Morphology and Molecular Motion of Poly(ethylene terephthalate) in Polymer/Oligomer Gel

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ABSTRACT: The structural heterogeneity and molecular motion in a thermoreversible gel consisting of poly(ethylene terephthalate) (PET) and a liquid ethylene glycol oligomer (PEG) was investigated by solid-state NMR and FT−Raman spectroscopies. PET was dissolved in PEG at elevated temperatures to form a concentrated solution (30 wt %), and the solution formed a gel rapidly on cooling. For the purpose of comparison, a PET/phenol binary system and PET crystallized by annealing methods were also investigated. The longest solid-state NMR relaxation times of ^{13}C ($^{13C}T_1$) in PET of PET/PEG gel among the samples indicated the slowest molecular motion and the highest rigidity PET chains. The structural heterogeneity of the PET/PEG gel investigated by $^{H}T_1$ measurement and confirmed by FT−Raman spectroscopy indicated phase transition during gelation. The crystallinity of PET recovered from polymer/oligomer gels is near 70% as measured by wide-angle X-ray diffraction, which is about 20% higher than that for PET samples crystallized by solution crystallization and high-temperature annealing techniques.

Introduction

Poly(ethylene terephthalate) (PET) is a slowly crystallizing material at atmospheric pressure. A number of physical methods have been developed to grow crystals of PET, such as crystallization from the melt, annealing samples at elevated temperature, hot-drawing film or fibers, crystal growth in dilute solution, etc.[1−7] Degrees of crystallinity in an annealed PET typically vary between 20 and 50%, measured by wide-angle X-ray diffraction.[3] Roland has investigated the annealing of PET at higher temperature.[4] The crystallinity of PET was found to increase from about 45% to 60% for samples annealed at 260 °C for 700 h.[4]

Recently, we found an effective method for preparing highly crystalline PET. PET was first dissolved in a low molecular weight poly(ethylene glycol) (PEG). At elevated temperature, a homogeneous solution consisting of PET and the oligomer was obtained, which rapidly formed a thermoreversible gel on cooling.[8] After the solvent was removed, a highly crystalline PET was recovered. It is well-known that both flexible and stiff macromolecules can form thermoreversible gels under certain conditions.[9] Micromolecular solvents are usually used in these gel systems. The thermoreversible gelation of solutions of PET in PEG oligomer differs in a number of respects from earlier reports of gel forming solutions. First, PET is a semicrystalline condensation polymer of low flexibility, and almost no investigations were concerned with its gelation. Second, the solvent, PEG oligomer, is a fairly large molecule with an average molar mass of approximately 400. Third, the system appears to gel easily on cooling the solution to room temperature. Here we report the molecular motion and structural heterogeneity in PET/PEG gel characterized by solid-state NMR and FT−Raman spectroscopies.

Experimental Section

The three major materials used in this study were poly(ethylene terephthalate), poly(ethylene glycol), and phenol. The homopolymer PET was available in the form of small beads having a viscosity-average molecular weight of 24 000, kindly supplied by Yizheng Chemical Fiber Company in China. PEG, with an average molar mass of 400, and phenol were supplied by Liming Chemical Institute in China. The terminal group of PEG as received was the hydroxyl group. In this experiment, PEG was reacted with acetyl chloride before use, to change the terminal hydroxyl group to the unreactive methyl group.[10]

For the gel preparation, the desired amount of PET and PEG solvent was added into a 10-mL Erlenmeyer flask. The mixture was initially heated to 230 °C while being stirred in a silicon oil bath and then held at this temperature for 10 min to ensure that all of the PET pellets have fully dissolved in the PEG and a homogeneous solution was obtained. The solution was then cooled to room temperature in the oil bath at a rate of 10 °C/min without further agitation. Gelation became evident visually on inverting the Erlenmeyer flask. The gels quickly dissolved above 180 °C reverting to a transparent homogeneous solution. Gels of 10, 20, and 30 wt % PET were prepared, but it is mainly the 30 wt % composition that is discussed. PET/phenol binary system was prepared by dissolving the polymer in phenol at 230 °C and then cooling the reaction to room temperature.

A specimen that had gelled and could support its own weight at room temperature was examined by polarized light microscopy, using a Leitz Ortholuz II microscopy. A gel drop was placed on a microscope slide, covered with a glass platelet, and examined at room temperature. The sample was kept in a sealed box to avoid dust contamination prior to observation.

The Chemagnetics CMX 200 NMR spectrometer was used to measure the NMR spectra for PET/PEG gel and for PET/phenol system with radio frequency fields of 58 kHz. The proton-enhanced spin−lattice relaxation times of ^{13}C ($^{13C}T_{1\rho}$) was measured by the use of a NMR pulse sequence originally proposed in 1978,[11] and the spin−lattice relaxation time of ^{1}H in the rotating frame ($^{H}T_1$) was studied by the pulse sequence proposed by M.G.[12] The FT−Raman spectra of PET/PEG gel

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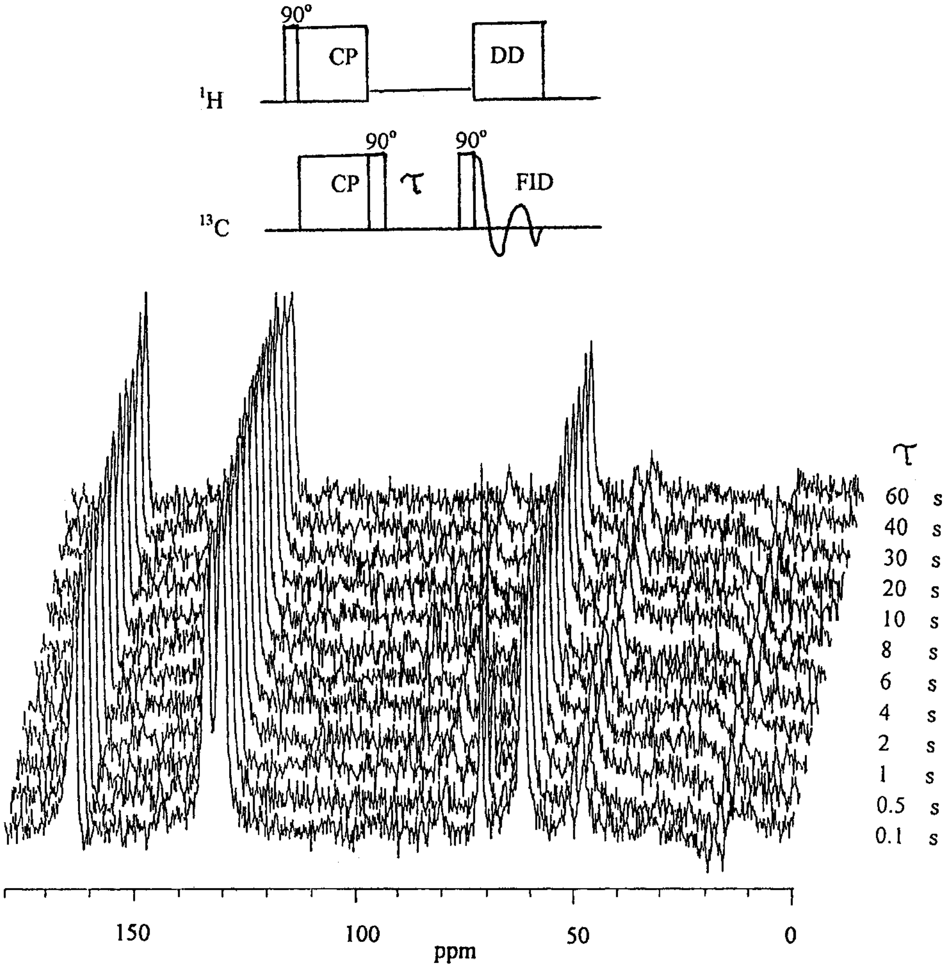

Figure 1. Pulse sequence used to observe $^{13C}T_1$ and the stack NMR spectra of PET/PEG gel recorded at various delaying times.

and PET/phenol solid were recorded with 1.064 nm excitation, using a Bruker RFS100 FT–Raman spectrometer.

Powdered PET was recovered by washing the PET/PEG gel with ethanol to remove the PEG. The gels were extracted with ethanol by adding one part of gel to five parts of nonsolvent. After the initial extraction, the slightly swollen PET was extracted overnight in a large excess of ethanol. This procedure was repeated three times. The dried PET samples were examined by means of a wide-angle X-ray diffractometer (Rigaku D/Max-Ra) using Ni-filtered CuKα radiation detected by a scintillation counter with single-channel discrimination. Differential scanning calorimetry (DSC) was run on a Perkin-Elmer model DSC-2C system with a data station. The heating rate was 20 °C min^{-1}.

Results and Discussion

Cross-polarization/magic-angle spinning/dipolar decoupling solid-state NMR spectroscopy was used to study the molecular motion and the structural heterogeneity in PET/PEG gel, PET/phenol binary system, and a PET sample precipitated from PET/phenol solution. Figure 1 shows the pulse sequence used to observe the spin–lattice relaxation times for ^{13}C ($^{13C}T_1$) and the stack NMR spectra of PET/PEG gel recorded with various delaying times values. Figures 2 and 3 are the stack NMR spectra of a solution precipitated PET and a PET/phenol binary system, respectively. One can easily see that the NMR signals decay quickly in Figures 2 and 3 as the delaying time is increased. The NMR pulse sequence for the measurement of proton-enhanced carbon-13 T_1 values was shown in Figure 1.[11] The low-power saturation of protons has been used in the pulse sequence to suppress the transient Overhauser effect. Theoretically, the longer delay time should be several times T_1. In this experiment, a very long delay time, 60 s, was used. The linear nature of more than 10 experimental data points with different delay times shows that the T_1 data extracted from the slope of the semilog plots illustrated in Figure 4 is reliable. The

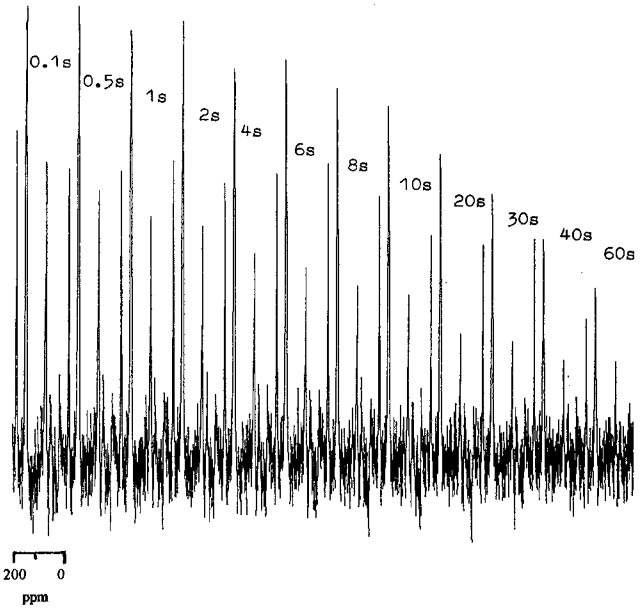

Figure 2. Stack NMR spectra of a solution precipitated PET recorded at various delaying times.

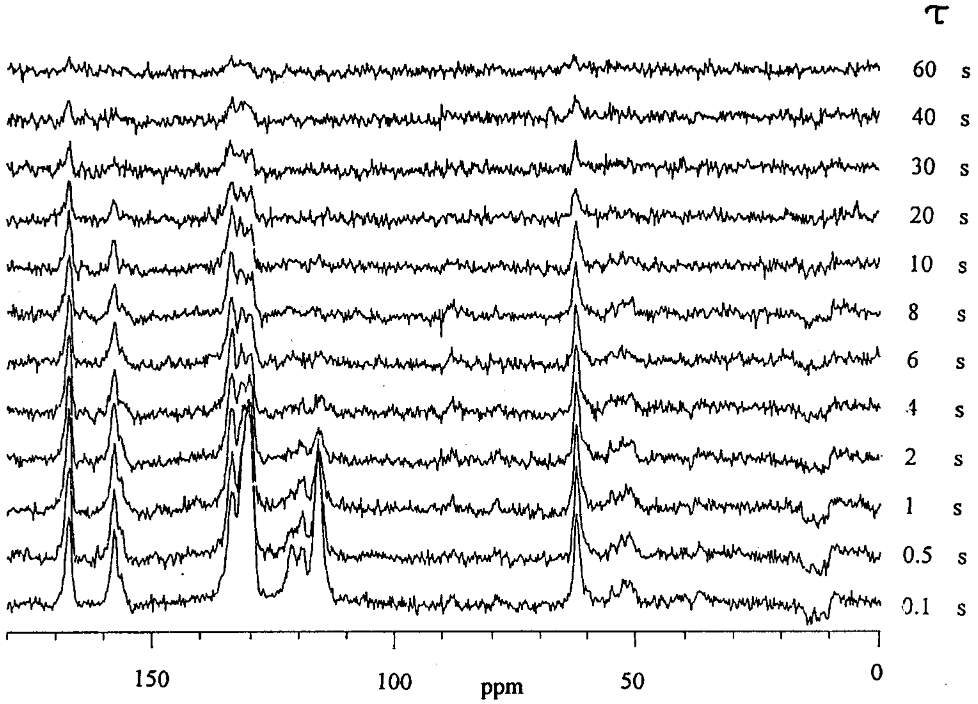

Figure 3. Stack NMR spectra of PET/phenol binary system recorded at various delaying times.

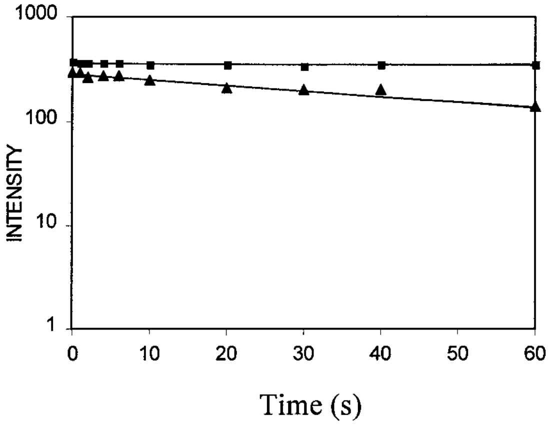

Figure 4. Semilog plots of the signal intensities in the proton-enhanced carbon-13 T_1 experiment for the carbonyl carbons of PET/PEO gel (■) and the solution pricitated PET (▲). The lines drawn in the figure were determined by a least-squares fit to the data and their corresponding slopes yields the T_1 values discussed in the text.

Table 1. Spin−Lattice Relaxation Times (s) of ^{13}C in Various PET

	spin-lattice times			
samples	$^{13}C{=}O$	Ar−^{13}C	Ar−^{13}CH	$^{13}CH_2$
PET/PEG gel	339	173	130	135
PET/phenol	23.3	20	20.6	
solution-precipitated sample	89	60	55	36.2
Annealed sample	170	94	88.5	67

$^{13C}T_1$ values were calculated for these four systems and are listed in Table 1. The $^{13C}T_1$ values for PET in PET/PEO gel are much higher than those in PET/phenol and in the annealed PET. Table 2 compares the spin−lattice relaxation in the rotating frame ($T_{1\rho}$), recorded from the PET/PEG gel and from PET/phenol solid.[12] $T_{1\rho}$ for PET in the PET/PEG gel is longer than that in PET/phenol.

A typical T_1 and $T_{1\rho}$ curve has a minimum in its relaxation time vs correlation time (τ_C) plot, as shown in Figure 5.[13] For the studies to correlate the experimental relaxation time to the molecular motion and morphology of the system, it is important to know whether the correlation time of the studied system is located on the slow side or on the fast side of the minimum. That is because the slow side of the curve can be interpreted in such a way that a decrease in T_1 or $T_{1\rho}$ value indicates increased molecular motion, while the fast side of the curve can be interpreted in such a way that a decrease in T_1 or $T_{1\rho}$ value indicates decreased molecular motion. For normal semicrystalline polymers, especially for those polymers where the

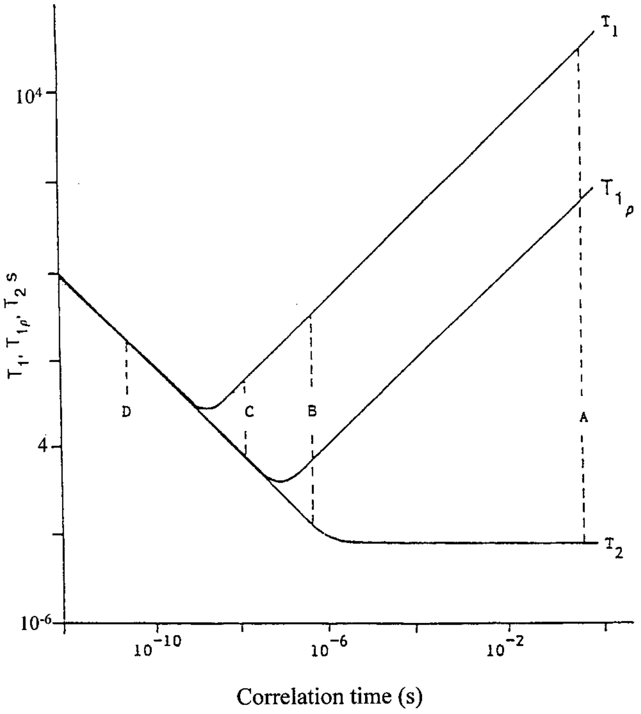

Figure 5. Dependence of T_1 and $T_{1\rho}$ on the molecular correlation times for relaxation determined by dipole−dipole interactions

Table 2. Spin–Lattice Relaxation Time in Rotating Frame (ms) of H in Various PET and Solvents

samples	$^{H}T_{1\rho}$ in PET	$^{H}T_{1\rho}$ in solvent
PET/PEG gel	28.9	50.2 (PEG)
PET/phenol	10.3	11.4 (phenol)

Table 3. $^{13C}T_1$ (s) of PET Recorded under Different Temperatures (°C)

		$^{13C}T_1$			
samples	temp	^{13}C=O	Ar–^{13}C	Ar–^{13}CH	^{13}CH$_2$
solution precipitated PET	20	89	60	55	38.2
	60	61.7	41.2	48.2	28.3
PET/PEG gel	20	339	173	130	135
	60	217	115	109	82.4
PET/phenol	20	23.3			20.6
	60	15.2			11.9

T_g of the amorphous phase is above room temperature, the motional correlation time lies on the slow side of the minimum, PET, PBT, and PNT for example.[12,13] However, this relation for the gel system of PET/PEG should be confirmed by experiments. An experimental way to find out which side of the T_1 minimum the system is located in is to measure the T_1 at two different temperatures. Table 3 shows $^{13C}T_1$ values for the PET samples in PET/PEG gel, PET/phenol, and the solution precipitated polymer at 20 and 60 °C with radio frequency fields of 58 kHz, respectively. The fact that $^{13C}T_1$ decreases as the temperature increases indicates that the correlation time lies on the slow side of the minimum. So we can conclude that the longest $^{13C}T_1$ for PET/PEG gel among the samples investigated indicates the slowest molecular motion and the most rigid chains of PET in the gel. It seems that PET in PET/PEG gel is in a highly crystalline phase.

NMR relaxation studies of polymer morphology for complex systems such as semicrystalline polymer in an oligomer gel are seldom reported in the literature due to the system complexity. Further research remains the subject of active investigation. To confirm the highly crystalline phase in PET/PEG gel, the gel was dried and was investigated by the use of WAXD. Figure 6A shows the wide-angle X-ray scattering pattern recorded from a PET powder sample which had been recovered from a 30 wt % PET/PEG gel. For the purpose of comparison two PET samples crystallized by conventional methods were also studied. The diffractogram of Figure 6B was recorded from a PET sample which had been crystallized from a 30 wt % solution in phenol, and the sample had been annealed at 200 °C for 24 h before measuring. Figure 6C was recorded from a PET film quenched from the melt and annealed at 220 °C for 48 h. Crystallinities were obtained by dividing the crystalline intensity by total diffracted intensity.[2] The crystallinity for the sample recovered from PET/PEG gel was 70% measured by wide-angle X-ray scattering. The diffractograms of parts B and C of Figure 6 exhibit lower crystallinity than that of Figure 6A. It is well-known that a highly crystalline phase can be obtained for polymers from their dilute solutions. However, we found here that PET with a high crystallinity could be obtained from a concentrated solution in PEG.

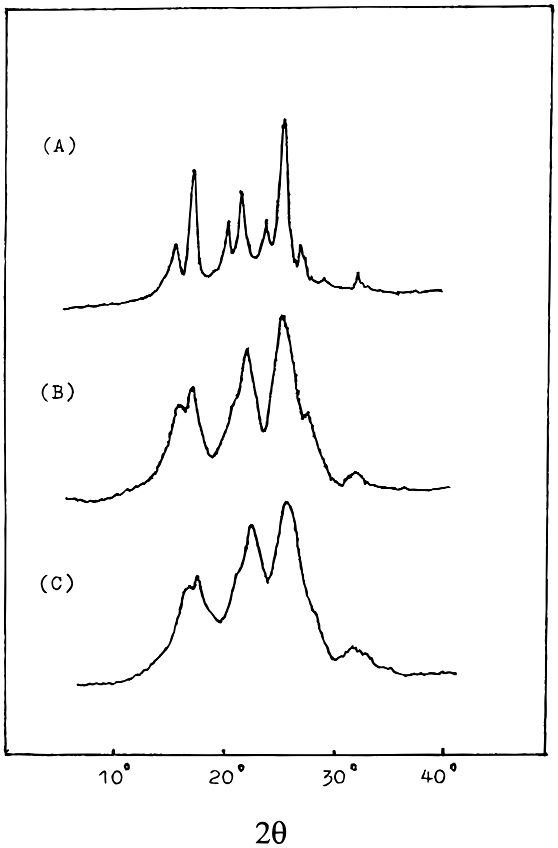

Figure 6. Wide-angle X-ray diffraction curves of PET recorded from (A) dried PET/PEG gel, (B) crystallized PET from phenol solution and annealed at 200 °C for 24 h, and (C) PET film quenched from the melt and annealed at 220 °C for 48 h.

It is clear that PET in PET/PEG gel is more highly crystalline than samples prepared by other physical techniques, such as annealing, stretching, solvent-induced crystallization, and their combinations. The degradation of the amorphous region of a draw PET fiber with aqueous methylamine resulted in a 66% crystalline phase of the PET residual,[5] but this etching procedure made the sample lose more than 80% of its original weight.[5] A recent study showed that crystallization of PET from the melt under high pressure (400 Mpa) in the temperature range 295–320 °C resulted in a material with a melting enthalpy of about 121 J g^{-1} and a density of about 1.46 g cm^{-3}.[6] Assuming the usual values for the melting enthalpy and the density of ideal crystals of PET (135 J g^{-1} and 1.490 g cm^{-3}, respectively), the degree of crystallinity of this high-pressure-crystallized material is about 90% whereas a 70% crystallinity was measured by wide-angle X-ray scattering.[7] Such a high value has never been obtained in PET before. However, the high-pressure and high-temperature crystallization resulted in a substantial reduction in the molecular weight of PET from M_w = 30 000 to M_w = 8000.[6,7] We found that the polymer is unchanged in molecular weight during gelation in PEG or in an epoxy resin, since the intrinsic viscosity remained unchaged as did the chemical shifts in the NMR spectra. The identical nature of the NMR spectra of the PET sample as received and that of the dried gel excluded the chemical reaction between PET and the solvent under our experimental conditions.

Figure 7 shows the DSC curves for the PET sample recovered from PET/PEG gel and for the sample quenched from the melt and crystallized 48 h at 220 °C. It can been seen that the gel crystallization in the PEG oligomer gives rise to a narrower melting peak which is shifted to higher temperature. This suggests the occurrence of thicker crystals in the dried gel showing a narrower distribution of crystal thickness than in the normally crystallized material. Table 4

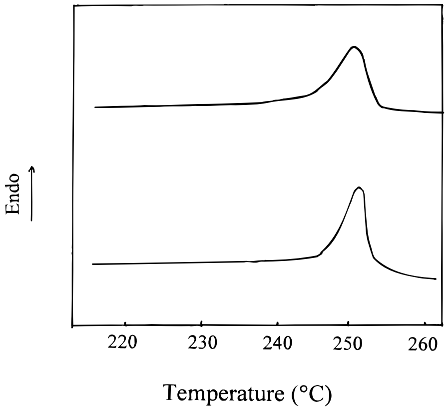

Figure 7. DSC scans of PET crystallized from the melt (upper) and the dried gel (lower).

Table 4. Melting Temperature (T_m) and Crystallinity X_c of PET Samples Measured by DSC Experiment

sample	crystallization	T_m (°C)	X_c (%)
PET dried gel	15 wt % PET/PEG	251	64
PET dried gel	20 wt % PET/PEG	250	65
PET film	220 °C/48 h	245	46

shows the values of the melting points and the corresponding degrees of crystallinity obtained from the melting enthalpy,[14] respectively.

The structural heterogeneity of PET/PEG gel was investigated by solid-state NMR spin–lattice relaxation in a rotating frame,[12] as shown in Table 2. In the sample of PET/PEG gel, the $T_{1\rho}$ value for PET is 28.9 ms and for PEG is 50.2 ms, while in the sample of PET/phenol $T_{1\rho}$ value is 10.3 ms for PET and is 11.4 ms for phenol. Determination of the proton spin–lattice relaxation times in the rotating frame $T_{1\rho}$ through analysis of the average decay rate of the protons of all carbon atoms can be used to study the polymer–polymer or polymer–solvent miscibility on a molecular scale.[12] In the case of phase separation the two values of $T_{1\rho}$ of the single components are found. In contrast, if miscibility occurs, a single relaxation time is found for the blend or solution, lying between the relaxation times of the two components.[12] The big difference in $T_{1\rho}$ values shown in Table 2 between PET and PEG clearly indicated that PET/PEG gel is heterogeneous. A nearly single $T_{1\rho}$ was observed for the binary system of PET/phenol as shown in Table 2, which suggests the homogeneity of mixing of PET and phenol. The heterogeneity of PET/PEG gel can be confirmed by FT–Raman spectroscopic studies. Parts A, B, and D of Figure 8 are the Raman spectra recorded from a PET/PEG gel, a pure PEG, and a PET film, respectively. The spectrum of Figure 8C is the subtraction spectrum (Figure 8A – Figure 8B), which is similar to the spectrum of a PET film except for the doublet bands at 1290 and 1286 cm^{-1} caused by a crystal field splitting effect.[16] Parts A and B of Figure 9 are the Raman spectra recorded from a PET/phenol system and a pure phenol, respectively. The spectrum of Figure 9C is the subtraction spectrum (Figure 9A – Figure 9B). The difference spectrum of Figure 9C is quite different from that of PET film (Figure 8D), indicating the existence of a very strong interaction between PET and phenol which caused most Raman lines of PET to shift from their original positions, while in the PET/PEG gel little solvent–solute interaction existed. The small molecular interaction between PET and PEG led to phase separation as the solution was cooling from high temperature.

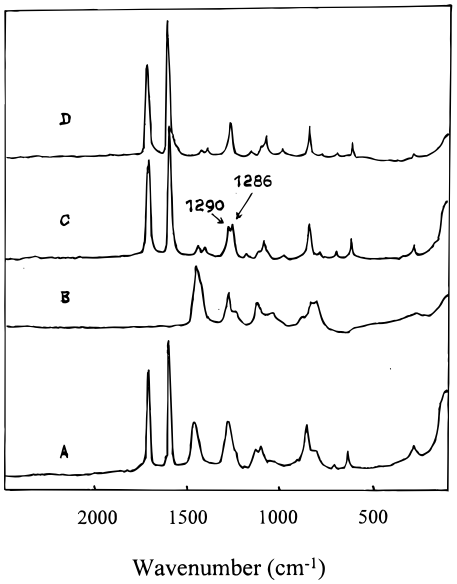

Figure 8. FT–Raman spectra recorded from (A) PET/PEG gel, (B) PEG, (C) subtraction of A – B, and (D) a PET film.

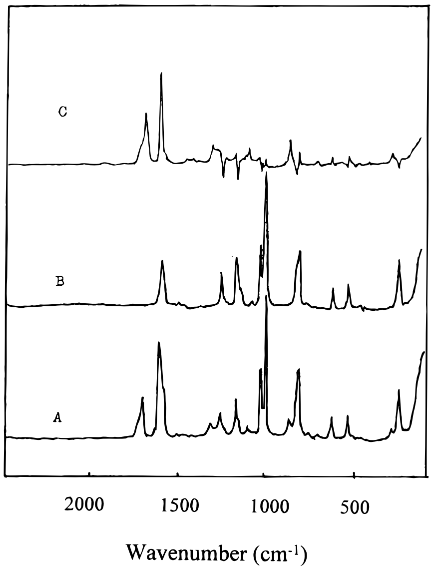

Figure 9. FT–Raman spectra recorded from (A) PET/phenol, (B) phenol, and (C) subtraction of A – B.

When the PET/PEG gel was observed at room temperature by use of a polarizing microscope with crossed polars, a sample with a spherulite-like supermolecular structure shows high birefringence, for example, Maltese cross extinction patterns. Figure 10 displays a polarized light micrograph of wet PET/PEG gel. Maltese cross extinction patterns, which are obvious characteristic of spherulites, can be seen clearly in the photohraph of Figure 10. Since the extinction cross pattern remained unchanged, when the sample was rotated, the texture could be attributed to crystal spherulites.[15]

The spherulite texture of PET develops in the high concentration PET/PEG sample, and is associated with two gelation processes. First, a liquid–liquid-phase separation creates a bicontinuous phase, one richer in PEG and the other richer in PET. This liquid–liquid-phase demixing was evidenced by the turbidity, which is due to the difference in refractive index between the concentrated polymer solution and the liquid "matrix" of dilute solution and was investigated by DSC.[8] At a

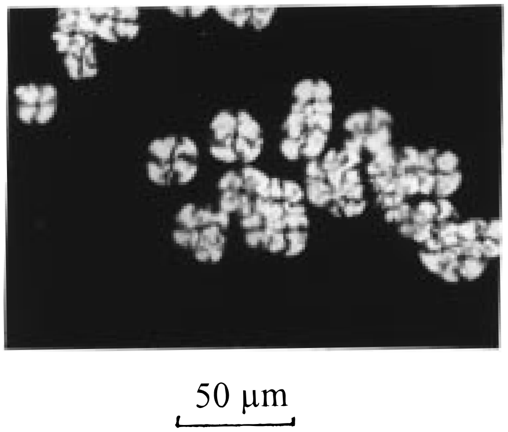

Figure 10. Polarized light micrograph of PET/PEG gel with a PET concentration of 20 wt %.

critical PET concentration, an anisotropic phase may develop. Second, these anisotropic domains grow further into the spherulite textures that are observed under polarized light scattering and small-angle light scattering.[8] This mechanism of a two-step gel formation has also been reported in synthetic random coil polymers and in some biological systems,[17] as well as in rigid-rod polymers.[18] Liquid−liquid-phase separation is a common characteristics in polymer solution and has been studied extensively. However, the phase behavior of the PET/PEG system is more complex than that of many polymer/solvent systems, due to the ability of the PET to crystallize. A similar behavior was suggested by Kim and Lloyd for mixtures of isotactic polypropylene.[19]

The formation of polymer spheres has already been related to liquid−liquid-phase separation. These crystalline globules have been reported for a number of polymers.[17−19] They are consistently obtained when using a rather poor solvent. For example, the formation of polymer globules has often been observed in association with epitaxial crystallization for a benzoic acid solution of PE or polyamides.[19] The PET spheres distributed in mixtures in our polarized light microscopy studies give strong evidence that phase-phase separation occurred in the PET/PEG system during the cooling.

PET prepared from PET/PEG oligomer gel is highly crystalline with fewer intermolecular segmental interaction. The chain movement of PET in the environment of PEG molecules may be represented by the reptation model proposed by De Gennes.[20−22] In a normal polymer melt, the constraints imposed by the long chain molecule are strong and the molecule diffuses slowly. In PET/phenol solution, the constraints imposed by the solvent are strong, as evidenced by the NMR data shown in Table 2. The PEG oligomer ($M_t = 400$) chain is shorter than PET molecules but is longer than a monomer. In PEG solution, PET interchain entanglements were partially replaced by PET/PEG interpenetration. For a PET molecule, PEG imposes only a weak constraint and allows the long chain to move in a rapidly renewed tube, while other PET chains which entangled with the chain of interest can only translate slowly due to the restriction of PEG chains. When the binary system was cooling, phase separation occurs and PET molecules continuously diffused into the polymer-rich domains. These are conditions suitable for chain disentanglement and for growing crystals.[1] Well-organized crystallite in spherulites of PET were formed on further cooling, resulting in a thermally reversible PET/PEG gel. The recovered PET is highly crystalline with fewer entanglements. We also obtained PET with 70% crystallinity from PET/epoxy resin through gelation crystallization.

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