Pulsed n.m.r. relaxation study of a polystyrene/poly(ethylene oxide) diblock copolymer: Evidence for interaction at the phase boundary

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(*Received* 5 *February* 1980; *revised* 25 *April* 1980)

Pulsed nuclear magnetic resonance relaxation measurements are presented for a hydrophobic-hydrophilic diblock copolymer of polystyrene and poly(ethylene oxide) along with results for the individual homopolymers. Although observation of the thermal transitions of the homopolymer components in the copolymer reveals a gross incompatibility, the n.m.r. data suggests strong interfacial effects. From the T_1 and T_2 data below the melting point of PEO(T_m=335K), it was concluded that polystyrene creates localized defects which reduce PEO domain crystallinity to 75% from 93% in the homopolymer. Above T_m in the copolymer three motional domains can be distinguished, isolated rigid polystyrene, isolated molten PEO and an intermediate domain. The composition of the intermediate domain suggests that 23% of the polystyrene is plasticized whereas 80–90% of the molten PEO is motionally constrained. The results are interpreted in terms of a spatial segregation of the homopolymer components with a forced interaction at the phase boundary as a result of the covalent linkages tying the two components together.

INTRODUCTION

The technological promise of block copolymers and other composite materials emanates from the potential for controlling their structure and creating materials with desirable combinations of properties[1]. A wide variety of techniques has been used to study the detailed structure of composite systems with particular focus on the phase boundary, because of its influence on physical properties. Phase separation or domain formation can be measured over different characteristic dimensions using various spectroscopic methods such as microscopy, light scattering, dielectric or dynamic mechanical response and nuclear magnetic resonance (n.m.r.). In the present study we use n.m.r. relaxation measurements, sensitive to short range interactions, to study the effect of block copolymerization on the behaviour of the individual homopolymer components in a diblock copolymer of polystyrene (PS) and poly(ethylene oxide) (PEO).

The PS–PEO system is interesting because it is composed of two dissimilar polymers — polystyrene, which is hydrophobic and glassy, and poly(ethylene oxide), which is hydrophilic and semicrystalline. Previous studies of PS–PEO copolymer bulk morphologies have demonstrated microphase separation of the individual components[2–4]. However, covalent bonds linking the two incompatible polymers prevent macroscopic phase separation, which occurs in physical blends of the same components. The bulk copolymer has been previously characterized by differential scanning calorimetry (d.s.c.)[2], transmission electron micrographs (*TEM*)[3] and rheological melt flow behaviour[4].

D.s.c. measurements of blocks as well as blends of the individual homopolymers demonstrate the incompatibility of the PS and PEO domains by showing thermal transitions at the melting point of crystalline PEO (335K) and the glass transition of PS (373K). A melting point suppression, which increases with PS content in the block systems but is not observed in the blends, is explained in terms of the macroscopic phase separation in the blends which cannot occur in the blocks. Transmission electron micrographs[3] reveal that the size and perfection of PEO crystal lamellae depend upon copolymer composition — increasing PS content decreases lateral dimensions and distorts the lamellae. Heat of fusion measurements[2] show a reduction in crystallinity of PEO domains with increasing PS content. In the melt, the viscosity of the block system[4] is higher than that of either component, suggesting partial phase separation. This behaviour is common to incompatible block copolymers and results from increased resistance in the flow of one component through domains of the other.

We report here on n.m.r. spin–spin (T_2) and spin–lattice (T_1) relaxation data, which show that, although the component homopolymers are spatially segregated, polymer chain motions of one domain influence the behaviour of the other domain.

EXPERIMENTAL

Sample materials

Polystyrene in a Pressure Chemical Co. narrow molecular weight distribution polymer with $\bar{M}_w = 10K$. Poly(ethylene oxide) is a Union Carbide Carbowax with $\bar{M}_w = 25K$. Synthesis of the PS–PEO diblock copolymers involves a two step anionic polymerization technique described in detail elsewhere[2]. The copolymer used for the present study is identical to sample 84 of reference 2. It is composed of 39.3 wt % polystyrene and has a number

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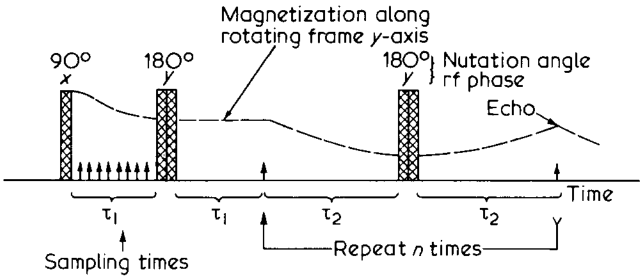

Figure 1 Split time base Carr-Purcell-Meiboom-Gill pulse sequence used to digitize in a single scan a free induction decay consisting of widely different relaxation times. The fast component is captured with high speed digitization following the 90°, *x* phase r.f. pulse. After a time τ_1, when the fast decay is essentially complete, a 180°, *y* pulse is applied generating an echo at time $2\tau_1$. Subsequent echoes are formed with a train of 180°, *y* pulses separated by $2\tau_2 (\tau_2 \gg \tau_1)$. The envelope of echo peaks are digitized to give the slow component response

average molecular weight $\bar{M}_w = 33.5\text{K}$ with $\bar{M}_n$ (PEO) $= 20.3\text{K}$ and $\bar{M}_n$ (PS) $= 13.2\text{K}$. A reference blend, composed of a physical mixture of the two homopolymers, is of the same composition as the copolymer. Samples were degassed using the freeze–pump–thaw technique, where the 'thaw' step involved heating to above the polystyrene glass transition, and sealed under vacuum.

Pulse sequences and data analysis

Proton T_1 and T_2 relaxation times were measured from 140K to 500K on a Bruker CXP pulsed spectrometer operating at 90 MHz. T_2 data was acquired in three separate modes depending upon the nature of the free induction decay (*FID*). Low temperature *FID*'s (<335K), displaying short decay components, were obtained by high speed digitization of the magnetization response to a 90° pulse. High temperature (>430K) slowly decaying *FID*'s were measured by digitizing echo peaks in a Carr–Purcell–Meiboom–Gill (CPMG) pulse train. In the intermediate temperature range (between 335K and 430K), where component relaxation times are spread over several orders of magnitude, data was acquired using a split time base pulse sequence illustrated in *Figure* 1. The fast component was captured by high speed digitization after a 90° pulse and the slowly decaying portion by a subsequent echo train. The CPMG sequence was carried out using the procedure recommended by Haberlen, *et al*[5]. The 180° pulse separation ($2\tau_2$ in *Figure* 1) was always adjusted to exceed the width of the echoes in order to minimize the tendency that $T_{1\rho}$ is obtained. In order to determine the possible influence of spin locking and self-diffusion on the T_2 values, additional measurements were made at 350K and 400K mapping signal amplitudes vs time for a Carr–Purcell single echo experiment. Relaxation times calculated in this way showed small differences from the CPMG pulse train values and these differences assisted in establishing data error bars.

Measurement of the true *FID* signal shape requires adjustment for exact resonance frequency and correct r.f. phase at each temperature in order to compensate for magnet drift and temperature effects on the probe and external lock tuned circuits. Readjustment at each temperature is a time consuming process, particularly in view of the long (up to 40 s) spin–lattice relaxation times at low temperatures. Diode detectors, often employed to give signals independent of phase and offset frequency, are notoriously non-linear, and therefore the following scheme was used to circumvent these problems. *FID* data was acquired with a two channel quadrature phase detector. Since the signals $A(t)$ and $B(t)$ from the two channels are 90° phase shifted, the *FID* envelope $S(t)$ can be calculated from $S(t) = (A^2(t) + B^2(t))^{1/2}$. This magnitude calculation is independent of phase misadjustment and resonance offset frequency and does not have the linearity problems of a diode detector. At higher temperatures this procedure proved unnecessary since spin–lattice relaxation times were conveniently short.

Spin–spin relaxation times were calculated by a least squares fitting of the *FID*. As the T_2 values obtained depend upon the shape function one selects, and choice of a Lorenzian or Gaussian lineshape is arbitrary, the data was fitted to the Weibull function[6,7], $\exp[-(t/T_2)^E]$, where t is time, T_2 is the spin–spin relaxation time and E is a generalized shape parameter. The Weibull function is a convenient though empirical representation of the *FID*. It can assume Lorenzian ($E = 1$), Gaussian ($E = 2$) or intermediate character. For a two component decay, relaxation times were determined by applying a 6 parameter non-linear least squares regression analysis (Fortran program No. BMDX85, Health Sciences Computing Facility, UCLA) of the observed time evolution of the magnetization $M(t)$ to obtain the following equation,

$$M(t) = A_r \exp[-(t/T_{2r})^{E_r}] + A_m \exp[-(t/T_{2m})^{E_m}] \quad (1)$$

where r and m denote the rigid and mobile components, respectively. The proton mole fraction associated with the mobile component, F_m, is calculated from

$$F_m = A_m/(A_m + A_r) \quad (2)$$

A 6 parameter iterative curve fitting procedure may converge to different solutions depending upon initial parameter estimates. However, for the PS–PEO copolymer of this study the decay time constants, T_{2r} and T_{2m}, are sufficiently different for unambiguous fits to be obtained. We found the Weibull coefficient, E, to behave generally as expected, ranging from 2.0–2.7 in the rigid solid at low temperatures and from 0.7–1.0 in the melt at high temperatures. Above the PEO melting point, a fit of the decay to two components using equation (1) gave very low values for E_m (~ 0.5). Examination of the mobile component revealed a long exponentially decaying tail with T_2 equal to that of the PEO homopolymer. This long component, as determined by a linear least squares fit to an exponential function, was then subtracted from the original signal before reapplying the regression analysis of equation (1), giving an adequate description of the total magnetization behaviour in terms of a three component decay.

Spin–lattice relaxation times were measured by the 180°–τ–90° inversion recovery pulse sequence. There was no deviation in any T_1 determination from a single exponential recovery.

RESULTS AND DISCUSSION

At the lowest measured temperatures, the *FID* of the PEO homopolymer exhibits a beat structure which transforms into an ~100 kHz splitting in the frequency domain. This behaviour, attributed to a resolved dipolar structure[8], reflects the very high degree of chain alignment within

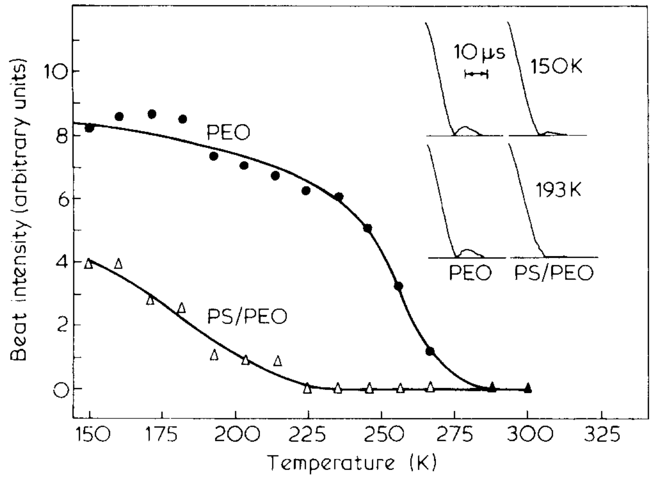

Figure 2 Temperature dependence of the resolved dipolar beat intensity. Selected *FID*'s are shown in the inset

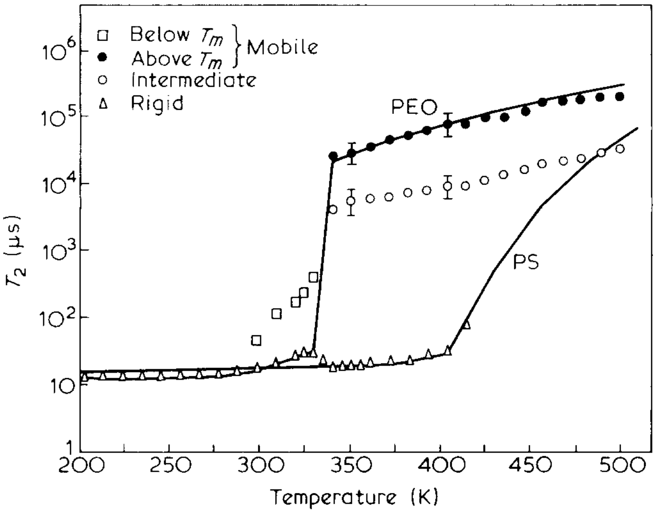

Figure 3 Temperature dependence of spin-spin (T_2) relaxation times of the various motional components of the PS/PEO diblock copolymer. Homopolymer data are indicated by solid curves. Error bars for the mobile and intermediate components are based on single echo experiments (see text) and on the range of results from several measurements

crystalline domains combined with the relative isolation of groups of proton spins. *Figure* 2 shows some typical *FID*'s and the temperature dependence of the beat intensity for PEO and for the PS–PEO copolymer normalized for equal PEO content. We see that the copolymer beat intensity is reduced in comparison with that of the PEO homopolymer. Localized defects in the PEO regions near the PS interface distort crystalline lattice dimensions and smear out the observed dipolar structure. *Figure* 2 demonstrates that, with increasing temperature, molecular motion enhances these distortions, and the resolved structure disappears.

Temperature dependence of the T_2 relaxation data, determined by regression analysis of equation (1), is shown in *Figure* 3. Spin–spin relaxation times of the rigid, intermediate and the mobile copolymer phases as well as relaxation times of the individual homopolymers (solid curves) are plotted. Homopolymer transitions associated with the onset of large scale molecular motion with correlation times $\tau_c < 10^{-5}$ are clearly observed at 335K and at over 400K owing to the crystalline melting point of PEO and the glass transition of PS, respectively. At low temperatures the copolymer shows only a single component with a rigid lattice T_2 of ~12 μs. At 250K, the temperature associated with the PEO glass transition[9] at 10^5 Hz, a mobile component emerges. The spin–spin relaxation times of this component increase by more than a decade over the temperature range from the PEO homopolymer glass transition to the melting point at 335K. This behaviour is suggestive of a premelting phenomenon and is discussed below. Above T_m the *FID* can be separated into three distinct phases. The mobile fraction T_2 follows the behaviour of the PEO homopolymer while the rigid component relaxation times maintain continuity through T_m and are identical to those of the polystyrene homopolymer. It is evident that above T_m there exist domains of rigid polystyrene and domains of molten PEO which are unperturbed by the presence of the other polymer. The intermediate component, attributed to interfacial chains, exhibits T_2's, and thus mobilities, between the homopolymer values.

From the temperature dependence of the mole fraction of each phase (*Figure* 4), we see that the individual homopolymer transitions are manifested by dramatic changes in the relative fractions of the copolymer phases. This behaviour is a reflection of the gross incompatibility (i.e. domain segregation) of the two chemically dissimilar homopolymers. However, a detailed examination of the data reveals evidence for interaction at the phase boundary. In the temperature range from the PEO glass transition (250K) to the melting point (335K), the mobile fraction steadily increases as PEO chains of increasing crystalline perfection melt. PEO at the phase boundary is truly amorphous and exhibits a glass transition, whereas those chains in the interior of PEO domains are highly crystalline and melt at T_m. Between these two extremes we observe intermediate 'melting' temperatures.

Concurrent with the increase in the mole fraction of the mobile phase there is a rise in its T_2, which can be explained by the removal of physical constraints imposed on segments of the polymer as neighbouring segments pass through their melting temperatures. It is for this reason, as well, that there is a discontinuity in the T_2 of the amorphous regions at T_m. Unlike in the copolymer, the

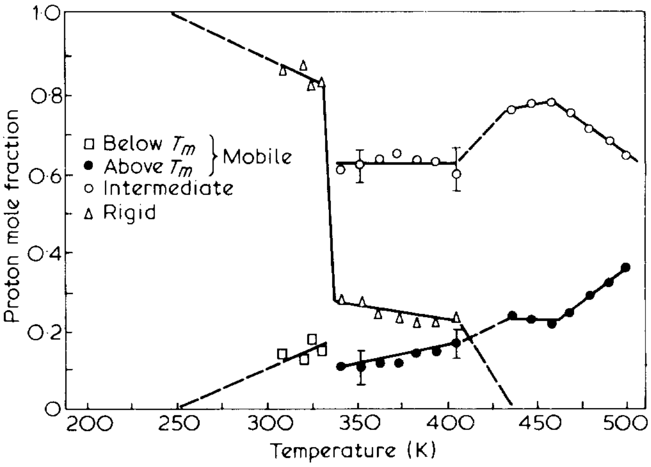

Figure 4 Temperature dependence of the mole fractions of each of the components in the diblock copolymer of *Figure 3*. Solid line connects experimental points and dashed lines represent estimated behaviour over regions where measurement accuracy was low. Error bars are established as in *Figure 3*

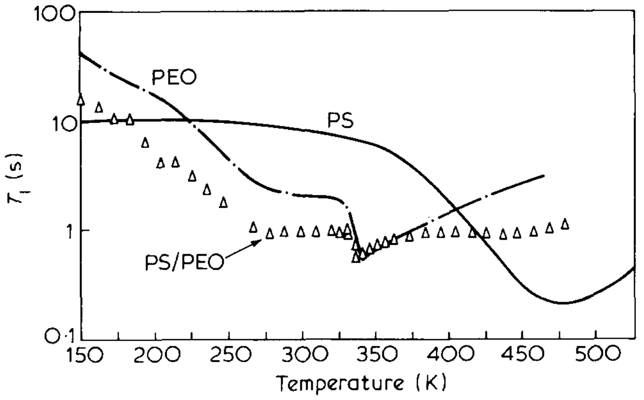

Figure 5 Temperature dependence of spin-lattice (T_1) relaxation times of the copolymer as well as the individual homopolymers

mobile (i.e. amorphous) phase is barely discernible below T_m in the PEO homopolymer. Even upon rapid quenching of the homopolymer from the melt, only a small mobile component emerges, which diminishes with room temperature annealing. From this observation it is concluded that crystallization of pure PEO occurs readily, whereas crystallization of PEO domains in the copolymer is inhibited at the phase boundary by the presence of polystyrene. From the mole fraction data, crystallinity of our copolymer sample can be determined. Assuming that just below T_m the mobile phase, which accounts for 0.16 of the proton signal, represents the amorphous PEO, crystallinity of the PEO domains in the diblock copolymer can be estimated at 75%. Agreement with the crystallinity obtained by heat of fusion measurements on the same sample[2] lends support to this assumption.

Above the melting point of PEO the rigid T_2 component accounts for 0.27 of the proton signal, which is lower than the 0.35 mole fraction of polystyrene protons in the copolymer. The remaining polystyrene must be accounted for by the intermediate relaxation component. Thus, above T_m, 77% of the polystyrene behaves like the pure homopolymer, whereas the remaining 23% has enhanced mobility imposed by the molten PEO at the phase boundary. On the other hand, only 10–20% of the PEO in the copolymer can be ascribed to unperturbed domains, while 80–90% has reduced mobility hindered by the presence of polystyrene. From this data one can calculate that the intermediate T_2 component reflects an approximately 14 to 1 molar ratio of PEO to polystyrene. This ratio is much too large to be a realistic composition for a homogeneous domain at the PS–PEO interface. Furthermore, we know from the magnitude of the individual homopolymer transitions in the copolymer that physical mixing is small. Thus we can conclude that most of the PEO which is responsible for the intermediate component is not mixed spatially with polystyrene. In order to explain the reduced mobility for the bulk of the PEO, we conjecture that over the duration of the T_2 experiment most of the PEO chains spend some small portion of time near the interface, where their motion is restricted. Thus, a reduced average mobility, as measured by T_2, is determined for these chain segments. Separation of the molecular motions into discreet domains is only a crude approximation of the true physical state. There is probably a distribution of relaxation times reflecting the distribution of mobilities, which are a function of the distance from the interfacial tie point. Those segments farthest removed are responsible for the mobile PEO component.

In contrast to the PEO, the behaviour of the polystyrene in the copolymer suggests a localized effect at the interface since only ~23% of the polystyrene is plasticized. Most of the polystyrene chain segments are rigid and display a glass transition near that of the homopolymer. A physical blend with identical composition to the copolymer shows no intermediate phase but only a two component decay with relaxation times which are the same as for the individual homopolymers. The mole fractions in the rigid and mobile phases correspond exactly to the polystyrene and PEO contents, respectively. Unlike the copolymer data, the blend data is consistent with complete phase separation. The liquid phase, composed entirely of molten PEO, and the solid phase, composed entirely of polystyrene, occupy separate non-interacting regions.

Spin–lattice relaxation times, T_1, for the copolymer and the homopolymer are illustrated in *Figure* 5. Polystyrene exhibits a single minimum at ~480K, its glass transition temperature (at 10^8 Hz). PEO and the copolymer show two minima, one at $T_m = 335$K and a less well-defined one at around 280–290K which is associated with the PEO glass transition. A notable feature of the spin–lattice relaxation is the parallel temperature dependence of the copolymer and PEO T_1 values below T_m. Such behaviour implies that the protons of PEO relax all other protons through spin diffusion[10]. What is interesting about the present T_1 data is that copolymer relaxation times are not intermediate between the homopolymer values, but are, in fact, even lower than the corresponding PEO values. This data can be explained satisfactorily by analogy with a previous study on polyethylene[11], which is a semi-crystalline polymer like PEO. In polyethylene near the T_1 minimum, the spin–lattice relaxation can be shown to occur primarily in the amorphous regions, which are sufficiently mobile as to dominate the relaxation process. Protons in the crystalline regions relax via spin diffusion to the more quickly relaxing amorphous protons. Such a mechanism must prevail for the PEO homopolymer in order to explain the presence of a T_1 minimum at the glass transition while no corresponding T_2 transition is observed. The small number of amorphous sites is insufficient to produce a noticeable effect on the rigid lattice T_2, yet through spin diffusion can dominate T_1 behaviour. The lower copolymer T_1's, in comparison with pure PEO, are a consequence of increased amorphous content of the PEO domains in the copolymer. As with polyethylene, it is likely that we are in the fast diffusion limit[12] where the effective T_1 is proportional to the inverse of the mole fraction of relaxing sites. From the T_1 data at the PEO glass transition minimum and the previously measured fraction of amorphous PEO in the copolymer, 93% crystallinity is estimated for our homopolymer sample.

CONCLUSION

Despite the incompatibility of polystyrene and poly(ethylene oxide) arising from chemical dissimilarities and revealed by the presence of individual thermal transitions in a diblock copolymer, evidence is presented for a substantial degree of interaction at the phase boundary. Polystyrene perturbs the PEO crystal structure, thereby reducing crystallinity of PEO domains in the copolymer to 75% from 93% in the homopolymer. Also, above the PEO melting point it has been demonstrated that, on the basis of molecular motions, the copolymer can be separated into three domains, a rigid phase consisting of unperturbed polystyrene polymer, a mobile phase containing unperturbed PEO polymer and an intermediate phase which consists of plasticized polystyrene and motionally constrained PEO.

ACKNOWLEDGEMENTS

We would like to thank Dr W. M. Prest, Jr, for helpful discussions on the nature of the crystallization process and for his critical comments on the manuscript. The assistance of M. Nowacki in writing some of the data reduction software and B. Fornalik for typing the manuscript are gratefully acknowledged.

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