OAc)_2/Sb_2O_3$ as catalysts. Details on the synthesis were given in the previous papers,[25] and the synthesis of deuterated PEN was given elsewhere.[26]

The blends were obtained by dissolving both polymers in hexalfluoro-2-propanol and coprecipitating in ethanol. The final coprecipitants were dried completely in vacuum at 40 °C. The weight ratios of PBT to PEN in the system tested were 100/0, 80/20, 50/50, 0/80, and 0/100.

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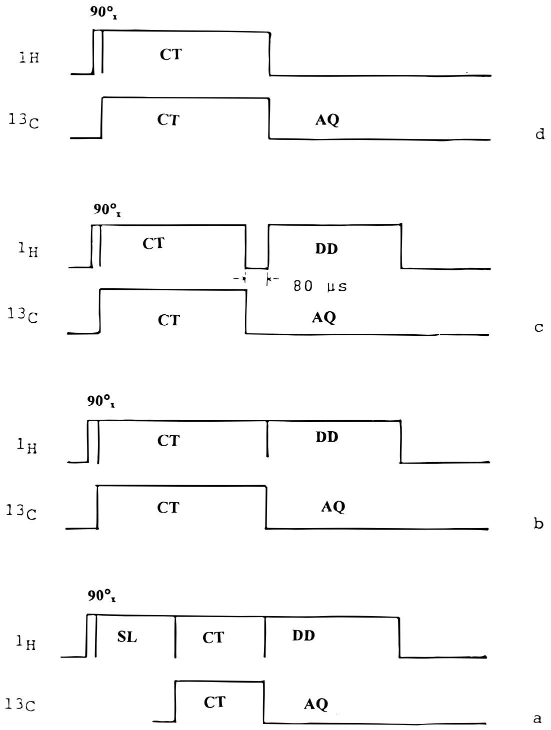


Figure 1. Pulse sequence used in ^{13}C CP/MAS NMR experiments: (a) pulse sequence for proton $T_{1\rho}$ measurement; (b) full decoupling ^{13}C CP/MAS NMR pulse sequence; (c) delayed decoupling ^{13}C CP/MAS NMR pulse sequence; (d) no decoupling ^{13}C CP/MAS NMR pulse sequence. SL: spin lock. CT: contact. DD: dipolar decoupler. AQ: acquisition.

The glass transition temperature T_g and melting point T_m were investigated by a Perkin-Elmer DSC IV. The NMR experiments were performed at room temperature on a Bruker MSL 300 NMR spectrometer operating at 75 MHz. Proton $T_{1\rho}$ was measured as the slope of the intensity of the ^{13}C CP/MAS NMR spectra vs the time of proton spin locking. The pulse sequence employed, Figure 1a, was ^{1}H $(90^\circ_x)(\tau_y)$ followed by simultaneously 3 ms ^{13}C and ^{1}H spin locks and then acquisition of the ^{13}C magnetization with proton dipolar decoupling. The length of τ ranged from 0.1 to 10 ms. Ten τ values were usually taken to determine each slope.

The CP/MAS/DD pulse sequence, Figure 1b, consists of a cross polarization followed by a proton dipolar decoupling. The delay decoupling CP/MAS pulse sequence, Figure 1c, contained an 80 μs delay between cross polarization and proton dipolar decoupling to cause irreversible defocusing of the protonated carbon resonance. The no decoupling CP/MAS pulse sequence is shown in Figure 1d.

For all four pulse sequences, the proton 90° pulse length was 4 μs, the sample spinning frequency was 4.5 kHz, the contact time was 3 ms, and the recycle time of the pulse was 4 s. The proton spin locking field, proton and carbon magnetic field, employed for the matched spin lock cross polarization transfer was 62.5 kHz. Proton decoupling was provided at the same strength as the spin locking field. Spin sidebands were suppressed by using the pulse sequence TOSS.[27] A total of 500 transients were accumulated for the normal spectra and relaxation spectra, 2000 for the delay decoupling spectra, and 5000 to 10 000 for the no decoupling spectra. Chemical shifts were referenced to tetramethylsilane via the carbonyl carbon atom line of glycine (176.03 ppm).

Results and Discussion

DSC Measurements. Figure 2 shows the differential scanning calorimetry (DSC) curves of different PBT/PEN blends. One can see the weak step in the specific heat in the region from 50 to 120 °C, corresponding to the glass transition temperature. The peaks in the region from 140 to 170 °C are caused by crystallization. The peaks following the endothermal peak correspond to the melting point. The crystallization peak of PBT does not appear because PBT crystallizes very quickly and it happened during the precipitation. This agrees with the result of the NMR observation that the line width of all the resonance lines of PBT is narrower than that of PEN. The glass transition step of PBT is relatively weak.

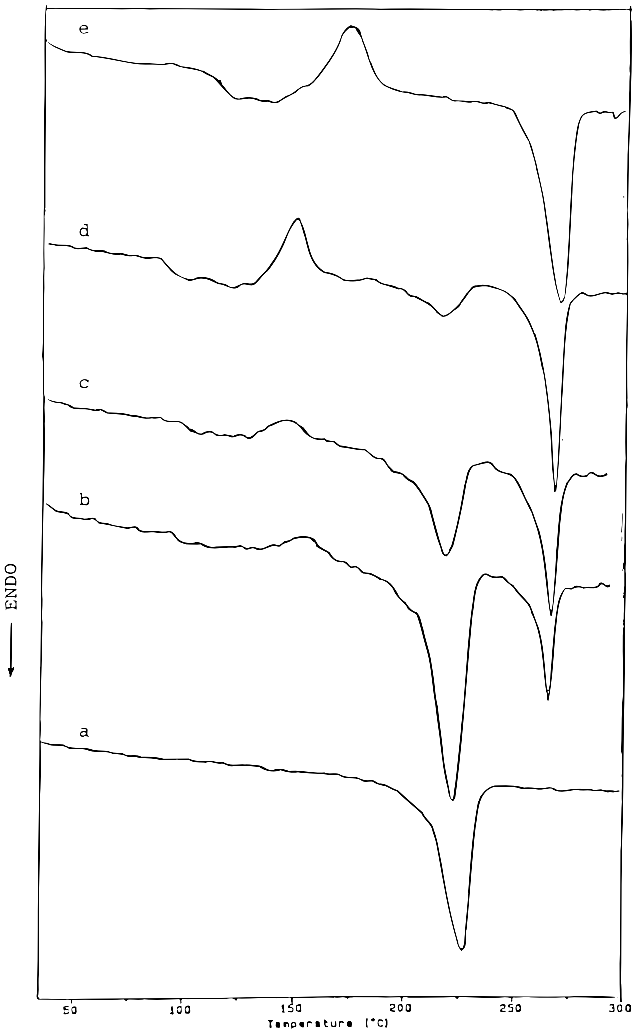
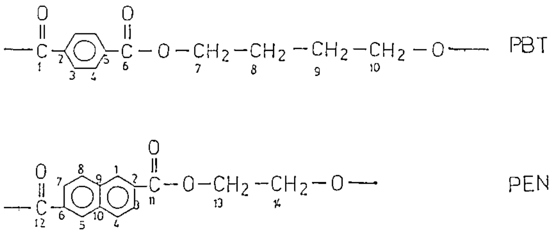


Figure 2. Differential scanning calorimetry (DSC) curves of different PBT/PEN blends (heating rate: 10 °C min^{-1}): (a) PBT/PEN (100/0); (b) PBT/PEN (80/20); (c) PBT/PEN (50/50); (d) PBT/PEN (20/80); (e) PBT/PEN (0/100).

Table 1. Glass Transition Temperatures and Melting Points of Binary Polyester Blends

PBT weight fraction	PEN			T_m		ΔH_m (J/g)	
	T_g	T_c	ΔH_c (J/g)	PEN	PBT	PEN	PBT
100	51.8				226.8		57.3
80	99.2	153.6	2.9	265.4	221.5	8.9	40.5
50	96.1	146.2	8.3	266.1	218.4	16.6	20.4
20	93.7	147.2	12.3	266.4	216.6	32.1	5.6
0	113.9	172.8	30.2	269.0		34.2	

The glass transition temperature, T_g, the crystalline temperature, T_c, the melting point, T_m, the heats of fusion, and the crystalline enthalpy of both components are displayed in Table 1. The glass transitions of the blends were lower than that of PEN and higher than that of PBT. But the change in T_g of the blends coupled with the change in the composition is not observed in the system because the weak specific heat effect prevents such observation. The crystallization tempera-



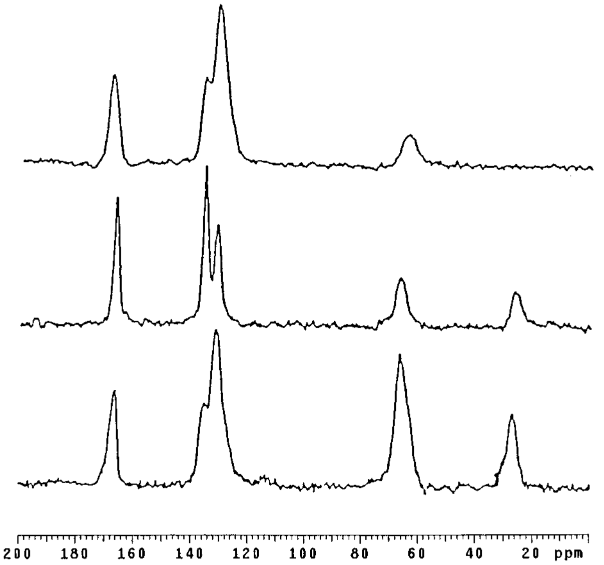


Figure 3. ^{13}C CP/MAS NMR spectra of (a) the 50/50 blend of PEN/PBT, (b) PBT, and (c) PEN.

ture, T_c, of PEN is lower in the blends than in the homopolymer case, and the crystalline enthalpy, ΔH_c, of PEN decreases continuously as the amount of PEN decreases. This implies that the mechanism of crystallization of PEN is affected by mixing. From the data in Table 1 we find also that the melting points and the heats of fusion of PBT decreased continuously as the PEN ratio was increased. In the same way, the melting point and the heats of fusion of PEN were lowered continuously as the PBT ratio was increased. These results imply that PEN is compatible with PBT.

CP/MAS NMR: Proton Spin−Lattice Relaxation. The ^{13}C CP/MAS NMR spectra of PEN, PBT, and the blend of PEN/PBT are shown in Figure 3. The chemical shift assignment results,[28] supported by the application of the short contact time pulse sequence and the interrupted decoupling pulse sequence,[29] are displayed in Table 2. The line widths of all the resonance lines of PBT are narrower than those of PEN. This implies that PBT quickly crystallized during the precipitation process.

Measurement of rotating frame proton spin−lattice relaxation times was made by using a 90°_x-τ_y spin-locking pulse sequence, shown in Figure 1a. The carbon signal intensity decay curves were fitted to a standard first-order kinetic expression. Use of this procedure allowed the determination of the proton spin−lattice relaxation times for the blends and the component polymers by monitoring the change in carbon signal intensity as a function of delay times.

In testing the miscibility of the 50/50 blend of PEN/PBT, a linear fit of the intensity from such a set of data for the pure PEN, the pure PBT, and the 50/50 blend of PEN/PBT is shown in Figure 4 with a common axis. For this particular fit, the peak at approximately 64 ppm is chosen because it is both large and highly resolved in the spectra. However, the same results are obtained for any of the peaks, since they all decayed with the same rate constant. We measured the proton relaxation behavior of different carbon atom resonances for the three samples. The results show that the relaxation times were independent of the peak chosen for the calculation. The proton $T_{1\rho}$ values of the pure homopolymers PEN and PBT are 6.65 and 2.23 ms, respectively. For the 50/50 blends of PBT/PEN the decay is best fitted by a single exponential with the proton $T_{1\rho} = 3.83$ ms, which is between the relaxation time value of the two pure homopolymers. The observation of a single $T_{1\rho}$ shows that spin diffusion occurs quickly among the chemically different constituents, which equilibrates the magnetization, and the chains are intimately and homogeneously mixed.

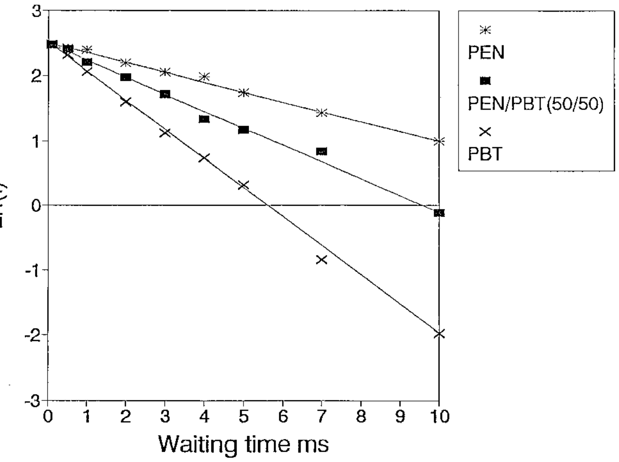


Figure 4. Semilog plot of the carbon atom resonance signal intensity as a function of delay time for PBT, PEN, and the blend 50 PBT/50 PEN at ambient temperature. The slope yields the proton spin−lattice relaxation time in the rotating frame.

Useful semiquantitative information about the domain size can be obtained from the equation $\langle r^2 \rangle = 6 D_s \tau$[15] (where $\langle r^2 \rangle$ is the mean square diffusive path length, D_s is the spin diffusion constant, and τ is the time for a fundamental step in the random walk); equating τ with $^{H}T_{1\rho}$ provides a reasonable order of magnitude estimation of the spatial dimensions involved. In a dense rigid proton system, the spin diffusion constant D_s is of the order of $(2-4) \times 10^{-16}$ $m^2\ s^{-1}$ in the rotating frame. The calculated communication distances or maximum diffusive path length in the PEN/PBT blend is on a scale of 20−40 Å. This experiment indicates that the two polymers, PBT and PEN, 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 a relaxation time. Therefore, the polymer blend is miscible on a 20−40 Å scale.

We are also interested in the morphology of the blend system on a smaller scale. That is, whether the blend system is miscible at a molecular level. In order to investigate the miscibility of the system further, deuterated PEN was blended with different amounts of PBT and the intermolecular cross polarization of the systems was examined.

Intermolecular Cross Polarization. We know that the efficiency of cross polarization depends on the strength of the ^{1}H−^{13}C magnetic dipolar decoupling and thus on the proximity of the protons to the ^{13}C nuclei. Of course, the absence of protons, as in the deuterated

Table 2. Chemical Shift of PEN and PBT Resonance Lines

PEN		PBT	
chemical shift δ (ppm)	assignment	chemical shift δ (ppm)	assignment
167.60	C11, C12	166.19	C1, C6
135.58	C9, C10	135.49	C2, C5
130.94	C1−4	131.45	C3, C4
	C5−8	66.71	C7, C10
63.89	C13, C14	27.06	C8, C9

polymer, deprives the system of this benefit. Fortunately, cross polarization can also occur if the average $^1H-^{13}C$ distances in two different molecules are on the order of 6 Å or less. In the circumstance where carbon atoms on deuterated chains can be spectrally distinguished from carbon atoms on the proton chain, the observation of a intermolecular cross polarization between carbon atoms in the deuterated polymer and the proton atoms of the other polymer provides strong evidence for intimate mixing.

1. Full Decoupling ^{13}C CP/MAS NMR Spectra. From the fully decoupled ^{13}C CP/MAS NMR spectra of PBT, PEN, and the three blends of PBT and deuterated PEN spectra, we can see that the higher the content of the PEN-d_{10} in the blends, the higher the aromatic carbon atom resonance signal at 130 ppm, and the wider the methylene carbon atom resonance signal at 64 ppm. These changes in the signal in the blends come from the contribution of the intermolecular cross polarization of the carbon atoms in the deuterated polymer, i.e. PEN-d_{10}, which are enhanced by the proton in the PBT chain. This experiment demonstrates the occurrence of a significant intermolecular cross polarization of the carbon spins of PEN-d_{10} by the proton spins of PBT. This is only possible when the proton−carbon intermolecular distances are on the order of 6 Å or less. From this result one could conclude that there is a molecular scale mixing in these blends at any composition.

However, judging from the results from Figure 3, and Table 2, we find that carbon atoms in deuterated chains, PEN-d_{10}, are not spectrally well distinguished from the carbon atoms in the proton chain, PBT. Therefore, the observation of intermolecular cross polarization between carbon atoms on the deuterated PEN and the protons of PBT is not proven by the results described above.

Recently, we used two other ^{13}C CP/MAS NMR methods,[21] the delayed decoupling and no decoupling ^{13}C CP/MAS measurements, to investigate the miscibility of the blends of PEN and PET. By using the two methods, the intermolecular cross polarization of the deuterated carbons of one polymer and the protons of the another polymer can be distinguished regardless of whether the chemical shift of both cross polarization signals (the signal from the intramolecular cross polarization between the protonated polymer and the signal from intermolecular cross polarization between the deuterated polymer and the protonated polymer) are the same or not.

We used these two methods here to study the miscibility of the blends of PEN-d_{10} and PBT, by observation of the intermolecular cross polarization in the blends, in which the chemical shifts of both components are very close.

2. ^{13}C CP/MAS NMR Spectrum without Dipolar Decoupling. Without dipolar decoupling during data acquisition, shown in Figure 1d, it is known that high-resolution cross polarization carbon signals from protonated carbons are not observed.[30] Magic angle spinning by itself, however, is sufficient to produce high-resolution cross polarization signals from the quaternary carbons and from the carbons in the deuterated chains which are well mixed with the protonated polymers.

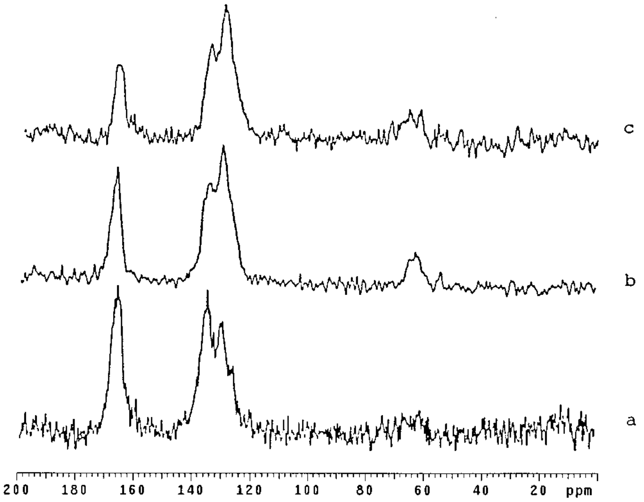


Figure 5. No decoupling ^{13}C CP/MAS NMR spectra of (a) blend 80 PBT/20 PEN-d_{10}, (b) blend 50 PBT/50 PEN-d_{10}, (c) blend 20 PBT/80 PEN-d_{10}.

The ^{13}C CP/MAS spectra, without dipolar decoupling during data acquisition, of different PBT/PEN-d_{10} blends are shown in Figure 5. The resonance signals at 63 and 131 ppm come from the contribution of the intermolecular cross polarization of the methylene carbon atoms and the ternary aromatic carbon atoms in deuterated PEN with the protons in PBT. This experiment clearly demonstrates the occurrence of a significant intermolecular cross polarization of the carbon spins of PEN-d_{10} by the proton spins of PBT. This is only possible when the proton−carbon intermolecular distances are on the order of 6 Å or less. It is concluded that there is a molecular scale mixing for those blends at any composition.

3. ^{13}C CP/MAS NMR Spectrum with Delayed Decoupling. In the delayed decoupling experiment, following the contact time, an extra delay, T_{DD}, is inserted before data acquisition. The pulse sequence is shown in Figure 1c. The delay, normally 50−100 μs, allows those carbon atoms with strong coupling to protons to dephase, so that the signals of carbons without directly attached protons can be selectively observed. This method is often called the dipolar dephasing experiment[14] and interrupted decoupling ^{13}C CP/MAS NMR experiment, which are very useful in isolation of protonated and nonprotonated signals,[14,28,29] and in partitioning the ^{13}C resonance of rigid and mobile phases.[14,31] By using the pulse sequence with the present studied system, blends of PEN-d_{10}/PBT, the contributions from deuterated carbons, when they are well mixed with the protonated polymers and the proton−carbon intermolecular distances are on the order of 6 Å or less, are, of course, unaffected by the delay.

The ^{13}C CP/MAS spectra, with an 80 μs dipolar dephasing delay before data acquisition, of different PBT/PEN-d_{10} blends and homopolymer PBT are shown in Figure 6. When the amount of deuterated PEN increases, the intensity of the resonance signals at 63 and 131 ppm increases correspondingly as a consequence of the contribution of the intermolecular cross polarization of the methylene carbon atoms and the ternary aromatic carbon atoms of deuterated PEN with the protons in PBT. Obviously, the higher the amount

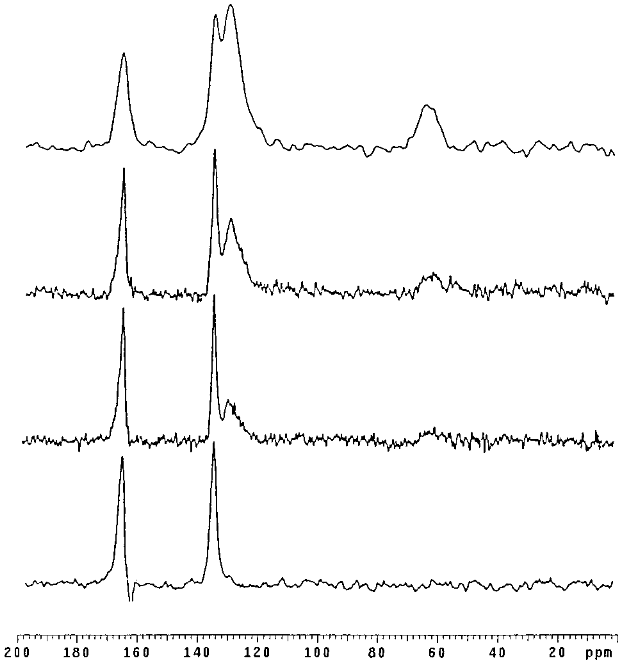


Figure 6. Delayed decoupling ^{13}C CP/MAS spectra of (a) homopolymer PBT, (b) blend 80 PBT/20 PEN-d_{10}, (c) blend 50 PBT/50 PEN-d_{10}, and (d) blend 20 PBT/80 PEN-d_{10}.

of the deuterated PEN in the blends, the more deuterated carbon spins in the systems, the higher the intensity of the two peaks when the deuterated carbon spins in PEN-d_{10} are close enough to the protons of a PBT polymer. This experiment again clearly demonstrates the occurrence of a significant intermolecular cross polarization of the carbon spins of PEN-d_{10} by the proton spins of PBT. This is only possible when the proton−carbon intermolecular distances are on the order of 6 Å or less. It is concluded that there is a molecular scale mixing for these blends at any composition.

Conclusions

The miscibility of the PEN/PBT blends has been investigated with DSC and four different ^{13}C CP/MAS NMR measurements. The T_m and ΔH_m of PBT decrease continuously, while the T_m, ΔH_c, and ΔH_m of PEN are increased continuously as the PEN ratio is increased. A single $^{H}T_{1\rho}$ was observed for the 50 PEN/50 PBT blend. This indicates that the polymer blend is miscible on a 20−40 Å scale. For the blends of deuterated PEN with different components of PBT, intermolecular cross polarization from the protons in PBT to carbons in deuterated PEN was observed on the ^{13}C CP/MAS NMR spectra under the conditions of full decoupling, no decoupling, and delayed decoupling. When the chemical shifts of the resonance signals from the intramolecular cross polarization between the protonated polymer and the resonance signals from intermolecular cross polarization between the deuterated polymer and the protonated polymer are the same or very close, the full decoupling ^{13}C CP/MAS NMR method cannot distinguish the intermolecular cross polarization resonance from the intramolecular ones, while the latter two decoupling techniques are still effective in this case. The investigations lead to the conclusion that PEN and PBT form miscible signal phase blends at the molecular level at any composition.

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