

LIQUID-LIQUID PHASE SEPARATION BY NUCLEATION AND GROWTH IN SOLUTIONS OF POLY(2,6 DIMETHYL-1,4 PHENYLENE OXIDE) IN TOLUENE

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Abstract—In solutions of poly(2,6 dimethyl-1,4 phenylene oxide) in toluene, the nucleation of the newly formed phase during liquid-liquid phase separation takes place after induction periods which vary between several minutes (at temperatures close to the spinodal) and several hours (at temperatures close to the cloudpoint). The growth of the nuclei in the initial stages is diffusion controlled. The diffusion coefficients and the activation energy of diffusion were calculated. From these values, together with the calculated volume free energies and the experimental induction times, an estimate could be made of the size of a critical nucleus and of the surface free energy of the nuclei.

INTRODUCTION

DIRECT measurements of homogeneous nucleation rates have been possible in inorganic glass-forming systems in which non-crystalline phase separation occurs below the liquidus.⁽¹⁾ By electron microscopy, direct measurements could be performed of nucleation rates during transient times, as well as in the steady-state. The kinetics of these separations occurring within the miscibility gap were described in terms of an induction period, followed by nucleation and growth or by spinodal decomposition.

Phase separation phenomena of poly(2,6 dimethyl-1,4 phenylene oxide)-toluene solutions proceed along analogous ways.^(2,3) Upon cooling a homogeneous solution, liquid-liquid phase separation will take place either by the nucleation and growth mechanism or by the spinodal decomposition. Electron-microscopy has shown that nucleation takes place after induction periods which, depending upon temperature and concentration, can reach values up to several hours.⁽⁴⁾ In contrast with most other liquid polymer systems, the growth rates of the nuclei, once formed, have such relatively small values that the growth of the nuclei can be followed under the light microscope.

A survey of the observations of nucleation and growth of solutions of poly(2,6 dimethyl-1,4 phenylene oxide) in toluene is presented in this paper.

EXPERIMENTAL

Appropriate amounts of poly(2,6 dimethyl-1,4 phenylene oxide) and toluene were weighed into glass tubes with two parallel sides, the tubes being sealed at liquid nitrogen temperature under vacuum. Complete dissolution was obtained by heating in a thermostat bath at 150°. Subsequently these tubes were brought into an air thermostat at the temperature at which phase separation by nucleation and growth was known to occur. The temperature control was within 0.1°. The growth of the nuclei was studied under the light microscope with photographic means.

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THEORETICAL CONSIDERATIONS

Induction times

The rate of formation of nuclei at a certain time t after changing the stability conditions is given by:^(5,6)

$$J(t) = J_0 \exp(-\tau/t) \quad (1)$$

$J(t)$ = number of nuclei formed per unit time at time t

J_0 = nucleation rate in the steady state

τ = induction time.

For the induction time, the following expression is valid:^(6,7)

$$\tau = kT/4s(n^*)\nu\lambda \quad (2)$$

k = Boltzmann constant

T = absolute temperature

$s(n^*)$ = surface of a critical nucleus that contains n^* particles

ν = transport frequency

$$\lambda = - \left[\frac{d^2 \Delta G(n)}{dn^2} \right]_{n=n^*}$$

The free enthalpy of formation of a spherical nucleus that contains n particles, $\Delta G(n)$, is given by:⁽⁷⁾

$$\Delta G(n) = (36\pi)^{1/3} n^{2/3} v^{2/3} \sigma - n kT \ln \beta \quad (3)$$

v = volume of a molecule

σ = interfacial free energy

β = a measure of the supersaturation of the system.

From (3) one can derive that

$$\lambda = \left(\frac{32\pi}{81} \right)^{1/3} v^{2/3} \sigma n^{*-4/3} \quad (4)$$

and

$$n^* = \left(\frac{32\pi}{3} \right) v^2 \sigma^3 (kT \ln \beta)^{-3}. \quad (5)$$

Substitution of (5) in (4) gives

$$\lambda = (32\pi)^{-1} v^{-2} \sigma^{-3} (kT \ln \beta)^4. \quad (6)$$

For a condensed system, the supersaturation of the system is related to the volume free energy, controlling phase separation, by:

$$\Delta G_v = \frac{kT \ln \beta}{v}. \quad (7)$$

The expression for λ therefore can be written as

$$\lambda = (32\pi)^{-1} v^{+2} \sigma^{-3} (\Delta G_v)^4. \quad (8)$$

The transport frequency ν for a liquid polymer system is related to the jump frequency^(8,9) F of the segments of the polymer.

For a volume unit of the polymer system one can write⁽¹⁰⁾

$$\nu = N_1 \delta F_0 \exp(-\Delta G_a/kT) \quad (9)$$

N_1 = number of molecules in a volume unit

δ = interparticle distance

F_0 = a factor proportional to kT/h (h is Planck's constant) and dependent upon the stiffness of the polymer chain.⁽¹¹⁾

ΔG_a = activation energy for diffusion.

Substitution of (8) and (9) in (2) results in:

$$\tau = \frac{32\pi kT \sigma^3 \exp(\Delta G_a/kT)}{4s(n^*) N_1 \delta F_0 (\Delta G_v)^4 v^2} \quad (10)$$

Since $s(n^*)$ can be expressed in terms of r^* , the size of the critical nucleus, and since this latter quantity is related to σ and ΔG_v by

$$r^* = \frac{2\sigma}{\Delta G_v} \quad (11)$$

Eqn. (10) can be written as:

$$\tau = \frac{kT r^* \exp(\Delta G_a/kT)}{4 N_1 \delta F_0 \Delta G_v v^2} \quad (12)$$

For our system τ can be obtained directly from experiments, ΔG_v can be calculated and ΔG_a can be obtained from experimental growth data of the nuclei. Therefore r^* can be calculated from Eqn. (12) if suitable values for N_1 , δ , F_0 and v are inserted. This calculated value for r^* will be compared with an experimental value obtained earlier by electron microscopy.⁽⁴⁾

Using Eqn. (11), σ can be calculated also.

Calculation of ΔG_v

The volume free energy, ΔG_v , can be calculated if, for the system, the Gibbs free energy of mixing, ΔG_m , is known as a function of concentration and temperature.

For a polymer solution, ΔG_m , expressed in weight fractions, in a volume element, ΔV , is given by:⁽¹²⁾

$$\Delta G_m/RT = \left[w_0 \ln w_0 + \sum_i \frac{M_0}{M_i} w_i \ln w_i + g w_0 w \right] \frac{\rho \cdot \Delta V}{M_0} \quad (13)$$

w_0 = weight fraction of the solvent

w_i = weight fraction of the polymer component i

w = total weight fraction of the polymer

M_0 = molecular weight of the solvent

M_i = molecular weight of component i of the polymer

ρ = density of the solution

R = universal gas constant

g = free enthalpy correction parameter.

ΔG_m for the system poly(2,6 dimethyl-1,4 phenylene oxide) toluene can be calculated⁽¹³⁾ with a temperature- and concentration-dependent interaction parameter g , given by

$$g = g_0 + g_1 w_1 \quad (14)$$

in which

$$g_0 = \frac{566.0 - 6.7(T - 273)}{RT} \quad (15)$$

and

$$g_1 = \frac{1251.8 - 0.7(T - 273)}{RT}. \quad (16)$$

Taking $\rho\Delta V/M_0 = 1$ in Eqn. (13), the free energies driving phase separation at various concentrations and temperatures can be obtained using the following expression:⁽¹⁾

$$\Delta G_v = \{\Delta G_m(w_2) - \Delta G_m(w_1) + (w_3 - w_2) d\Delta G_m/dw_2 - (w_3 - w_1) d\Delta G_m/dw_1\}/V_{M_0} \quad (17)$$

where

w_2 = weight fraction of polymer in the homogeneous solution (i.e. before phase separation)

w_1 = weight fraction of polymer in the dilute phase at equilibrium

w_3 = weight fraction of polymer in the concentrated phase at equilibrium

V_{M_0} = volume of M_0 of the homogeneous solution.

Diffusion coefficient and activation energy of diffusion

The diffusion coefficient for a particular process can be calculated if the rate of growth of a spherical particle can be measured and the degree of supersaturation is known.⁽¹⁴⁾

In systems where liquid-liquid phase separation is known to occur, the degree of supersaturation is expressed as:

$$\frac{\Delta G_v \cdot v}{kT} = \ln \beta = f(S). \quad (18)$$

Here v again is the volume of a molecule (or polymer segment) and $f(S)$ is a complicated function of S , a measure of the supersaturation of the system. S is equal to $r/D^{\frac{1}{2}}t^{\frac{1}{2}}$, where r is the radius of the growing particle, D is the diffusivity and t is time. Frank⁽¹⁴⁾ has tabulated $f(S)$ over a wide range of values of S . Therefore, using Eqn. (18), S can be obtained from Frank's tabulated values.

Since

$$dA/dt = 4\pi DS^2 \quad (19)$$

in which dA/dt represents the growth of area of a spherical particle, D can be calculated.

From the plot of $\ln D$ vs $1/T$, the activation energy of diffusion can thus be obtained.

RESULTS

Experimental τ -values

The growth of the nuclei has been measured at temperatures between the cloud-point and the spinodal of solutions of 30, 40 and 50 per cent of weight poly(2,6 dimethyl-1,4 phenylene oxide) in toluene.

The growth data of a 30 per cent of weight solution at various temperatures are shown in Fig. 1. For that particular solution, the cloudpoint $T_{cip} = 60^\circ\text{C}$ and the spinodal temperature $T_s \approx 38^\circ\text{C}$. For a full cloudpoint curve and spinodal curve see Ref. 2.

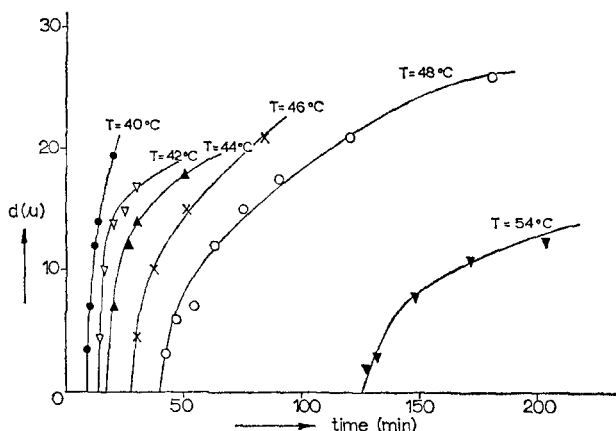


FIG. 1. Size of the nuclei vs time for a 30 per cent by weight poly(2,6 dimethyl-1,4 phenylene oxide)-toluene solution at various temperatures. d = dia. of the particle.

Nuclei were observed after a certain induction time which approached zero at temperatures near the spinodal temperature and which were several hours at temperatures close to the cloudpoint.

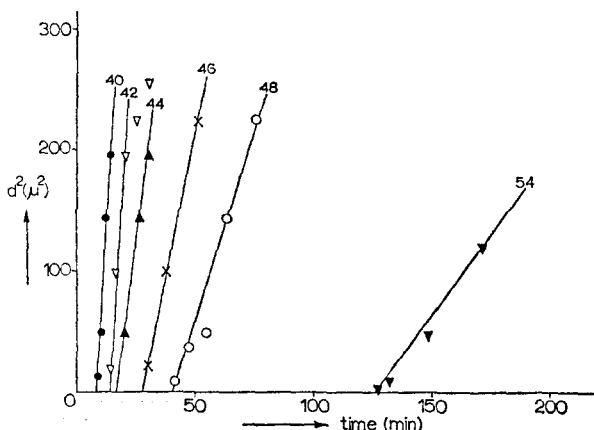


FIG. 2. Area of nuclei vs time for a 30 per cent by weight poly(2,6 dimethyl-1,4 phenylene oxide)-toluene solution at various temperatures; d = dia. of the particle.

To test the possibility that early in the induction period nuclei were formed and might be too small to detect under the light microscope, samples were studied at appropriate times and temperatures with the transmission electron microscope using the freeze etching technique during sample preparation.⁽⁴⁾ This investigation showed indeed that during the induction period no nuclei were formed.

By plotting d^2 vs t , as in Fig. 2, and extrapolating to $d^2 = 0$, the induction periods were obtained as a function of temperature (Table 1). The plot of $\ln \tau$ against $1/T$ is linear (Fig. 3). This is rather unexpected, given the complicated dependency of τ on temperature suggested by Eqn. (12).

TABLE 1. EXPERIMENTAL τ -VALUES AND CALCULATED VALUES OF THE VOLUME FREE ENERGY CONTROLLING PHASE SEPARATION FOR POLY(2,6 DIMETHYL-1,4 PHENYLENE OXIDE)-TOLUENE SOLUTIONS

w	T (K)	τ (min)	ΔG_v (J/cm ³)
0.3	313	8	3.51
	315	14	2.85
	317	17	2.22
	319	27	1.45
	321	40	1.27
	326	100	0.60
	327	125	0.57
0.4	328	4	1.73
	333	29	1.27
	335	43	1.00
	338	98	0.71
0.5	342	5	1.03
	345	6	0.99
	346	13	0.89
	348	28	0.71
	351	51	0.56

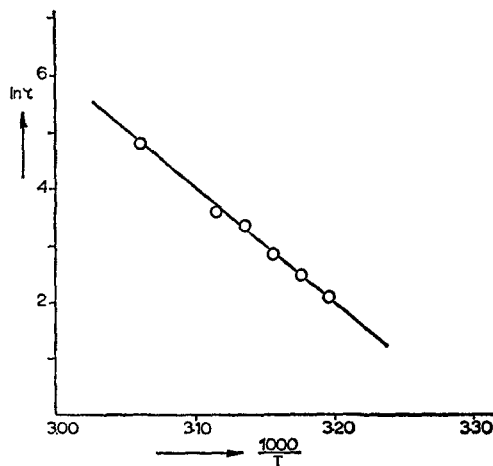


FIG. 3. The logarithm of the induction time vs $1/T$ for a 30 per cent by weight poly(2,6 dimethyl-1,4 phenylene oxide)-toluene solution.

Calculation of ΔG_v

Using Eqn. (17), the volume free energy associated with phase separation for a 30, 40 and 50 per cent of weight solution of poly(2,6 dimethyl-1,4 phenylene oxide) in toluene was calculated at various temperatures, while taking for V_{M_0} the values 100.10, 98.06 and 96.05 at the concentrations mentioned.

The results are given in Table 1.

TABLE 2. CALCULATED VALUES OF THE DIFFUSION COEFFICIENT AND THE ACTIVATION ENERGY OF DIFFUSION OF POLY(2,6 DIMETHYL-1,4 PHENYLENE OXIDE)-TOLUENE SOLUTIONS

w	T (K)	f (S)	S	$dA/dt \times 10^8$ (cm ² /min)	$D \times 10^9$ (cm ² /sec)	ΔG_a (kcal/mol)
0.3	313	0.143	0.73	82.74	2.06	2.07
	315	0.116	0.65	75.36	2.37	
	317	0.089	0.55	54.21	2.37	
	319	0.058	0.41	31.81	2.51	
	321	0.051	0.37	24.55	2.38	
	327	0.022	0.21	8.35	2.51	
0.4	328	0.067	0.45	70.60	4.63	3.08
	333	0.049	0.37	60.01	5.82	
	335	0.038	0.31	44.10	6.08	
	338	0.027	0.25	23.99	5.09	
0.5	342	0.039	0.31	40.01	5.56	4.14
	345	0.037	0.30	35.34	5.21	
	346	0.033	0.28	33.20	5.62	
	348	0.026	0.24	26.80	6.17	
	351	0.020	0.20	18.79	6.24	

Calculation of the diffusion coefficient and the activation energy of diffusion

From the plots of d^2 vs t , values of the growth of area of the formed nuclei could be obtained at each phase separation temperature. Using Eqn. (18) and taking the calculated values of ΔG_v from Table 1, $f(S)$ could be obtained. These data were converted to S using Frank's tabulated values.⁽¹⁴⁾

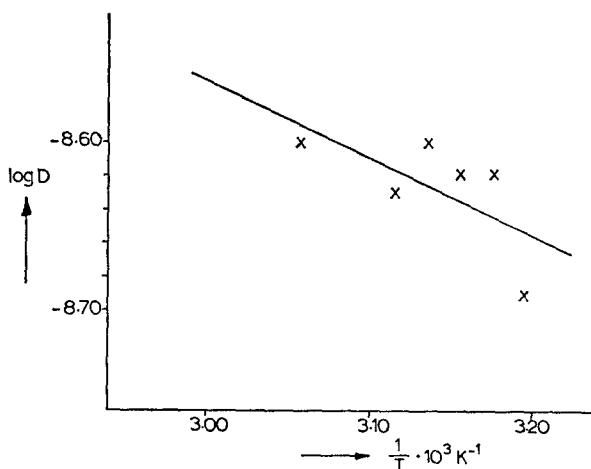


FIG. 4. A plot of the logarithm of the diffusion coefficient vs $1/T$ for a 30 per cent by weight poly(2,6 dimethyl-1,4 phenylene oxide)-toluene solution.

Substitution of these values in Eqn. (19) gave values of the diffusion coefficients (see Table 2). From the plot of $\ln D$ vs $1/T$ (Fig. 4), the activation energy of diffusion was obtained with the least squares method (see Table 2).

Calculation of the size of the critical nucleus and of the interfacial free energy

With the calculated values of ΔG_a and ΔG_v , r^* can be obtained if the experimental values of τ are substituted in Eqn. (12), taking $N_1 = 10^{18} \text{ cm}^{-3}$, the estimated number of polymer molecules in a volume unit of a 30 per cent polymer solution, $\sigma = 10^{-7} \text{ cm}$, the estimated interparticle distance and $v = 17.6 \times 10^{-23} \text{ cm}^3$, the volume of a polymer segment. The value of F_0 depends strongly upon the stiffness of the polymer.⁽¹¹⁾ For polyethylene $F_0 = 11 \times 10^{12}$, for polychlorotrifluoroethylene 5.2×10^{10} and for isotactic polystyrene 1.8×10^8 . The glass transition temperatures for these polymers are respectively 253°K, 325°K and 358°K.

TABLE 3. CALCULATED VALUES OF THE SIZE OF THE CRITICAL NUCLEI AND INTERFACIAL FREE ENERGIES OF A 30 PER CENT OF WEIGHT POLYMER SOLUTION.
 $T_{\text{clpt}} = 333^\circ\text{K}$; $T_{\text{sp1a}} = 310^\circ\text{K}$

w	T	r^* (Å)	σ (erg cm^{-2})
0.3	313	173	30.3
	315	249	35.5
	317	239	26.3
	319	252	18.3
	321	331	13.0
	326	405	12.1
	327	484	13.8

The T_g of poly(2,6 dimethyl-1,4 phenylene oxide) is 490°K, indicating the much higher stiffness of this polymer compared with, for example, isotactic-polystyrene.

As an estimate of F_0 for poly(2,6 dimethyl-1,4 phenylene oxide), the value of 10^4 has been chosen. In principle, one could obtain an experimental value for F_0 from measurements of the rate of nucleation. This type of measurements, however, for the system poly(2,6 dimethyl-1,4 phenylene oxide)-toluene failed with the available experimental means.

The calculated critical radii of the nuclei of a 30 per cent of weight poly(2,6 dimethyl-1,4 phenylene oxide)-toluene solution at various temperatures are given in Table 3, together with the values of σ . If suitable values for F_0 for 40 and 50 per cent solutions were known, the critical radii for these concentrations could be calculated in the same way.

DISCUSSION

1. Since the plot of the growth of area of the nuclei formed in poly(2,6 dimethyl-1,4 phenylene oxide)-toluene solutions versus time is linear (Fig. 2), the growth of the nuclei is a diffusion controlled process.

From differential scanning calorimetric experiments⁽¹⁵⁾ performed with these solutions, it has been concluded that the concentrated phase will crystallize if kept at

the demixing temperature for a certain time. Only in the initial stages of the demixing process, the growth of the nuclei is diffusion controlled.

2. The growth rates of the nuclei become larger at temperatures close to the spinodal. The activation energy of diffusion has a constant value for a given concentration, but the volume free energy increases at lower temperatures. As a result, induction times will be smaller and growth rates increase.

For $T = 52^{\circ}\text{C}$, r^* is calculated to be 405 \AA , a value which agrees very well with the size of nuclei found earlier by transmission electron microscopy.⁽⁴⁾ However, the value of σ seems to be rather high. This is probably due to the rough estimates used for the values of F_0 , N_1 , δ and v . Especially F_0 may be much smaller than 10^4 . This will have a very marked effect upon the calculation of r^* and σ . To conclude we can say that, although there still are some uncertainties about the true values of r^* and σ , the experiments are qualitatively in agreement with the theoretical considerations.

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Résumé—La nucléation d'une nouvelle phase, pendant la séparation de phase liquide-liquide des solutions toluéniques de poly(oxyde de diméthyl 2-6 phénylène 1,4) intervient après une période d'induction qui peut durer soit plusieurs minutes (pour des températures près de la température spinodale) soit plusieurs heures (pour des températures près du point de trouble). La croissance des noyaux dans les étapes initiales est contrôlée par diffusion. On a calculé les coefficients de diffusion et l'énergie d'activation de diffusion. A partir de ces valeurs, des énergies de volume libre calculées et des temps d'induction déterminés expérimentalement on peut estimer la taille d'un noyau critique et la valeur de l'énergie libre de surface des noyaux.

Sommario—In soluzioni di poli(2,6 dimetil-1,4 fenilene ossido) in toluene, la germinazione della nuova fase, durante la separazione di fase liquido-liquido, ha luogo dopo un periodo di induzione che varia da diversi minuti (a temperature vicine a quella spinodale) a diverse ore (a temperature prossime a quella di intorbidimento). La crescita del nucleo nelle fasi iniziali è controllata dalla diffusione. Si sono calcolati i coefficienti e l'energia di attivazione della diffusione. Partendo da tali dati, assieme ai valori calcolati di energia di volume libero e ai tempi di induzione sperimentali, si è potuto fare una stima delle dimensioni del nucleo critico e dell'ammontare dell'energia libera di superficie del nucleo.

Zusammenfassung—Die Keimbildung zur Entstehung der neuen Phase bei der flüssigflüssig-Phasentrennung in Lösungen von Poly-2,6-dimethyl-1,4-phenylenoxid in Toluol findet nach einer Induktionsperiode statt, die zwischen einigen Minuten (bei Temperaturen nahe dem Spinodalpunkt) und einigen Stunden (bei Temperaturen nahe beim Trübungspunkt) beträgt. Die Keimbildung ist im Anfangsstadium diffusionskontrolliert. Der Diffusionskoeffizient und die Aktivierungsenergie der Diffusion wurden berechnet. Aus diesen Daten konnte unter Zuhilfenahme der berechneten freien Volumenenergien und den experimentell erzielten Zeiten für die Induktion die kritische Keimgröße und die freie Oberflächenenergie der Keime abgeschätzt werden.