

# polymer communications

## Model calculations of the phase-behaviour of rod-like particles in solution and their application to the isotropic and anisotropic phases of poly(n-alkylisocyanates) in solution

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Aharoni and co-workers<sup>1-7</sup> have shown that concentrated solutions of certain poly(alkylisocyanates) exhibit lyotropic mesomorphic behaviour. Theoretical considerations of the formation and structure of concentrated solutions of rod-like macromolecules have been given by Flory and co-workers who have shown that anisotropic and isotropic phases may coexist above a minimum concentration of polymer. Recently Flory and co-workers<sup>8-14</sup> have published an important series of papers in which the earlier work is cited and is extended to the case of polydisperse systems. Specifically, Flory and Frost<sup>10</sup> and Frost and Flory<sup>11</sup> have made calculations for the 'most probable' and Poisson distributions of species, respectively. Their calculations predict that in the bi-phasic region there will be a partial fractionation of material between the two phases, the higher molecular weight species tending to concentrate in the anisotropic phase. The formation of lyotropic mesophases has been observed by Aharoni and Walsh<sup>2,3</sup> for certain poly(n-alkylisocyanates) in solution, and, further, they showed that under the correct experimental conditions, bi-phasic media involving poly(n-hexylisocyanate) separated into isotropic and anisotropic phases during which there was a partial fractionation of the original polydisperse material in the manner predicted by Flory<sup>8-11,14</sup>.

During the course of our studies of the dielectric relaxation behaviour of poly(n-hexylisocyanate)-toluene solutions<sup>15,16</sup> and of a copolymer of n-butyl and n-nonyl isocyanates in toluene solution<sup>17</sup>, covering isotropic and bi-phasic ranges, it became apparent that a knowledge, if only semi-quantitative, of the relative amounts of isotropic and anisotropic phases and their compositions would be desirable in order to assist in the interpretations of our data for the reorientations of molecules.

The calculations of Flory and Frost<sup>10,11</sup> were made for distributions having fixed half-width for a given average length of rod. We have extended the work of Flory and Frost<sup>10,11</sup> in order to include the effect of varying the distribution of molecular weight (rod-length) for a given degree of polymerization. This has been done using the theory of Flory and co-workers<sup>8-11,14</sup> together with a Gaussian distribution of rod-lengths. In this way we may

explore the phase-behaviour as a function of average rod-length, width of distribution and concentration of polymer. The details of the calculations and a complete set of results will be the subject of a further publication<sup>18</sup>. The present communication gives a portion of these data and indicates how they may be applied to such systems as the poly (n-alkylisocyanates) in solution.

### Theory

The theory of Flory and co-workers<sup>8-14</sup> is adopted in the present work. We use the same notation as these earlier workers and write the volume-fraction of  $x$ -meric species in the system as a whole as  $r_x^0$  and the mean volume-fraction of all polymer (solute) in both phases combined as  $r_2^0$ . The Gaussian distribution for particles consisting of  $x$  units leads to the following relation:

$$\frac{r_x^0}{r_2^0} = \frac{x}{\bar{x}} \exp \left[ -4 \ln 2 \left( \frac{x - x_0}{\Delta_{1/2}} \right)^2 \right] \quad (1)$$

where  $x_0$  is the value of  $x$  at the maximum of the Gaussian curve,  $\bar{x}$  is the mean value of  $x$ ,  $\bar{x} = (\sum x n_x^0 / n_2^0)$ ,  $n_x^0$  is the number of  $x$ -meric species in the total volume  $V$ . The total number of particles in  $V$  is given by the normalization condition  $n_2^0 = \sum_1^{\infty} n_x^0$ . The total half-width of the Gaussian distribution,  $\Delta_{1/2}$ , may be varied for each chosen value of  $x_0$ . Our calculations follow the procedure outlined by Flory and Frost<sup>10,11</sup> and yield:  $r_2$  and  $r_2'$ , being the volume-fractions of solute in the isotropic and anisotropic phases, respectively, and  $\Phi$ , being the ratio of the volume of the isotropic phase to the total volume, for given values of  $r_2^0$ ,  $x_0$  and  $\Delta_{1/2}$ . The solute concentration  $c$  (% w/w) is defined as 100 times the ratio of the weight of solute to the weight of solution, and may be expressed as

$$c = 100 \times \left[ 1 + \frac{\rho_1}{\rho_2} \left( \frac{1}{r_2^0} - 1 \right) \right]^{-1} \quad (2)$$

$\rho_1$  and  $\rho_2$  are solvent and solute density respectively.

For the present calculations we took  $\rho_1/\rho_2 = 0.86/1.00$ , to conform with values for poly(n-hexylisocyanate) in toluene<sup>3</sup>. We calculate  $\Phi_A = (1 - \Phi)$ , being the volume

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fraction of the anisotropic phase, as a function of  $c$  (equation (2)) for  $x_0 = 50$  and different values of  $\Delta_{1/2}$ . This value of  $x_0$  was chosen in order to conform with a rod-like poly(n-hexylisocyanate) at a molecular weight of about  $10^5$  (see ref. 19). The correctness of our procedures and calculations were first checked by verification of Table 1 of ref. 10 and Table 1 of ref. 11. All calculations were made using the College Honeywell 6080 main-frame computer.

Figure 1 shows  $\Phi_A$  for  $x_0 = 50$  as a function of  $c$  for  $\Delta_{1/2}$

equal to 10, 30 and 50. For  $\Delta_{1/2} = 10$ , the wholly isotropic phase persists up to  $c = 17.8\%$ . In the range  $17.8 < c < 28.2\%$  the system is bi-phasic with  $\Phi_A$  increasing monotonically with  $c$ . For  $c > 28.2\%$  the system is wholly anisotropic. As  $\Delta_{1/2}$  is increased two effects are observed: (i) there is a lowering of the concentration at which the bi-phasic system first appears, (ii) the range of the bi-phasic region is considerably extended. For  $\Delta_{1/2} = 30$  the formation of the wholly anisotropic phase is extended up to  $c \sim 37\%$ .

In addition to the volume fraction of anisotropic phase  $\Phi_A$ , we obtain the distribution curves for the composition of the isotropic and anisotropic phase for given values of  $x_0$ ,  $\Delta_{1/2}$  and  $c$ . From the curves of Figure 1 it is of interest to see the form of these distributions at different values of  $c$ . We note that in Figure 1 for  $c = 21\%$  the values of  $\Phi_A$  are independent of  $\Delta_{1/2}$ . Thus we chose to show in Figures 2 the distributions for  $c$  below, above and equal to  $c = 21\%$ . Here  $f_x$  and  $f'_x$  are the quantities of  $x$ -mer in the isotropic and anisotropic phases respectively, as defined by Flory and Frost<sup>10,11</sup>.

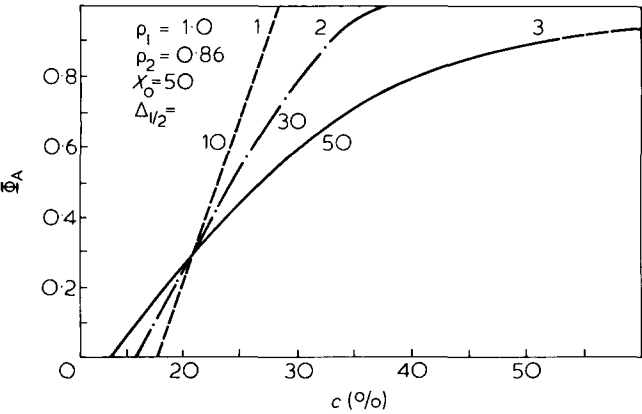


Figure 1  $\Phi_A$  against  $c$  (% w/w) for  $x_0 = 50$  and for different values of  $\Delta_{1/2}$ . Curves 1, 2 and 3 correspond to  $\Delta_{1/2}$  equal to 10, 30 and 50 respectively

$f_x = \Phi v_x/v_2^0$  (3a)

$f'_x = (1 - \Phi)v'_x/v_2^0$  (3b)

and

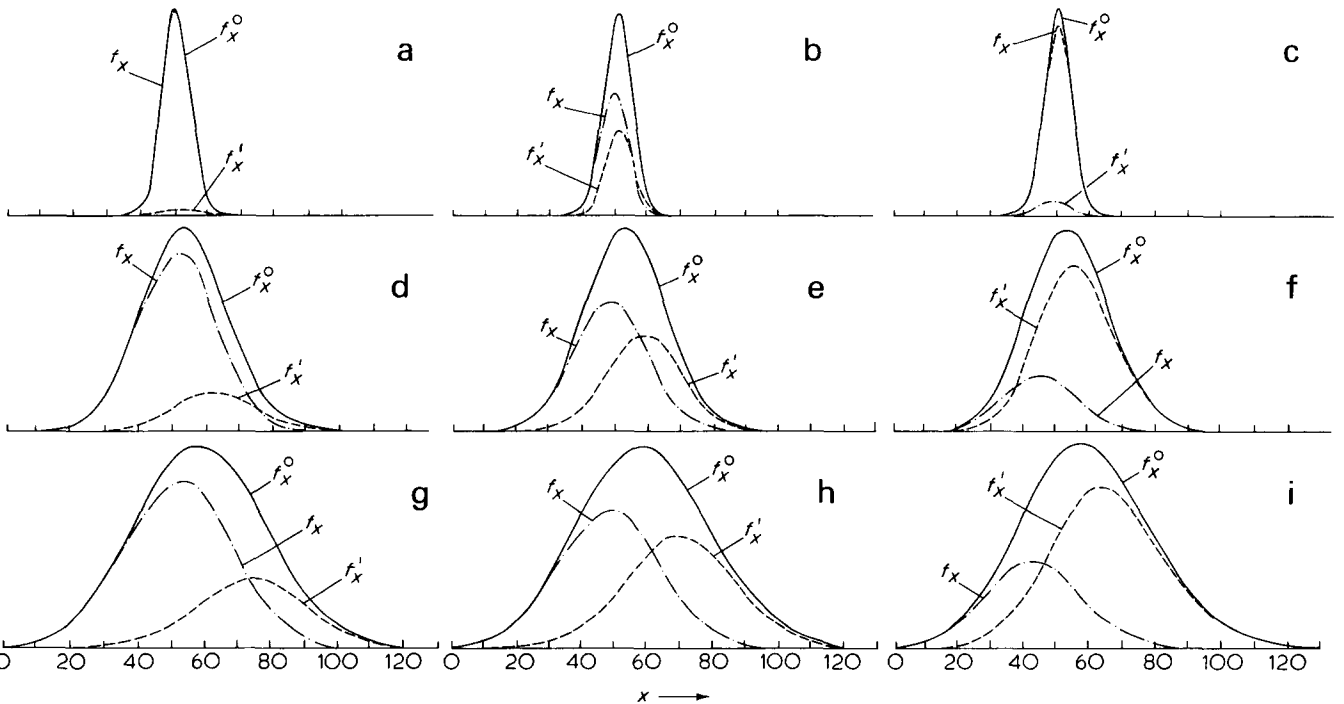


Figure 2  $f_x^0$ ,  $f_x$  and  $f'_x$  against  $x$  for  $x_0 = 50$  and different values of  $\Delta_{1/2}$  and  $c$

Figure	$\Delta_{1/2}$	$c$ (% w/w)	$\Phi_A$
a	10	18	0.017
b	10	21	0.310
c	10	27	0.890
d	30	18	0.115
e	30	21	0.310
f	30	27	0.640
g	50	18	0.183
h	50	21	0.310
i	50	27	0.520

$f_x^0 = f_x + f'_x = v_x^0/v_2^0$  (4)

Consider first Figure 2e. At this concentration,  $c = 21\%$ ,  $x_0 = 50$  and  $\Delta_{1/2} = 30$ . The plots of  $f_x^0$ ,  $f_x$  and  $f'_x$  are each essentially symmetrical about their maximum values. The original mixture partitions into isotropic and anisotropic phases with the high molecular weight species favouring the anisotropic phase and the low molecular weight

Table 1  $v_2$ ,  $v'_2$ ,  $\Phi$ ,  $\Phi_A = 1 - \Phi$  and  $\Phi_A v'_2 / (\Phi v_2)$  for all systems shown in Figure 2

$c$ (% w/w)	$\Delta_{1/2}$	$v_2$	$v'_2$	$\Phi$	$\Phi_A$	$\Phi_A v'_2 / (\Phi v_2)$
18	10	0.157	0.245	0.983	0.017	0.0270
18	30	0.146	0.250	0.885	0.115	0.222
18	50	0.136	0.260	0.817	0.183	0.429
21	10	0.159	0.248	0.69	0.310	0.700
21	30	0.153	0.262	0.69	0.310	0.769
21	50	0.145	0.279	0.69	0.310	0.864
27	10	0.160	0.252	0.11	0.89	12.74
27	30	0.164	0.284	0.36	0.637	3.06
27	50	0.160	0.316	0.48	0.520	2.14

species the isotropic phase. From equation (4)

$$\sum_{x=1}^{\infty} f_x^0 = 1 = \sum_{x=1}^{\infty} f_x + \sum_{x=1}^{\infty} f'_x \quad (5)$$

$$= \Phi \frac{v_2}{v_2^0} + \Phi_A \frac{v'_2}{v_2^0}$$

$v_2$  and  $v'_2$  are the volume fractions of solute in the isotropic and anisotropic phases respectively. Thus  $\Phi_A v'_2 / [\Phi v_2]$  is the ratio of the volume of solute in the anisotropic phase to the volume of solute in the isotropic phase. Table 1 lists  $v_2$ ,  $v'_2$ ,  $\Phi$ ,  $\Phi_A = 1 - \Phi$ , and the above ratio for all systems shown in Figures 2. We note that since the curves of  $f_x$  and  $f'_x$  for a given system, have essentially the same shape, the ratio of their areas,  $\Sigma f'_x / \Sigma f_x = \Phi_A v'_2 / [\Phi v_2]$ , is given, quite accurately, by the ratio of their peak heights, i.e.  $(f'_x)_{\max} / (f_x)_{\max}$ , so this ratio is readily judged by eye from the figures.

Consider now the sequence—Figures 2b, 2e and 2h, for which  $\Phi_A$  is constant (see Figure 1). As  $\Delta_{1/2}$  is increased the maxima in  $f_x$  and  $f'_x$  move apart; i.e. as the distribution is broadened the extent of partial fractionation between the phases is increased. Table 1, and the figures, show that the relative amount of polymer in the anisotropic phase increases as  $\Delta_{1/2}$  increases although  $\Phi_A$  is constant.

For the sequence—Figures 2a, 2d and 2g, the system starts as predominantly isotropic phase and ends up as predominantly anisotropic phase, with increasing  $\Delta_{1/2}$ , but with a steady increase in  $\Phi_A v'_2$  and a corresponding decrease in  $\Phi v_2$ . As  $\Delta_{1/2}$  increases the maxima in  $f_x$  and  $f'_x$  move apart, as for Figures 2b, 2e and 2h. For the sequence—Figures 2c, 2f and 2i the bi-phasic system starts off as predominantly anisotropic phase but as  $\Delta_{1/2}$  increases  $\Phi_A v'_2$  steadily decreases with a corresponding increase in  $\Phi v_2$ . Again the maxima in  $f_x$  and  $f'_x$  move apart as  $\Delta_{1/2}$  is increased. The variation of the amount of anisotropic phase with  $\Delta_{1/2}$  for Figures 2c, 2f and 2i contrasts with that for Figures 2a, 2d and 2g. Thus broadening the distribution for a bi-phasic material that is predominantly composed of anisotropic phase (Figures 2c, 2f, 2i) introduces more isotropic phase whereas for a bi-phasic material that is predominantly composed of isotropic phase (Figures 2a, 2d, 2g) broadening the distribution introduces more anisotropic phase.

We may examine the variations with  $c$  at fixed values of  $\Delta_{1/2}$ . For the sequence—Figures 2a, 2b and 2c, increase in  $c$  for a fairly-narrow distribution ( $\Delta_{1/2} = 10$ ) transforms

the bi-phasic material from essentially isotropic to essentially anisotropic phase (as expected from Figure 1) with very little partial fractionation with respect to molecular weight. For  $\Delta_{1/2} = 30$  Figures 2d, 2e and 2f show that as  $c$  is increased  $\Phi_A v'_2$  increases rapidly and there is a marked partial fractionation between the phases. Similar behaviour is seen for  $\Delta_{1/2} = 50$ , i.e. for Figures 2g, 2h and 2i, as  $c$  is increased. Note, however, that the maxima in  $f_x$  and  $f'_x$  move to lower values of  $x$  as  $c$  is increased for constant  $\Delta_{1/2}$ . Thus if we have a polymer of a given distribution of molecular weight and form two bi-phasic materials one of low overall polymer concentration,  $c_A$  say, in which the isotropic phase predominates, and one of high concentration,  $c_B$  say, in which the anisotropic phase predominates, then the average molecular weight of polymer in the two phases will obey the relations  $\langle M_{\text{iso},B} \rangle < \langle M_{\text{iso},A} \rangle$ ,  $\langle M_{\text{aniso},B} \rangle < \langle M_{\text{aniso},A} \rangle$ . More comprehensive calculations, including variation of  $x_0$  and their relation to our dielectric data for concentrated solutions of poly(n-hexylisocyanate) will be considered in a future publication<sup>16</sup>.

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