Anisotropy of motion in solutions of poly(ethylene oxide) in the presence of the crystalline phase

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Internal mobility of poly(ethylene oxide) molecules in the liquid phase of heterogeneous samples, prepared by cooling concentrated (70–90% w/w) solutions in $CDCl_3$ to room temperature, was characterized by n.m.r. techniques. In the liquid phase, which in all cases contained 45% (w/w) polymer, spatial restrictions of motion as well as a broadening of the distribution of correlation times were found to be induced by the presence of the crystalline phase with a dependence on morphology, as characterized by microscopic methods.

Keywords Poly(ethylene oxide); heterogeneous solutions; morphology; motional restrictions; ^{13}C n.m.r. relaxation; ^{1}H MAR n.m.r.

INTRODUCTION

To our knowledge, the effects of the crystalline phase on the dynamics of dissolved polymer molecules have not been studied by n.m.r. so far. Spatial restrictions of motion, induced in polymer solutions and gels by the presence of chemical (permanent) or physical crosslinks (entanglements, aggregates or microcrystallites) have been studied in this laboratory by ^{1}H and ^{13}C n.m.r. spectroscopy for several polymers (polystyrene[1], poly(methyl methacrylate)[2-5], poly(ethylene oxide)[6]). Spatial restrictions of motion generally cause the presence of near-static dipolar interactions, revealed by more or less super-Lorentzian (SL) line shapes in conventionally measured spectra, which are reduced to Lorentzian shapes by magic-angle rotation (MAR) experiments[2,6]. In some cases they may also lead to modifications of the rapid motional mechanisms characterized by MAR n.m.r. linewidths and ^{13}C n.m.r. relaxation parameters measured with strong dipolar decoupling[6]. Here we have attempted to characterize, by these n.m.r. methods, the motional anisotropy induced in concentrated solutions of linear poly(ethylene oxide) (PEO) by the simultaneous presence of the crystalline phase. The results are discussed on the basis of morphological evidence obtained from microscopic observations. In some respects this simple system may be regarded as a model of a semicrystalline polymer with a plasticized amorphous phase.

EXPERIMENTAL

The PEO polymers studied were commercial products; their molecular weight was determined by light scattering in methanol solution: Sample A: Polyäthylenglykol 6000 (Carbowax, LOBA-Chemie, Wien; M.wt. 8–9 × 10^3; m.p. 60°C); Sample B: Polyaethylenglykol 20 000 (FLUKA; M.wt. 21 × 10^3; m.p. 62°C). Samples for n.m.r. measurements were prepared by dissolving the polymer in $CDCl_3$ or $CHCl_3$, at the indicated w/w concentration in sealed n.m.r. tubes, above the melting temperature of the pure polymer. The resulting homogeneous solution was then either quenched by rapid immersion in a bath of solid CO_2–acetone, or left to cool slowly to room temperature over the course of several hours. Measurements of high-resolution (HR) ^{1}H n.m.r. line shapes indicated that the quenched samples gave irreproducible results, and in the course of time changed slowly and finally resembled the slowly crystallized samples. Therefore, only the slowly crystallized samples were studied in detail.

HR ^{1}H n.m.r. spectra without sample rotation were measured at 100 MHz using the PS-100 (JEOL) spectrometer. ^{1}H n.m.r. spectra, both static and with sample rotation at the magic angle (MAR n.m.r.) were measured at 60 MHz using the JNM-3-60 (JEOL) spectrometer with a MAR n.m.r. probe of our own construction[7]. The same probe and spectrometer were used for the measurement of broadline (BL) ^{1}H n.m.r. spectra[8]. ^{13}C n.m.r. spectra, *NOE* factors and both ^{1}H and ^{13}C T_1 relaxation times were measured using the FX-60 (JEOL) spectrometer, operating at 60 and 15 MHz for ^{1}H and ^{13}C, respectively. ^{13}C T_1 and T_2 relaxation times at 50 MHz were measured using the Varian XL-200 spectrometer. All T_1 relaxation times were measured by the inversion recovery method. At 50 MHz, the ^{13}C T_2 relaxation time was measured by the CPMG[9] pulse sequence. All other T_2 values were derived from linewidths after correction for field inhomogeneity effects. *NOE* factors were measured by the gated decoupling technique with planimetric evaluation of the peak areas. The ^{13}C relaxation parameters of the heterogeneous samples were measured under ^{1}H noise decoupling of sufficient strength

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Table 1 Basic characteristics of PEO–$CDCl_3$ systems

			^1H n.m.r. characteristics (60 MHz)		
			static		
System	Total composition of sample PEO %(w/w)	α^a	$\Delta\nu_{1/2}(Hz)^d$	$\Delta\nu_{1/10}:\Delta\nu_{1/2}{}^e$	MAR $(Hz)^d$
A1	45^b	1	$\_^f$	$\_^f$	2.3
A2	70^c	0.35	11.6	3.3	5.8
A3	80^c	0.205	14.8	4.2	7.6
A4	90^c	0.091	16.7	4.5	8.2
B1	45^b	1	5.5	4.0	4.5
B2	70^c	0.35	15.0	3.8	7.7
B3	80^c	0.205	14.4–23.5	4.2	6.9–8.7
B4	90^c	0.091	98–112	5.0–7.6	12.6–19.6

[a] Fraction of total polymer in solution
[b] Homogeneous solution
[c] Heterogeneous samples consisting of a crystalline phase and of a 45% (w/w) solution of PEO in $CDCl_3$
[d] Width at half-height
[e] Gaussian shape: 1.82; Lorenzian shape: 3.0
[f] Limited by instrument resolution

for the removal of near-static dipolar interactions as manifested in the static ^1H n.m.r. spectra.

For microscopic observations, crystallization of PEO from solutions was performed in sealed ampoules similarly as for n.m.r. measurements, and also in a planparallel cell on a heating stage of a light microscope. The morphology of the separated polymer was evaluated in the presence of the liquid phase by polarization microscopy (Photomicroscope III, OPTON), and after rapid removal of the liquid phase also by the scanning electron microscope JSM 35 (secondary electron mode, accelerating voltage 25 kV, after metallization by gold using a Balzers sputtering device).

NUCLEAR MAGNETIC RESONANCE MEASUREMENTS

The solid phase in samples prepared by cooling of solutions containing 70, 80 and 90% (w/w) of the polymer in $CDCl_3$ was characterized by measurement of the ^1H BL n.m.r. spectra. In all cases, both with the quenched and with the slowly cooled samples, and with both molecular weights investigated, BL n.m.r. spectra exhibited a single broad line very near Gaussian in shape, with a second moment equal, within experimental error, to that of pure crystalline PEO of equal molecular weight. From this it was concluded that the short-range geometrical order of the crystalline phase was independent of the concentration of the solution from which crystallization took place.

The concentration of PEO at room temperature in the liquid phase of samples, prepared by cooling solutions containing 70, 80 and 90% (w/w) PEO in $CHCl_3$, was determined from the ratio of integrated peak areas of $CHCl_3$ and PEO signals in HR ^1H n.m.r. spectra. For both molecular weights and all three sample compositions studied, the concentration of PEO in the liquid phase was equal to $45 \pm 2\%$. Therefore, for comparison, for both studied PEO samples A and B, homogeneous solutions containing 45% (w/w) polymer in $CDCl_3$ (A1, B1) were prepared and measured in similar way to the heterogeneous systems (A2–A4, B2–B4).

The designation of the measured PEO–$CDCl_3$ systems and their basic characteristics are summarized in *Table 1*. From this table it is seen that in spite of equal concentration of polymer in the liquid phase, in the spectra measured without sample rotation, with increasing total contents of the polymer, linewidth and the SL character of the line shape (expressed as ratio of linewidth at 1/10 and 1/2 maximum height)[6] increase appreciably. This increase is more pronounced for the higher molecular weight polymer B. For the quenched samples, linewidths reached 125 Hz and $\Delta\nu_{1/10}:\Delta\nu_{1/12}$ reached 10.0 for system B4. From *Table 1* it can also be seen that the linewidths of the heterogeneous systems are greatly reduced by magic-angle rotation. This indicates the presence of magnetic heterogeneity effects and/or near-static dipolar interactions[10]. The SL character of static line shapes indicates that only part of the line broadening can be explained by the macroscopic inhomogeneity of the samples, and that the predominant contribution is evidently due to the near-static dipolar interactions caused by spatial restrictions of motion[11].

The ^1H MAR n.m.r. line shapes of the heterogeneous systems are near to Lorentzian, and they do not differ from the line shapes of the PEO signals in the homogeneous solutions A1 and B1. However, the ^1H MAR n.m.r. linewidths of the heterogeneous samples shown in *Table 1* are seen to be much larger than those of the homogeneous samples, and they increase appreciably with the increasing proportion of the solid phase. From previous experience[10,12–14] we know that even very severe effects of physical heterogeneity are always reduced to the resolution limit of our instrument (~3 Hz); as the near-static dipolar interactions are also removed by the MAR n.m.r. experiment, the observed trend of MAR n.m.r. linewidths indicates that even the rapid segmental motions are affected by the differing relation of the liquid and solid phase in the heterogeneous samples.

To compare the character of the rapid segmental motions in the homogeneous solutions and in the liquid phase of the heterogeneous samples, ^1H T_1 and MAR n.m.r. T_2 values at 60 MHz, ^{13}C T_1 and T_2 relaxation times at 50 and 15 MHz, and *NOE* factors at 15 MHz were measured and analysed. The values obtained for the 45% homogeneous PEO solutions are summarized in *Table 2*. In this table the $\tau_{c,eff}$ values estimated from both ^{13}C and ^1H T_1 relaxation times using the isotropic motional model[15] are also given, and are found to lie in the range 0.05–0.09 ns.

Table 2 Relaxation parameters of homogeneous PEO solutions (45% (w/w) of polymer in $CDCl_3$)

	^{1}H (60 MHz)		^{13}C (15 MHz)		^{13}C (50 MHz)
Sample	A1	B1	A1	B1	B1
T_1 (ms)	360	380	410	420	537
T_2 (ms)	–	–	–	–	235
NOE	–	–	2.95	2.85	–
$\tau_{c\,eff}$ (ps)	88	84	59	61	46

^{13}C relaxation parameters of homogeneous polymer solutions are conventionally analysed using the model of the log χ^2 distribution of correlation times[16], characterized by a mean correlation time $\bar{\tau}$, and the width parameter p increasing with the width of the distribution. In terms of this model, the T_1 and T_2 values of the homogeneous sample B1 measured at 50 mHz yield $\bar{\tau}=7$ ps, $p=11$. ^{13}C T_1 values and linewidths of samples A1 and B1 measured at 15 MHz are consistent with either $\bar{\tau}=6$ ps, $p=11$; or $\bar{\tau}=7$ ps, $p=12$. However *NOE* values measured at 15 MHz (*Table 2*) are higher than would correspond to the found distribution width, and indicate a very near to isotropic type of motion. Therefore, it appears that the model of the log χ^2 distribution of correlation times is not fully adequate for the analysis of ^{13}C relaxation data in concentrated solutions of PEO in $CDCl_3$.

The ^{13}C T_1 and T_2 (linewidth) values of the heterogeneous samples, measured at 15 MHz with sufficient ^{1}H decoupling power to remove the near-static dipolar broadening, are summarized in *Table 3*. When analysed by means of the log χ^2 distribution of correlation times, in heterogeneous samples, the distribution estimated from T_1 and T_2 values is seen to be broadened by 2–3 units of p, accompanied by rather minor changes of $\bar{\tau}$, as compared with the homogeneous samples, where values of $p=11$–12 were found. Values of $p=9$, 10 should correspond to $NOE \sim 2.5$. Similarly as for the homogeneous samples, also for the heterogeneous samples, experimental *NOE* values are somewhat higher than values expected for the model; they increase from 2.62 for samples A4, B4 to 2.74 for samples A2, B2. Nevertheless, they are much lower than the *NOE* values of the homogeneous samples in *Table 2*, indicating likewise a broadening of the distribution of correlation times by at least 3 units of p. For characterizing the motional behaviour in heterogeneous samples, ^{13}C relaxation data have the drawback, as compared to MAR n.m.r., that some effects resulting from macroscopic sample heterogeneity must be assumed to be present. Because of this, and because of the observed inadequacy of the applied motional model, our analysis of the ^{13}C relaxation data is presented illustratively only and as such quantitative data should be regarded with caution.

The T_2 values derived from ^{1}H MAR n.m.r. linewidths of the heterogeneous samples are also shown in *Table 3*. They are much smaller than the ^{1}H T_1 values measured for the homogeneous solutions A1 and B1 (*Table 2*), and also smaller than the ^{1}H T_2 values estimated from ^{1}H MAR n.m.r. linewidths for the homogeneous samples ($\gtrsim 200$ ms). The ^{1}H MAR T_2 values exhibit a trend which is remarkably similar to that of the ^{13}C T_2 data. As in our equipment, T_1 relaxation times cannot be measured with MAR, the ^{1}H MAR T_2 data cannot be evaluated in terms of a model involving a distribution of correlation times. The similarity of the ^{1}H MAR and ^{13}C T_2 data indicates that the effect of macroscopic sample heterogeneity on ^{13}C T_2 values is not serious.

MICROSCOPIC OBSERVATIONS

The process of crystallization of PEO from concentrated solutions in $CDCl_3$ and the morphology of the resulting heterogeneous systems were also directly studied by microscopic methods, visually in the n.m.r. cells, and under similar conditions in a planparallel cell with an optical microscope. The polymer separated from solutions of various concentrations melted in the range 57°–65°C. After temperature equilibration at 80°C for 10 min, crystallization was followed at a cooling rate of 1°C/min. It was found that the rate of crystallization decreased in the order of systems B4, A4, B3 ... A2; separation of the solid phase took place at 52°C for system B4, at 45°C for B3 and at 39°C for B2; with series A, separation temperatures were lower by 6°C. The crystals formed from the most concentrated solutions, especially from sample B4 in n.m.r. cell, have finely dispersed particles consisting of irregular dendritic spherulites with a highly developed lamellae surface and a coarse fold surface (*Figure 1a, c*). To the contrary, however, the polymer crystallized from a less viscous medium (A2) has a structure consisting of more regular spherulites and aggregates of lamellar crystals (*Figure 1b, d*).

The extremely perfect crystals of system A2 evidently occlude only a smaller part of the liquid phase, the major part of which remains separated in larger domains between the spherulites. On the contrary, in systems formed from the most concentrated solutions (e.g. B4) the size of the domains of the liquid phase is evidently below the resolution limit of the optical microscope. The saturated PEO solution in these systems is probably occluded in the large surface of the dendritic crystals with irregular chain folds.

DISCUSSION

From the above results of the n.m.r. measurements of saturated solutions of PEO in $CDCl_3$ it is clear that the internal mobility of PEO molecules in solution is modified by the presence of the solid phase of the polymer. The deviations from the behaviour of a homogeneous solution depend on the overall composition of the solution from which the crystallization has taken place, and also on the rate of the crystallization process.

The experimentally observed differences in the morphology of the polymer separated from samples B4

Table 3 Relaxation parameters of heterogeneous PEO samples

	^{13}C (15 MHz)				^{1}H (60 MHz)
Sample	T_{1C} (ms)	$T_{2C}{}^a$ (ms)	$\bar{\tau}^b$ (ps)	p^b	$T_{2H,MAR}{}^c$ (ms)
A2	370	111	6	10	114
A3	350	76	4	9	69
A4	334	56	5	9	61
B2	420	101	3	9	68
B3	340	56	4.5	9	82–56
B4	300	43	6	9	33–19

[a] $T_{2C} = 1/[\pi(\Delta\nu_{1/2} - 1.5\text{ Hz})]$

[b] Calculated using the log χ^2 distribution of correlation times

[c] $T_{2H} = 1/[\pi(\Delta\nu_{1/2,MAR} - 3\text{ Hz})]$

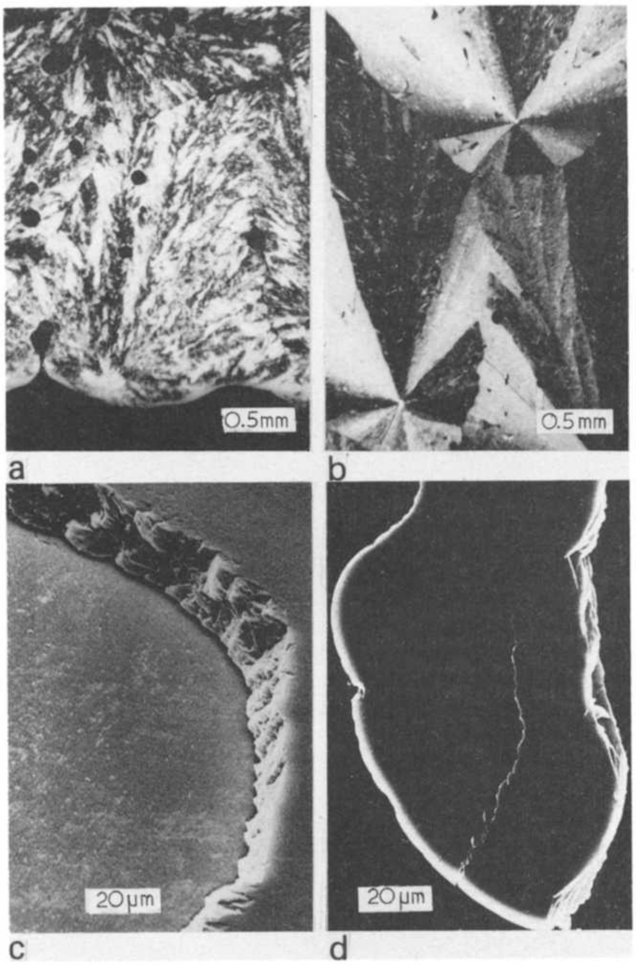

Figure 1 Poly(ethylene oxide) crystallized in a planparallel cell. Front view between crossed nicols of the polarizing microscope (a, b); side view of the growth front in the scanning electron microscope (c, d) Samples: B4 (a, c); A2 (b, d)

and A2 can be well understood on the basis of the theory of Keith and Padden[17]. It is known that for semicrystalline polymers, like PEO (maximum crystallinity 90%, ref 18) segregation of the noncrystallizing matter ahead of the growth front of the crystal takes place. The impurity layer has a width δ proportional to the diffusion constant and inversely proportional to the growth rate. Owing to this phenomenon, fibrous crystals of thickness δ are developed from a smooth growth front. In agreement with this theory, in the viscous system B4, with a lower diffusion coefficient of impurities and a higher growth rate compared to the system A2, the growth front of the crystal is finely dendritic, and the separated polymer solution is in a more intimate interaction with the polymer surface. In addition, loose loops are expected to be more frequent in crystals of system B4 compared with system A2.

The hindrance of internal mobility of the liquid phase in contact with the solid is manifested in two ways: (1) By the presence of near-static dipolar interactions, indicating spatial anisotropy of motion, similar to that observed in swollen crosslinked polymer gels. (2) A widening of the distribution of rapid internal motions. Some idea about the spread of the correlation times of the rapid segmental motions which is generated by the presence of the solid phase, may be obtained from analysis of ^{13}C relaxation data by means of the model of the log χ^2 distribution of correlation times[16], which, though not quite adequate for the system studied, indicates a widening of the distribution corresponding to ~ 3 units of p.

The morphological observations described above indicate that the motional hindrance is caused by the presence of the large surface of dendritic crystals holding the occluded liquid phase. In systems prepared by crystallization from solutions containing 90% polymer, the size of the liquid domains is such that it cannot be decided if the liquid phase is formed by free dissolved polymer molecules, or merely by large chain folds or chain ends protruding from the crystal surface, plasticized by the solvent. Alternatively, in systems crystallized from solutions containing 70% polymer, regions of a separated liquid phase are clearly visible under the optical microscope. In spite of this, the n.m.r. behaviour is continuous in the studied series, and the MAR n.m.r. line shapes are similar and very near to Lorentzian in all the systems studied. Therefore, a dynamic equilibrium, rapid on the n.m.r. scale, between molecules in a true liquid phase and those which are motionally hindered on the crystal surface is implied. As a dynamic equilibrium between truly dissolved polymer molecules and solubilized large chain folds and protruding chain ends is hard to visualize, it must be concluded that even in the systems crystallized from the most concentrated solutions of our series, the signal in HR and MAR n.m.r. spectra corresponds to free dissolved polymer molecules. The motional hindrance manifested in these spectra must, therefore, be caused by mere physical interaction or steric hindrance of motion of the dissolved polymer molecules in narrow intercrystalline cavities of the large and highly irregular surfaces of the crystals.

In a more general sense it may be concluded that the effect of the crystalline phase on the mobility of a plasticized polymer phase with which it is in contact depends largely on the morphology of the crystalline phase, and on the relative amounts of the two phases. Both the spatial anisotropy of motion, and the distribution of rapid segmental motions of the plasticized polymer phase are affected by the presence of the crystalline surface.

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