# Crystallization kinetics of poly(ethylene oxide) diluted with xylene

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The crystallization kinetics of poly(ethylene oxide)–xylene mixtures with volume fractions of solvent $\nu_1 = 0.52$, 0.93 and 0.99 has been investigated by means of dilatometry. At low extents of crystallinity, isotherms are well expressed by the free growth approximation with exponent $n = 3$ for the concentrated systems ($\nu_1 = 0.52$ and 0.93) and $n = 4$ for the more dilute solution ($\nu_1 = 0.99$). The overall rate temperature coefficient was analysed using the theory pertinent to polymer–diluent mixtures. Assuming that the product $\sigma_e'\sigma_u$, where $\sigma_e'$ is the apparent basal free energy and $\sigma_u$ is the lateral free energy of the critical nucleus, is independent of concentration, the dissolution temperature for different dilutions as well as the interaction parameter $\chi_1$ have been estimated.

## INTRODUCTION

For many years, attention has been drawn to the different crystallization behaviour of polymers as compared to material of low molecular weight. Assuming that the crystallization process of polymers is governed by the nucleation of the system, theories pertinent to the nucleation act for finite molecular weights have been developed[1,2]. Nucleation theories were also extended to study the influence of the solvent in the crystallization of polymers[3]. By using these theories in the analysis of the crystallization of polyethylene in presence of diluents, one finds that the phase transformation is described by a function of the free energy required for the nucleation[4,5].

It is desirable to apply the nucleation theories to the crystallization of other polymer–diluent systems. Poly(ethylene oxide) is a molecule suitable for this purpose. In the extensive studies that have now been reported for the crystallization of this polymer, much of the effort has been focused on the crystallization kinetics of poly(ethylene oxide) from the bulk[6–14]. However, very few studies have been made dealing with the influence of the volume fraction of diluents on the crystallization of poly(ethylene oxide)[15,16]. In this paper the results of a dilatometric investigation of the crystallization kinetics of poly(ethylene oxide)–xylene mixtures at high, moderate and low concentrations are reported.

## EXPERIMENTAL

The high concentration mixtures were prepared using bubble-free films of a PEO fraction of number-average molecular weight 20 000. An accurately weighed amount of polymer and the desired amount of diluent were put in a glass tube which was placed in a silicone bath maintained at a predetermined temperature, well above its melting temperature. The sample tube was so constructed that it could either be evacuated or oxygen-free nitrogen could be introduced. Temperatures ranging from 80° to 110°C were used to prepare the mixtures. The time of heating and mixing in the molten state was about 24 h. The glass tube and its contents were allowed to cool slowly to room temperature and then reweighed. A correction to the concentration was made to allow for the slight loss of diluent. The mixture was removed from the tube and a weighed sample was transferred to the dilatometer bulb. In the case of dilute solutions, a weighed amount of polymer was directly introduced into the bulb of the dilatometer as well as the desired amount of solvent. The composition, on a volume basis, was computed at the respective melting temperatures of the mixtures from the density of the diluent and the density of the polymer in the liquid state at the appropriate temperature, assuming additivity of volumes.

The dilatometers were so constructed that, after introducing the mixtures, the bulb was sealed and filled with mercury in a high vacuum line[3–5]. The total change in the mercury height upon completion of the crystallization was about 3 cm. Prior to the initiation of the crystallization the polymer–diluent mixture was heated to remove all traces of crystallinity. The dilatometer was then quickly transferred to a water bath whose temperature was thermostatically controlled to within ±0.01°C. The contraction due to crystallization was followed by means of a cathetometer (±0.01 mm).

## RESULTS AND DISCUSSION

The crystallization behaviour of PEO–xylene mixtures with compositions: $\nu_2 = 0.48$, 0.07 and 0.01, where $\nu_2$ is the volume fraction of polymer, have been studied. Measurements were made at temperatures from 30.5° to 44.4°C, the wide temperature range reflecting the strong influence of the volume fraction of diluent on the polymer crystallization. The prior thermal history strongly influences the crystallization kinetics at all concentrations. As an example, the crystallization isotherms of the more dilute solution ($\nu_2 = 0.01$) are shown in *Figure 1*, using the dilatometer contraction data. In these experiments the solution was heated to 100°C for 4 h before crystallizing at 31.3°C; the polymer redissolved (100°C, 4 h) and recrystallized at 32.3°C, and this process repeated successively for $T_c = 33.3$°C and = 30.3°C. If the data of *Figure 1* are examined carefully, it is observed that as the temperature increases the isotherms show a tendency to superpose one upon another; in other words,

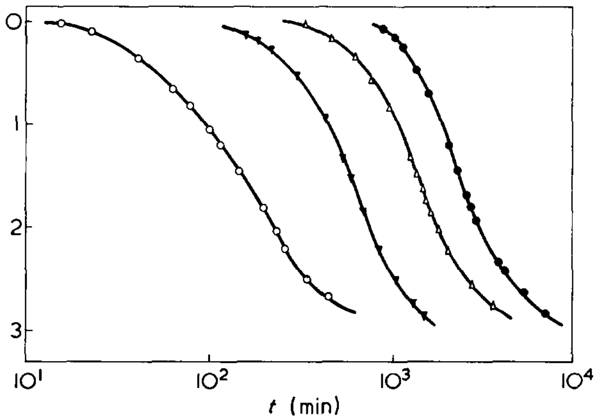

*Figure 1* Influence of the thermal history on the crystallization of the solution $\nu_2 = 0.01$. In all the experiments, the solution was heated at 100°C prior to subsequent crystallization at the given temperatures: ○, 30.3; ▼, 31.3; △, 32.3; ●, 33.3°C

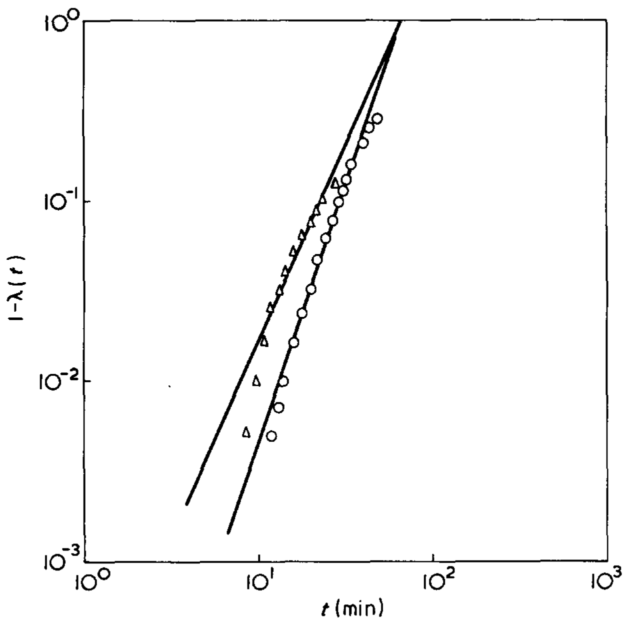

*Figure 2* Plot of degree of crystallinity as function of log *t* at 41.4°C for the system in which $\nu_2 = 0.48$. Prior to crystallization the system was kept in a bath at 130°C for 4 h (△) and 15 h (○)

the difference in the crystallization rates is not as large as it should be when the experiments proceed from low to high temperatures. The isotherms show a greater tendency to superimpose when the previous crystallization temperature is higher. Moreover, the isotherm at 30.3°C indicates that the crystallization rate is higher than it should be if it is compared with other isotherms. In view of these results, it would appear that a very high solution temperature is necessary to obtain completely homogenized solutions. The same behaviour occurs in high concentration mixtures. In *Figure 2* the degree of crystallinity $1 - \lambda(t)$ is plotted against log *t* at 41.4°C, for $\nu_2 = 0.48$. Prior to the crystallization the dilatometer was kept in a bath at 130°C for 4, 15 and 24 h. The slope of the isotherms and the induction time increases as the time interval increases from 4–15 h. *Reproducible isotherms were obtained for all concentrations once the dilatometers were melted in a bath at 130° C for 15 h.*

The completion of crystallization depends also on the concentration of polymer. Thus, for the more dilute solution ($\nu_2 = 0.01$), the end of crystallization is relatively sharp, in contrast to the crystallization of moderate and high concentration solutions where a slow increase in crystallinity is evident over a long period of time after a degree of crystallinity of about 20% is achieved. These observations seem to indicate that secondary processes are absent in most of the crystallization of poly(ethylene oxide) from very dilute solutions, in agreement with the early findings of Beech and Booth[16].

Crystallization isotherms obtained for the three concentrations studied here are illustrated in *Figures 3–5*, where a double logarithmic plot of the degree of crystallinity against time has been made for several temperatures. The kinetic data can be analysed using the Göler–Sachs free growth approximation[17]. The theory suggests that in the early stages of the transformation a straight line is obtained by plotting $\log[1 - \lambda(t)]$ against log *t*. The slope of the plot depends

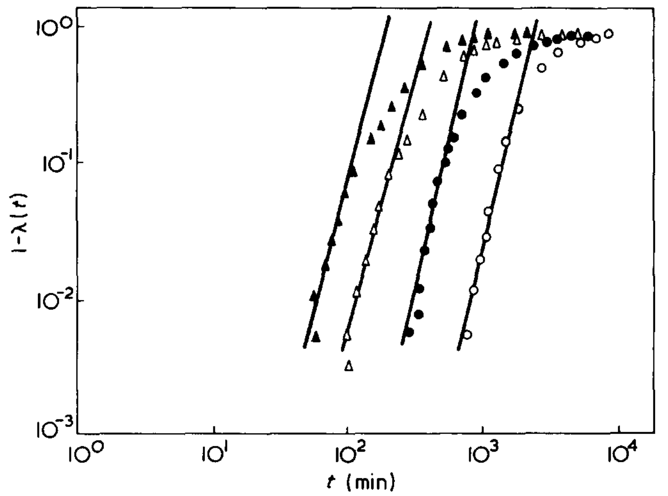

*Figure 3* Double logarithmic plot of degree of crystallinity against *t*, at different crystallization temperatures, for $\nu_2 = 0.01$; ▲, 30.5; △, 31.4; ●, 32.5; ○, 33.5°C

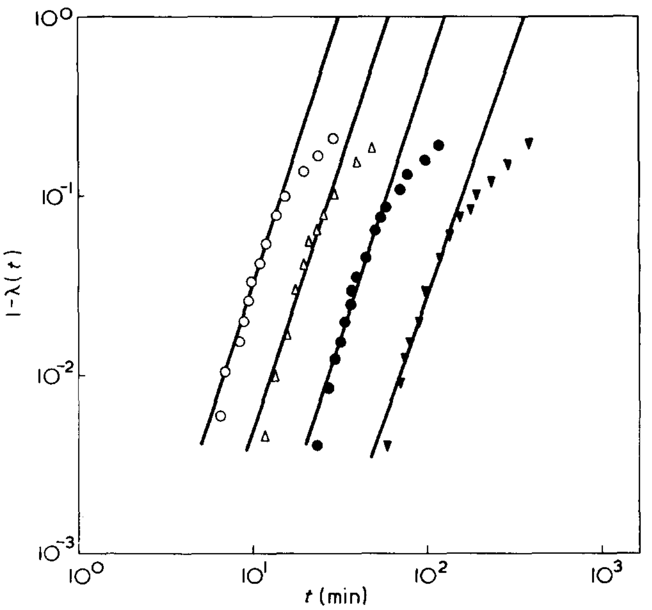

*Figure 4* Double logarithmic plot of degree of crystallinity against *t*, at different crystallization temperatures, for $\nu_2 = 0.07$; ○, 33.4; △, 34.4; ●, 35.4; ▼, 36.4°C

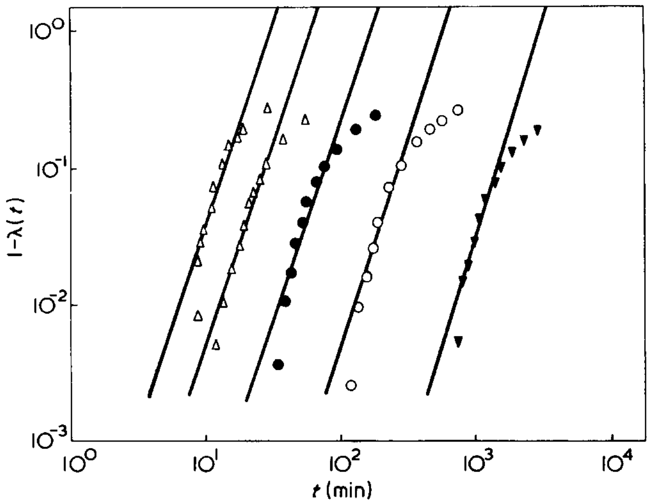

*Figure 5* Double logarithmic plot of degree of crystallinity against $t$, at different crystallization temperatures, for $\nu_2 = 0.48$; △, 40.4; △, 41.4; ●, 42.4; ○, 43.4; ▼, 44.4°C

on the respective growth geometries, so that slopes 4, 3 and 2 represent, respectively, three, two and one dimensional growth. The data of *Figures 3–5* indicate that for a given concentration, a linear relation is obtained for a significant part of the total transformation and the slope of these portions is found to be independent of the crystallization temperature. However, the slope of the double logarithmic plot $1 - \lambda(t)$ against $t$ is dependent on concentration. For the more dilute solution ($\nu_2 = 0.01$), the slope is four; for the moderate and high concentrated systems ($\nu_2 = 0.07$ and $\nu_2 = 0.48$), the slope is three.

The slope of the linear portion of the Göler–Sachs plot, corresponds to the exponent $n$ in the Avrami equation[18]. The simplest interpretation of the exponent $n = 3$ is the occurrence of a homogeneous nucleation accompanied by two dimensional growth, while the exponent $n = 4$, suggests an homogeneous nucleation with three dimensional growth. The exponent $n = 4$, also found for the crystallization of other very dilute solutions[5,16,19], cannot be explained at the present time and it must be reconciled with the lamella-like crystallites that are observed. We must emphasize that the very dilute solutions are precisely those which, at least in the early stages of the crystallization, meet the primary requirement of the Avrami analysis, i.e. that the rate of growth of the crystalline entities is independent of the extent of the crystallization. In early studies on the crystallization of very dilute solutions of polyethylene on several solvents[5], it was found that the exponent $n = 3$ corresponds to poor solvents, where the molecules freely interpenetrate one another, and $n = 4$ corresponds to better solvents. This conclusion apparently does not hold for very dilute solutions of poly(ethylene oxide) where the exponent is 4 for poor solvents. Therefore, we feel that the explanation of the exponent $n = 4$ needs further theoretical and experimental research.

In *Figure 6* the experimental isotherms, for each concentration, were superposed upon one another by shifting each one along the log time axis until the best composite isotherm was obtained. The superposition was performed on the basis of the absolute crystallinity*. For all the concentrations studied the isotherms are superposable over the complete extent of the transformation. Therefore, the temperature coefficient of the process in the retarded or tail portion of the isotherms is the same as for the initial part of the transformation. Moreover, the composite isotherms of the moderate and high concentration solutions are also superposable.

Overall rates of crystallization are given in *Table 1* in terms of the time necessary to achieve 10% of crystallinity, $\tau_{0.1}$. The rates increase with increasing concentration at a given temperature and for each concentration the temperature coefficient is negative. It is usual to discuss the rate–temperature relationship in terms of the nucleation theory, suitably modified for application to polymeric materials. If it is assumed that crystallization is controlled by a single nucleation step, then:

$$1/\tau_{0.1} = (1/\tau_{0.1})_0 \exp(-\Delta F/RT) \tag{1}$$

where $(1/\tau_{0.1})_0$ is constant over the temperature range considered and $\Delta F$ is the activation free energy, i.e. the free energy of critical size stable nucleus at the crystallization temperature.

If, as is possible, the rate determining step is the formation of a monolayer nucleus then, for a chain of high molecular weight[3]:

$$\ln(\tau_{0.1})^{-1} = \ln(\tau_{0.1})_0^{-1} - \frac{2\sigma_u \sigma_e'}{T\Delta f_u'} \tag{2}$$

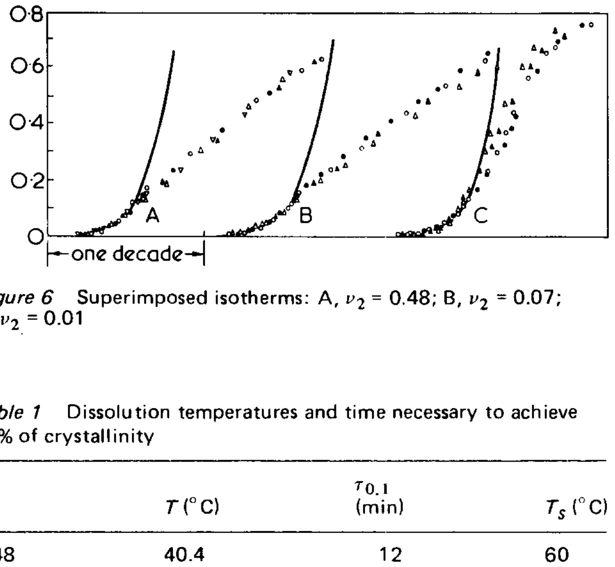

*Figure 6* Superimposed isotherms: A, $\nu_2 = 0.48$; B, $\nu_2 = 0.07$; C, $\nu_2 = 0.01$

*Table 1* Dissolution temperatures and time necessary to achieve 10% of crystallinity

| $\nu_2$ | $T$ (°C) | $\tau_{0.1}$ (min) | $T_s$ (°C) |
|---|---|---|---|
| 0.48 | 40.4 | 12 | 60 |
| | 41.4 | 30 | |
| | 42.4 | 80 | |
| | 43.4 | 280 | |
| | 44.4 | 1600 | |
| 0.07 | 33.4 | 13 | 55 |
| | 34.4 | 26 | |
| | 35.4 | 58 | |
| | 36.4 | 160 | |
| 0.01 | 30.5 | 120 | 52 |
| | 31.4 | 227 | |
| | 32.5 | 580 | |
| | 33.5 | 1600 | |

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* Absolute crystallinities were calculated using for pure PEO $\bar{\nu}_a = 0.8898 + 6.9 \times 10^{-4} (t - 25)$ and $\bar{\nu}_c = 0.8100 + 6.1 \times 10^{-4} (t - 25)$ according to Simon[23].

where

$$\sigma_e' = \sigma_e - T \ln \nu_2 \tag{3}$$

In equations (2) and (3) $\sigma_e$ and $\sigma_u$ are, respectively, the basal and lateral interfacial free energies and $\Delta f_u'$ is the depressed free energy of fusion for the units involved in the transformation. This last quantity may be written in the following way

$$\Delta f_u' = \frac{T_{m,0} - T}{T_{m,0}} \Delta H_u - RT(V_u/V_1)\nu_1(1 - g\nu_1) \tag{4}$$

where $g$ is a dimensionless interaction parameter which depends on temperature, pressure, concentration and molecular weight[5]; $T_{m,0}$ is the melting temperature of a crystal of infinite dimensions composed of polymer of infinite molecular weight, $\Delta H_u$ is the heat of fusion per repeat unit, $V_u$ and $V_1$ are the average molar volume of each repeat unit and the solvent, respectively.

The analysis of the data using equation (2) requires the knowledge of the interaction parameter $g$ which is not available for most of the polymers in solution. If we assume $g = \chi_1$, then we can calculate this parameter from the second virial coefficient $A_2$ by the Flory–Huggins formulation[20]:

$$A_2 = (1/2 - \chi_1)/V_1\rho_2^2 \tag{5}$$

where $\rho_2$ is the liquid polymer density and $V_1$ is the partial volume of the solvent. The second virial coefficient of poly(ethylene oxide) in xylene is not available, but data are available for solutions in benzene, a much better solvent. The second virial coefficient for poly(ethylene oxide) fractions[21] in benzene is about $30 \times 10^{-4}$ mol cm$^3$/g$^2$ for molecular weight of about 40 000. Using these data one obtains a value of about 0.20 for $\chi_1$ in benzene. The interaction parameter for poly(ethylene oxide) in xylene should be bigger than 0.20, but unfortunately we cannot determine *a priori* its exact value.

From nucleation theory it is easily shown that equation (2) can be written in the following way:

$$\ln \tau_{0.1}^{-1} = (\ln \tau_{0.1})_0^{-1} - \frac{2\sigma_e'\sigma_u}{\Delta H_u} \frac{T_s^0}{T\Delta T} \tag{6}$$

where $T_s^0$ is the equilibrium melting temperature or dissolution temperature of the solutions. A plot of $\ln \tau_{0.1}^{-1}$ against $T_s^0/T\Delta T$ should be a straight line provided the rate controlling step is the formation of a monolayer nucleus. For crystallization in bulk, plots of $\ln \tau_{0.1}^{-1}$ against $T_{m,0}/T\Delta T$, lie in a straight line and from its slope a value of 1.7 kcal/mol is obtained for the basal free energy (when $T_{m,0}$ = 349.2K, $\Delta H_u$ = 2000 cal/mol of repeat unit and $\sigma_u$ = 200 cal/mol). In order to analyse the temperature coefficient by equation (6) it is necessary to know $T_s^0$. However, as has been discussed in the literature, this quantity has evaded direct experimental determination[19,22]. Since the evaluation of $T_s^0$ is difficult we have chosen for the high concentration solution $T_s^0$ = 333.2K as a reasonable value on the grounds that this leads to a value of $\sigma_u\sigma_e'$ which is in the region of that obtained for poly(ethylene oxide) in bulk. We should stress that correspondence between the basal free energy $\sigma_e$ in crystallization from bulk and $\sigma_e'$ obtained from dilute solutions has been reported for polyethylene[5,19].

It is clear from the plots of *Figure 7* that equation (6) fits the experimental kinetic data of the high concentrated solution very well if we choose the value of 60°C for the equilibrium melting temperature of this solution. The slope of the straight line obtained is 338 cal/mol which agrees satisfactorily with the slope obtained for the polymer crystallized from the bulk using $T_{m,0}$ = 349.2K. This leads to a value of $2\sigma_e'\sigma_u$ of $6.76 \times 10^5$ cal$^2$/mol$^2$ when $\Delta H_u$ is set equal to 2000 cal/mol. In the same way, the experimental data of the middle and low concentrated solutions ($\nu_2$ = 0.07 and 0.01) adjust satisfactorily to straight lines with the same slope if we take as their dissolution temperatures the values of 55° and 52°C, respectively.

It may be worthwhile to compare the equilibrium melting temperature obtained for the more dilute system ($\nu_2$ = 0.01), with those previously reported by Beech and Booth[16] for different fractions of poly(ethylene oxide) in ethanol with concentration 0.27 g/dl. These authors have studied five fractions and have found that $T_s^0$ increases from 48.5° to 50°C in the molecular weight range $7 \times 10^4$ to $2 \times 10^6$. We can observe that these values are sensibly lower than that of 52°C obtained from our data. This difference may be qualitatively explained if we consider that in poor solvents, the dissolution temperature $T_s^0$ is related to the melting temperature $T_{m,0}$ of the undiluted polymer of infinite molecular weight by the familiar relationship[20]:

$$1/T_s^0 - 1/T_{m,0} = (RV_u/\Delta H_u V_1)[(-\ln \nu_2/s) + (1 - 1/s)\nu_1 - \chi_1\nu_1^2] \tag{7}$$

where $s = (xV_u/V_1)$, $x$ being the number of bonds per chain.

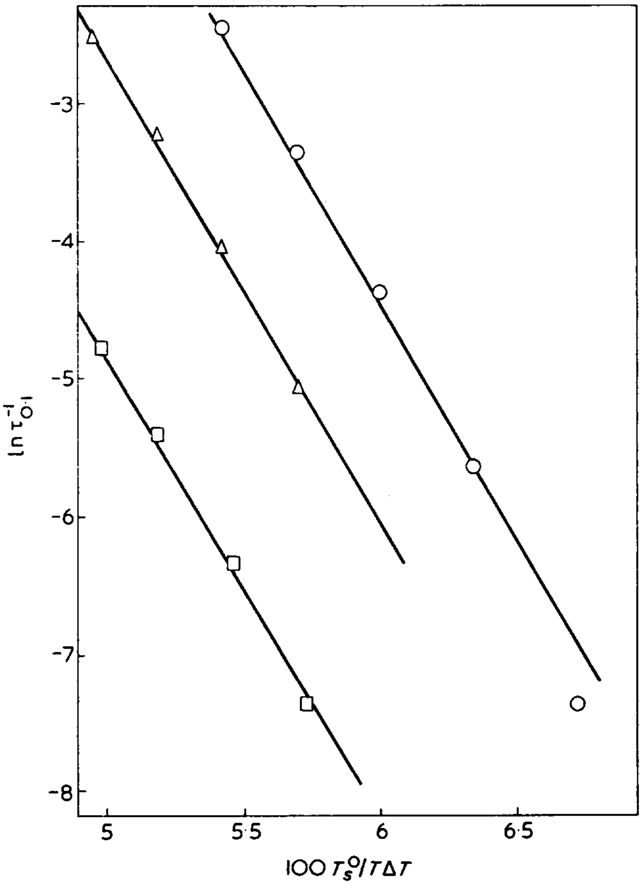

*Figure 7* Plot of $\ln \tau_{0.1}^{-1}$ against $T_s^0/T\Delta T$ for the indicated concentrations: ○, $\nu_2$ = 0.48; △, $\nu_2$ = 0.07; □, $\nu_2$ = 0.01

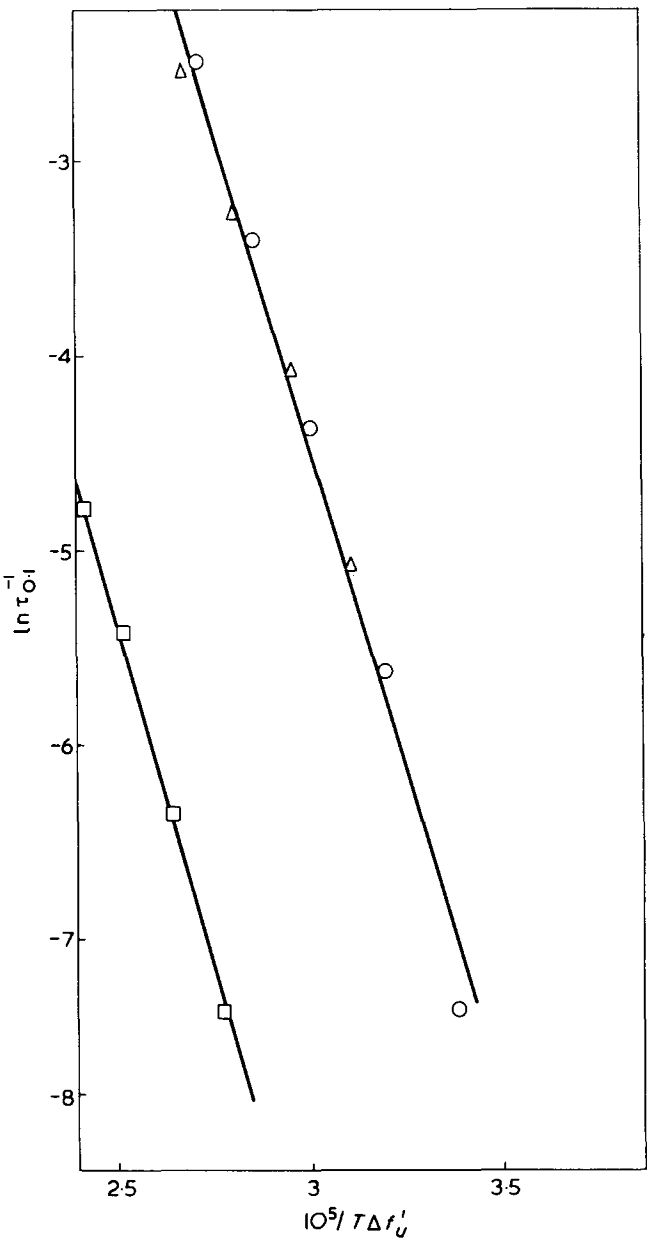

*Figure 8* Plot of $\ln \tau_{0.1}^{-1}$ against $1/T\Delta f_u'$ for indicated concentrations: ○, $\nu_2 = 0.48$; △, $\nu_2 = 0.07$; □, $\nu_2 = 0.01$

It is evident that, for a given concentration, the effect of the solvent on the depression of the melting temperature of the polymer is smaller when both the molar volume of the solvent and the interaction parameter $\chi_1$ are larger. Since the molar volume of ethanol is almost one half of that of xylene, the temperature depression in the former case should be larger than in the latter as the calculations show.

Equation (7) has also been used to obtain the interaction parameter $\chi_1$. As it is known, the validity of this equation is questionable for very dilute solutions in good solvents because in this case the macromolecules are more or less isolated and do not meet the requirements of the theory. In fact, equation (7) was obtained assuming that the system is composed of an enmeshed, intertwined and entangled assembly of chains. Therefore, the Flory–Huggins formulation can only be used with concentrated solutions in any solvent and with very dilute solutions in sufficiently poor solvents where excluded volume effects are negligible. The introduction of suitable values in equation (7) (i.e. $\Delta H_u$ = 2000 cal/mol, $T_{m,0}$ = 349.2K, $T_s^0$ = 333.2K, $\nu_2$ = 0.48), gives $\chi_1$ = 0.36, bearing out the former assumption that xylene is a relatively poor solvent for poly(ethylene oxide). Since $\chi_1$ has been estimated, we can also apply equation (2) to the analysis of the kinetic data. It is clear that $\sigma_u\sigma_e'$ can be obtained from the plot $\ln \tau_{0.1}^{-1}$ *versus* $1/T\Delta f_u'$. *Figure 8* shows the plots for the solutions here studied. It is observed that for the high and for the middle concentrated solutions, a single straight line is obtained. From the slope of the lines a value of $6.62 \times 10^5$ cal$^2$/mol$^2$ for $2\sigma_u\sigma_e'$ is obtained, which agrees satisfactorily with that evaluated from *Figure 7,* in spite of the simplifications that have been made in deriving equations (2) and (6).

It can be concluded that the product $\sigma_e'\sigma_u$ is independent of the concentration. Since the basal interfacial free energy $\sigma_e$ is related to $\sigma_e'$ by equation (3), $\sigma_e$ decreases as the dilution increases, as occurs in other systems[3]. The results also show that the crystallization process is described by a unique function of the free energy of nucleation when the variation of $\sigma_e$ with concentration is stipulated. However, there is a point which needs further clarification. This very important point is the change of the Avrami exponent with concentration and with the kind of solvent.

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