Static and dynamic light scattering studies of the crystallization of poly(ethylene oxide) from dilute solutions

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(Received 16 February 1988; revised 11 April 1988; accepted 18 April 1988)

We have monitored *in situ* the self-seeded crystallization of poly(ethylene oxide) from dilute toluene solutions by dynamic light scattering. In supercooled dilute solution, the radii (R) of the crystals grow linearly with time. The rate constant obtained from the slope of the plot R *versus* time depends on the temperature and the molecular weight of the polymer, both of which determine the degree of the supercooling. The maximum crystal size obtained from solutions of fixed concentration also depends on the temperature and the polymer molecular weight. It appears that crystal growth is limited because of molecular weight fractionation. Static light scattering from suspensions of stable crystals provides information on the crystal morphology. A comparison of experimental and theoretical particle scattering functions suggests that the crystals form short cylinders and that the crystal growth from the seeds is primarily two-dimensional. Some comparisons to melt crystallization are possible. The preparation and use of tiny seed crystals is critical to the success of these studies.

(Keywords: solution crystallization; crystal growth; light scattering; polyethylene oxide)

INTRODUCTION

The kinetics of polymer crystallization has been studied over the past two decades both theoretically and experimentally. Long before the discovery of chain folding in crystalline polymers, the kinetics of crystallization of bulk polymers was extensively studied[1]. The volume fraction of polymer crystallized was determined as a function of time, often by dilatometry, and interpreted in terms of the nature of nucleation and growth processes. Rate limiting steps of crystallization were believed to be either the rate of diffusion of molecules to and from the growth surface or the rate of their attachment to the interface. This Avrami-type analysis of dilatometric data has been extended to polymer crystallization from dilute solution[2]. For polyethylene crystallized from dilute xylene solution, it was reported that elongated three-dimensional lamellar crystallites were produced rather than single crystals. Moreover, deviations from linear Avrami crystallization behaviour was suggested to indicate diffusion controlled growth and changes in nucleation from instantaneous to sporadic. Crystallization studies were often focused on the morphology of polymer spherulites and lamellae[3]. However, theories of polymer crystallization involving chainfolding have been developed for predicting the lamellar thickness and the kinetics of crystallization[4]. Experimental data include the radial growth rate of spherulites from molten polymers and of lamellae formed from solution. For melt crystallization, different regimes of growth have been defined, corresponding to the relative rates of nucleation and growth of a crystalline layer at the growth front.

Experimental investigations of polymer crystallization from dilute solution have generally employed microscopy, either electron[5] or phase-contrast optical[6,7]. The inability of these techniques to measure crystal properties *in situ* poses a serious limitation to their application for monitoring instantaneous crystal growth. Work has continued in this area to develop new methods. For example, McHugh and Spevacek[8] have recently reported the use of a new technique, in which they monitored the flow-induced polymer crystallization from solution through a tubular geometry, using polarized light illumination and video recording. For the results presented in this paper, we apply instrumentation which is commercially available, laser light scattering, to the study of the kinetics of polymer crystallization from dilute solution.

EXPERIMENTAL

Instrumentation

All light scattering measurements were made using an Ar ion laser (Spectra Physics 2020-3) operating at 514.5 nm with 200–500 mW. A commercial light scattering goniometer (Brookhaven Instruments BI-200SM) was used with its original integrated optics to measure the scattering at angles between 10 and 150°. Alignment was very carefully controlled and it was necessary to add a diffusing filter before the photocathode of the photo-

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0032–3861/88/122121–05$03.00

multiplier tube (Thorn EMI 9863B) to improve the performance of the instrument for static light scattering measurements. A refractive index matching bath of filtered toluene surrounded the scattering cell and its temperature was controlled to $\pm 0.05°C$. The photon correlation measurements were performed with a 264 channel multibit autocorrelator (Brookhaven Instruments 2030). The total intensities were monitored concurrently with a separate 20 MHz counter. The correlator, counter and goniometer were all controlled by a microcomputer (IBM PC type) for automated data acquisition. The data were transferred to a VAX 11/780 for analysis with a nonlinear least squares fitting program.

Solution preparation

Poly(ethylene oxide) (PEO) samples of molecular weight 10^5 and 5×10^6 (Polysciences) were dissolved in reagent grade toluene which had been dried over liquid sodium, distilled and filtered. Stock solutions were prepared by weight at 0.01% and were dissolved in an oven at about 80°C with occasional gentle agitation. About 1 hour for the 5×10^6 sample and 20 minutes for the 10^5 sample were allowed, after which the solutions were filtered, in the 80°C oven, with a set of 3, 1 and 0.2 μm membrane filters (Millipore). As long as the solutions and filter apparatus were kept warm ($\geqslant 50°C$), we observed no significant loss of polymer in the filtration step. Scattering cells which could be easily sealed were prepared from selected and thoroughly cleaned 12 mm borosilicate reaction tubes. Immediately before use, the prepared cells were rinsed with distilled toluene vapour and inspected again for scratches and dust. The dilute solutions were sealed in the cells and allowed to equilibrate in the 80°C oven for several hours. Samples prepared in this way and included in these measurements showed no speckles, spurious scattering or irregularities in the scattering functions, when measured at temperatures above 35°C where the PEO remains fully dissolved.

Seed preparation

Preliminary measurements on samples prepared without hot filtration of the dilute solutions showed scattering functions which became very strong and indicated the formation of large PEO crystals when the temperature was brought below $\approx 25°C$. For more careful measurements, with meticulous sample preparation including hot filtration, the solutions no longer scattered much light and crystals did not grow, even when they were supercooled to below $-30°C$. With such deep supercooling, crystals did form, but they were on the walls of the cell and were therefore useless for scattering measurements. The spontaneous formation of nuclei required to grow crystals in suspension would require a very large activation energy, corresponding to the increased free energy due to the curvature of the surface of a small nucleus. For the PEO dilute solutions to crystallize reproducibly during scattering measurements, it was necessary to provide nucleation sites. We did this by preparing and introducing small PEO seed crystals.

Seeds were prepared from 0.01% PEO solutions which had been carefully cleaned and sealed into scattering tubes as described above. These tubes were quenched in liquid N_2, which caused the toluene to freeze. When they were warmed to room temperature ($\approx 20°C$, which is below the crystal dissolution temperature of $\approx 35°C$), light scattering clearly showed the presence of small suspended particles. Analysis of the dynamic scattering gave a particle radius of 0.18 μm for seeds formed from the 10^5 PEO and 0.19 μm from the 5×10^6 sample. These suspensions were stable with time over several days and with temperature up to about 35°C. In addition, the dynamic light scattering second cumulants indicated that the seeds were relatively monodisperse. This conclusion was also supported by optical and electron microscopy observations.

Microscopy

Dried suspensions of PEO seeds and crystals, grown from seeded solutions, were examined by scanning electron microscopy (Cambridge Stereoscan, Model S4-10) at several magnifications up to 20000. Such samples had been coated with a thin layer of gold and palladium to prepare a conductive surface before electron microscopy. Seeds resulting from PEO of molecular weight 10^5 were primarily small spherical bodies approximately 0.2 μm in radius. Occasionally, thin flat lamellar hexagons appeared to surround the seeds, perhaps due to some lamellar crystallization occurring on evaporation. For PEO of molecular weight 5×10^6, seeds were less uniform and varied in size from 0.1 to 0.3 μm.

RESULTS AND DISCUSSION

Before adding PEO seeds to the cleaned PEO solutions, we observed no scattering correlation function, and therefore no crystallization, when the solutions were held at 20°C for several days. After addition of a small aliquot (of the order of 0.05 ml, containing perhaps 10^8 seeds), we monitor the appearance of and subsequent changes in the dynamic light scattering (d.l.s.) correlation function. We accumulate and store correlation functions as quickly as possible, while still ensuring that the experiment duration is long enough for data to be well averaged. This means we can take data at 1–2 min intervals for early measurements. The correlation functions are analysed after the experiment by fitting to a second-order cumulant function with a baseline calculated from the correlator's monitor channels. The extracted decay constant, Γ, is related to the particle diffusion coefficient as $\Gamma = Dq^2$ where

$$q \equiv \frac{4\pi n}{\lambda_0} \sin(\theta/2)$$

is the scattering wavevector for scattering angle θ with n being the solvent refractive index, λ_0 the laser wavelength and D the diffusion coefficient. The decay constant decreases with time, so the diffusion coefficient also decreases and, applying Einstein's equation, $R_H = kt/6\pi\eta D$, the hydrodynamic radius increases. Indeed, we observe that $1/\Gamma(\propto R_H)$ increases linearly with time in the early time period, then deviates slightly from linearity and finally reaches a constant plateau value.

Before further discussion of this point, we note that Γ has been measured as a function of scattering angle for the stable suspensions of seeds and final crystals (after the plateau of the growth curve). The usual Γ *versus* q^2 dependence is shown in *Figure 1* and it demonstrates that we are measuring a mutual diffusion coefficient (from the

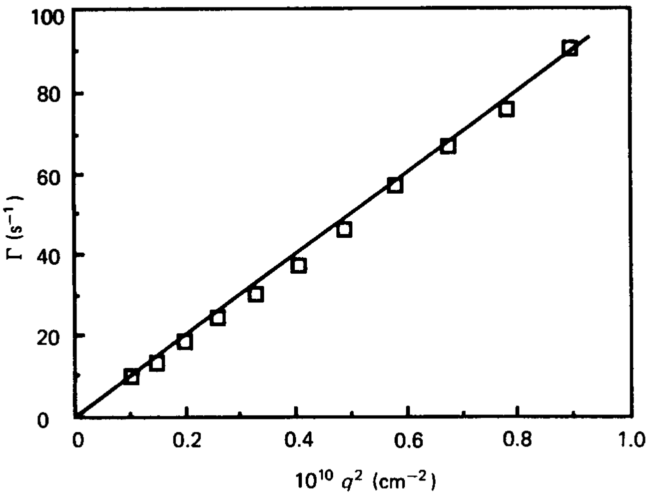

Figure 1 Dynamic light scattering decay constant Γ against q^2 for polyethylene oxide crystals grown from 0.01% (w/w) toluene solution at 25°C. Diffusion coefficient from slope is 1.0×10^{-8} cm^2 s^{-1}

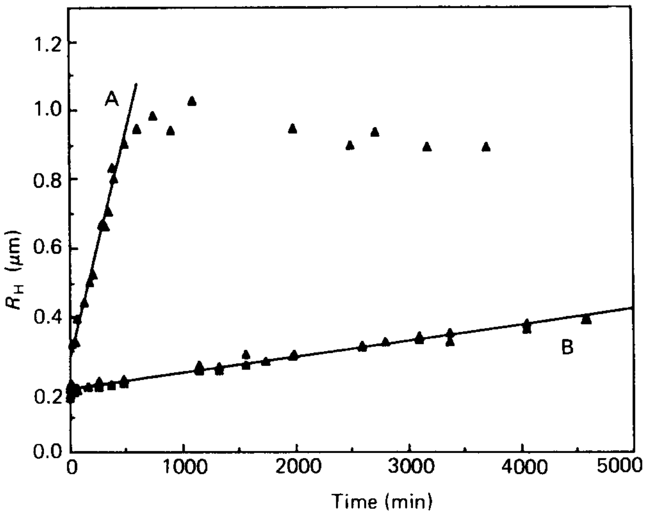

Figure 2 Hydrodynamic radius of PEO crystals growing at 25°C from 0.01% (w/w) toluene solutions as a function of growth time for starting PEO of two molecular weights: A, molecular weight $= 5 \times 10^6$, time $\times 10^{-1}$; B, molecular weight $= 10^5$, time $\times 1$. Growth of 5×10^6 molecular weight PEO is 35 times that of 10^5 molecular weight PEO

slope) of freely diffusing independent particles. Kinetic data is typically measured at scattering angles of 30 or 20° only. An example of kinetic data for the growth of crystals from seeds from PEO of molecular weight 10^5 is given in *Figure 2*, which shows instantaneous values of R_H *versus* time. The initial portion of kinetic data can be expressed as

$$R_H = kt + R_0 \tag{1}$$

where k is the slope of the line as shown and R_0 is the hydrodynamic radius calculated from the decay constant for the d.l.s. of the seeds.

This equation agrees with zero-order kinetics where the crystal growth rate dR/dt is equal to k. *Table 1* gives a summary of the analysis of crystal growth from the PEO sample of molecular weight 10^5 (see also *Figure 2*) with respect to temperature. The values of k, varying strongly with temperature from 10^{-4} to 10^{-1} nm s^{-1}, appear quite reasonable in comparison to the range (from 10^{-3} to 10^3 nm s^{-1}) deduced from the self-decoration method for melt PEO[9].

From scanning electron microscopy (SEM), PEO of molecular weight 10^5, crystallized at 25°C to completion after seeding, consisted of three-dimensional multilayer crystals composed of upright lamellar bundles on a hexagonal base and were 1.0–1.5 μm in diameter (*Figure 3*). For this same PEO, crystallized at 20°C, very large composite particles of many layers were observed, as well as small particles of 0.1–0.2 μm diameter, setting on lamellae. The former were never observed in light scattering and probably result from crystal agglomeration on prolonged storage or evaporation. The latter correspond to remaining seeds.

The data analysis gives rise to three notable features. First, the crystal growth rate obtained from the linear region of the plots increases significantly as the temperature drops, which implies that the diffusion of polymer molecules to the crystal surface is not the rate-determining step in this region. If it were, higher temperatures would increase the dissolved polymer diffusion coefficient and thus raise the overall crystal growth rate. The increased crystal growth rate with decreased temperature instead corresponds to a thermodynamic driving force. Second, the final crystal size decreases slightly as crystallization temperature increases. Fractionation of the polymer during the crystallization may contribute to this decrease, as lower molecular weight polymer will require a lower crystallization temperature. At a given undercooling, high molecular weight fractions have a stronger tendency to crystallize. This corresponds to a high molecular weight fractionation cut-off and thus yields a particular

Table 1 Temperature and molecular weight (*MW*) variation of crystal growth[a]

Sample	*MW*	*T* (°C)	$10^3 k$ (nm s^{-1})	R_{max} (μm)	Time to R_{max} (min)
PEO127	10^5	15.0	456.0	0.61	11
PEO107	10^5	20.0	24.7	0.53	270
PEO139	10^5	22.5	5.88	0.42	1000
PEO130	10^5	25.0	0.791	0.39	5600
PEO514	5×10^6	20.0	790.8	1.8	9
PEO529	5×10^6	25.0	27.9	0.89	75

[a] Poly(ethylene oxide) in toluene at 0.01 wt%

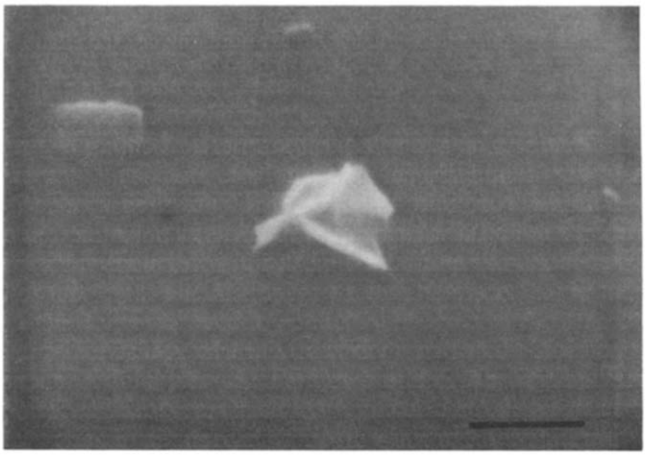

Figure 3 SEM photo of final PEO crystals grown from dilute toluene solution at 25°C. Scale bar ≡ 1 μm

Table 2 Static light scattering function analysis (cylinder model)[a]

Sample	T (°C)	Diameter (μm)	Height (μm)	R_H (μm)
PEO111	20.0	1.10	0.58	0.53
PEO140	22.5	1.00	0.58	0.42
PEO136	25.0	0.80	0.41	0.39

[a] Poly(ethylene oxide) in toluene at 0.01 wt%

stable crystal size. The final point is that a slight deviation from zero-order kinetics is observed near the turning point of the plot (*Figure 2*) for lower values of undercooling. Our data therefore verify the assumption of Point *et al.*[6] that a decrease in growth rate is found with decreasing concentration and possible fractionation.

The fractionation argument was checked by experiments with a higher molecular weight PEO. *Figure 2* and *Table 1* give the results. At the same temperature, crystallization of high molecular weight polymer is much faster than that of low molecular weight polymer. This means that the thermodynamic driving force is much greater and more than makes up for the fact that the polymer of molecular weight 5×10^6 would diffuse to the crystallization site much slower than would the polymer of molecular weight 10^5. The final crystal sizes are also much bigger than those from the low molecular weight polymer. (We note again that the seeds prepared from the polymers of the two molecular weights were of nearly the same size.) These findings strongly support the suggestion that molar mass fractionation limits the ultimate crystal growth because low molecular weight components remain in solution at a given crystallization temperature.

We have shown that the crystal radius is a function of growth time until it finally reaches a constant value. Static (total intensity) light scattering measurements were carried out on suspensions which had reached this zero growth rate. The experimental particle scattering function $P(\theta)$ was determined by measuring the total scattering intensity, $I_s(\theta)$. for $\theta = 16$–50° at 2° increments, according to

$$P_{\mathrm{exp}}(\theta) = \frac{I_s(\theta) - I_0(\theta)}{I_T(\theta)} \frac{\sin\theta}{\sin 30} \frac{I_T(30)}{I_s(30) - I_0(30)} \tag{2}$$

where I_0 is the scattering from the solvent blank, I_T is the transmitted intensity and the $P_{\mathrm{exp}}(\theta)$ function is normalized. The experimental particle scattering function was compared to theoretical functions for random coil, solid sphere, thin disk and cylinder. The cylinder function[10] is

$$P_c(\theta) = \int_0^{\pi/2} \frac{\pi}{hq\cos\beta} \left[J\left(\frac{hq\cos\beta}{2}\right) \frac{4J_1(\frac{1}{2}dq\sin\beta)}{dq\sin\beta} \right]^2 \sin\beta \, \mathrm{d}\beta \tag{3}$$

where $J(\ )$ and $J_1(\ )$ refer to zero-order and first-order Bessel functions. Adjusting the two parameters for height, h, and diameter, d, this cylinder model gave, by far, the best fit to the experimental data. We hesitate to put too much emphasis on the parameters derived from these fits because they are difficult to judge and not free of ambiguity. Nevertheless, the results for fitting $P_{\mathrm{exp}}(\theta)$ for crystals from PEO of molecular weight 10^5 grown to their limiting sizes at several temperatures are given in *Table 2*. An example of the quality of the fit is shown in *Figure 4*. The values of diameter and height are consistent with the hydrodynamic radii R_H determined by d.l.s. and with the SEM photos of the same crystals deposited from solution onto microscope slides.

In general, for a given PEO molecular weight, the height of the cylinder does not change much with growth temperature. The static light scattering of the seed solution could not be unambiguously fitted with a $P(\theta)$ model function. We note that the height of the grown crystals is nearly equal to twice the radius of the seeds. It may be that the crystallization of PEO can be described as primarily two-dimensional growth from the seed core. The cross sections of the cylinder (which is more like a disk than a rod) appear to be degenerate forms of the hexagonal habit of PEO crystals. Because the height of the crystal approximates twice the seed radius, we may suppose that growth occurs only in the width. Furthermore, the growth rate that we observe, which is proportional to $\mathrm{d}R/\mathrm{d}t$, directly reflects the lamellar growth rate G. During isothermal growth this rate remains invariant, independent of crystal size. The same conclusion was drawn by Buckley and Kovacs[9] for crystallization of melt PEO.

CONCLUSION

Static and dynamic light scattering allows us to measure the instantaneous crystal growth rate and comment on the morphology of the final crystals. At a given temperature the crystal growth rate is nearly constant within the range 10^{-4}–10^{-1} nm s^{-1}. The maximum crystal size depends on the temperature of crystallization, which in turn probably relates to fractionation. The crystal morphology suggests that the growth is two-dimensional. Thus, the growth rate $\mathrm{d}R/\mathrm{d}t$ is proportional to the growth rate normal to the lamellae. Further investigations are currently under way to establish the role of the molecular weight, its distribution, the number of seeds introduced and the temperature variation, as well as to develop a deeper theoretical understanding. In our continuing studies, we also hope to investigate other crystallizable polymers, such as linear polyethylene. We have demonstrated that light scattering can provide a means for studying *in situ* the kinetics of crystallization of polymers from dilute solution.

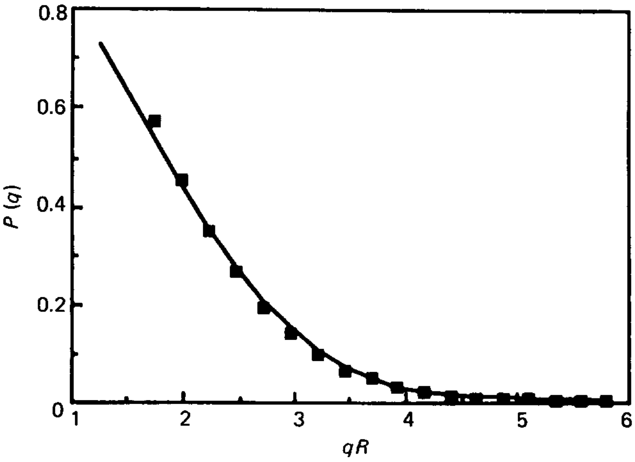

Figure 4 Fit of cylinder model (——) to static light scattering intensity data (■) for dilute suspension of fully grown PEO crystals

ACKNOWLEDGEMENTS

The work was supported by the 3M Corporation (E.J.A.) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society (E.J.A.).

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