Model calculations of the phase behaviour of rod-like particles in solution: Polydisperse systems having asymmetric distributions of rod-lengths

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Model calculations have been made of the phase behaviour, and compositions of the phases in the biphasic range, for polydisperse rod-like particles in solution. The special cases of a most-probable distribution (m.p.d.), an empirically modified most-probable distribution and asymmetric Gaussian distributions are considered. It is shown that the presence of species of very low molecular length in the m.p.d. result in $v_p^0{**}$, the volume fraction of polymer for which the system becomes wholly-anisotropic, being close to unity and thus the biphasic range for the case of this distribution is far larger than that normally found experimentally. The empirically-modified m.p.d. gives a narrower biphasic range than that for the m.p.d. Calculations for the asymmetric Gaussian distribution make it clear that $v_p^0{**}$ is determined by the low molecular length species in the distribution whilst $v_p^0{*}$, the volume fraction of polymer at which the system goes from isotropic to biphasic, is determined by the high molecular length species of the distribution. It is suggested that these distributions and those considered earlier are unable to adequately explain the observed dielectric and viscosity behaviour of rod-like molecules in solution. It is necessary to introduce a small high molecular weight tail to a chosen distribution in order to obtain agreement betwee between the calculate and the observed behaviour.

Keywords Phase behaviour; liquid crystal polymers; rod-like particles; asymmetric molecular weight distribution

INTRODUCTION

It is now well-established for certain rod-like molecules in solution that isotropic, anisotropic and biphasic (isotropic + anisotropic) media may be formed. The early studies of poly-γ-benzyl-L-glutamate in concentrated solution by Robinson and coworkers[1,2] established the essential features of the phase-behaviour of such systems and many investigations were subsequently made[3,4]. More recently it was shown that certain aromatic polyamides[5-10] and poly(alkylisocyanates)[11-16] form lyotropic liquid crystals. The work for polyamides is of special interest since ultra high modulus fibres may be formed *via* the liquid-crystalline phase. There is now extensive documentation of the phase behaviour[1-17] and, importantly, it has recently been shown that a physical separation of the isotropic and anisotropic components of a bi-phasic system may be achieved by the force of gravity[11-15] or by ultra-centrifiguration[9,10].

The observed phase behaviour of rod-like molecules in solution has been successfully rationalized by Flory and coworkers[18-25] using a statistical mechanical model for rod-like particles in solution. They considered monodisperse and polydisperse systems where the latter involved either a 'most-probable'[23] or Poisson[23] distribution of rod-lengths. In addition, their calculations took into account temperature-dependent interactions between particles. The model calculations yield the critical concentration for the formation of the bi-phasic system, the critical concentration for the formation of wholly anisotropic phase, the volume fractions of polymer in the isotropic and anisotropic phases and the volume fraction of anisotropic phase in a bi-phasic system, and the distribution of species between isotropic and anisotropic phases. They showed that in a bi-phasic system composed of polydisperse rods the high-molecular length species favour the anisotropic phase. This important effect has been confirmed experimentally[9-16].

Whilst studies of concentrated solutions of rod-like molecules using polarized optical microscopy and bulk flow viscosity yield important information on the phase behaviour, further information is required at the molecular level in order to obtain a fuller understanding of the structure and dynamics of such systems. Moscicki and coworkers[26-28] made dielectric studies of two poly(alkylisocyanates) in solution covering the isotropic, bi-phasic and anisotropic ranges. As an aid to the interpretation of their results Moscicki and Williams[29,30] extended the calculations of Flory and coworkers to the case of a Gaussian distribution of rod-lengths where the average length and width of distribution were varied over wide ranges. In addition, the motion of the rods in the anisotropic phase was modelled by the theory of Warchol and Vaughan[31] and Wang and Pecora[32] which considers the free angular diffusion of rods within a virtual cone. Whilst the model calculations give a broadly-correct representation of the dielectric behaviour: i.e. the relaxation magnitude $\Delta\varepsilon$ and average relaxation time $\langle\tau\rangle$

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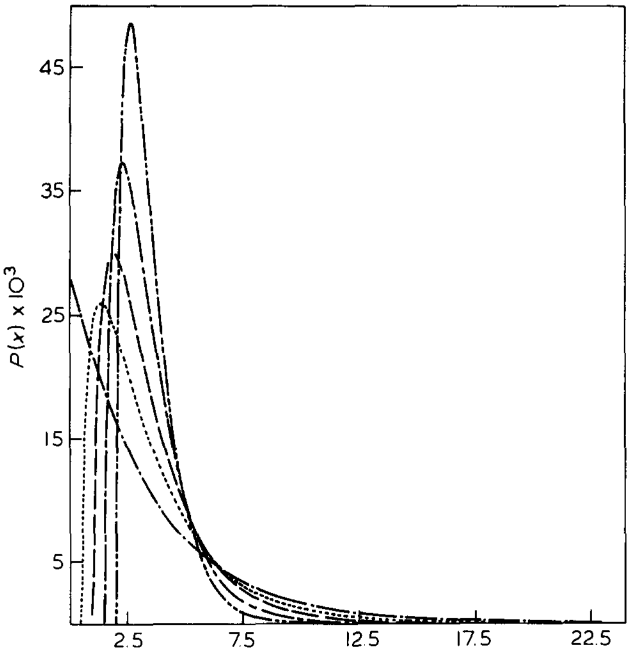

Figure 1 $P(x)$ against x for the most probable distribution with $p = 0.9714$ (—·—·—) and for a m.p.d. empirically-shifted from the origin (see equation (2)): curves indicated as (····), (— — — —), (- — -) and (— - - —) correspond to C_0 equal to 5, 10, 15 and 20 respectively

both increase to maximum values as polymer concentration increases but then decrease in the bi-phasic range. However the maximum value of the relaxation magnitude $\Delta\varepsilon_m$ occurred well within the biphasic range and this was not predicted using Gaussian or Poisson distributions since such distributions predict that $\Delta\varepsilon_m$ occurs exactly at $v_p^\circ = v_p^{\circ *}$ where $v_p^{\circ *}$ is the volume fraction of polymer at which the anisotropic phase forms in the isotropic phase. Similarly $\langle\tau_m\rangle$ was predicted to occur at $v_p^{\circ *}$. In order to obtain an improved simulation of the observed dielectric behaviour Moscicki and Williams[33] further extended the model calculations of the phase behaviour to the case where the total distribution comprises a 'basic' distribution (Gaussian, asymmetric Gaussian or Poisson) to which it added a high molecular weight 'tail'. It was shown that $v_p^{\circ *}$ was substantially reduced by inclusion of only a small relative amount of the high molecular length species, the reason being that the anisotropic phase formed in the initial part of the biphasic range is composed predominantly of those species. The subsequent simulation of the dielectric behaviour[34] incorporating the tail was found to be much improved over that which involved only a simple basic distribution. In particular, both $\Delta\varepsilon_m$ and $\langle\tau_m\rangle$ now occurred well within the biphasic range.

It was thus apparent[33,34] that the calculated phase behaviour of rod-like particles in solution could be significantly changed by incorporation of relatively small amounts of high molecular weight species. The experimental data for the viscosity of concentrated solutions of poly(n-alkylisocyanates)[11-16] and polyamides[9,10] showed that samples of approximately the same *average* molecular weight yielded very different plots for flow viscosity (η) against polymer concentration. In some cases the peak in η occurred at the concentration at which anisotropic phase first appears (optically) in the isotropic phase, but in the majority of studies η_m occurred well within the biphasic range. The interpretations of the experimental viscosity behaviour have been considered by Aharoni[16], Matheson[17] and Mosciki and Williams[33]. It is evident that the variations of the viscosity curves are closely associated with variations in molecular weight distribution on going from one sample to another. It is therefore of some interest to use model calculations based on the Flory model, as developed to date[18-25,29,30,33,34], to examine the phase behaviour and its variation as the form of the distribution is systematically varied. This has already been done to some extent for the most-probable Poisson and Gaussian distributions. For the most-probable distribution the parameter p which defines the number average rod-length *via* the relation[22,35] $\bar{x} = (1-p)^{-1}$ also determines the overall width and asymmetry of the distribution function. Thus as p is increased towards unity both $\bar{x}$ and the half-width of the distribution increase. For the Gaussian distribution Moscicki and Williams[29,30] varied the half-width $\Delta_{\frac{1}{2}}$ systematically for each given value of x_0 ($x_0 \simeq \bar{x}$, see ref. 30), for x_0 in the range 30 to 70 and also examined the variations as the amount of a high molecular weight tail (of variable form) was changed[33,34]. In the present paper we further examine the results for the most probable distribution (see following section) and, in view of recent experimental data for the distribution function for a model condensation polymer[36], examine the effects of empirically-shifting the origin of a most probable distribution to higher molecular weights and of varying the degree of asymmetry for an asymmetric Gaussian distribution. The aim of our model calculations is to see the trends in the phase behaviour and the compositions of the phases as the distributions are varied systematically so that a general physical understanding of such systems may be obtained which may aid interpretations of the optical, dielectric and viscosity data, independent of the detailed form of the distribution function.

THE MOST-PROBABLE DISTRIBUTION

Figure 1 shows, as one example, the number distribution function $P(x) = n_x/n_p^0$ for a most probable distribution (m.p.d.) function characterized by $p = 0.9714$. This value was chosen so that $\bar{x} = (1-p)^{-1} = 35$. Here n_x and n_p^0 are the number of x-meric species and the total number of polymer species, respectively, in a volume V. The resultant volume distribution is $f_x^0 = v_x^0/v_p^0$, where v_x^0 and v_p^0 are the volume fractions of x-meric species and polymer species, respectively, in the volume V and f_x^0 is given by[22]

$$f_x^0 = \frac{v_x^0}{v_p^0} = x(1-p)^{-2}p^{x-1} \qquad (1)$$

Figure 2 shows f_x^0 against x for $p = 0.9714$. We have calculated the volume fraction of anisotropic phase in a biphasic medium, Φ_A, and the volume fractions of polymer in the isotropic phase (v_p) and anisotropic phase (v_p'), and the Flory disorder parameter[22] y as a function of volume fraction of polymer v_p^0. The results are shown in *Figures 3–5*. Consider first the results for Φ_A, as shown in *Figure 3*. $\Phi_A > 0$ for $v_p^0 \geq 0.068$ (i.e. c.8% polymer): i.e. the isotropic range extends up to $v_p^{0*} = 0.068$ beyond which the system becomes biphasic. As v_p^0 is increased, Φ_A increases steadily, tending towards unity as $v_p^0 \to 1$. Thus for this case the biphasic range is extremely broad and is far broader than

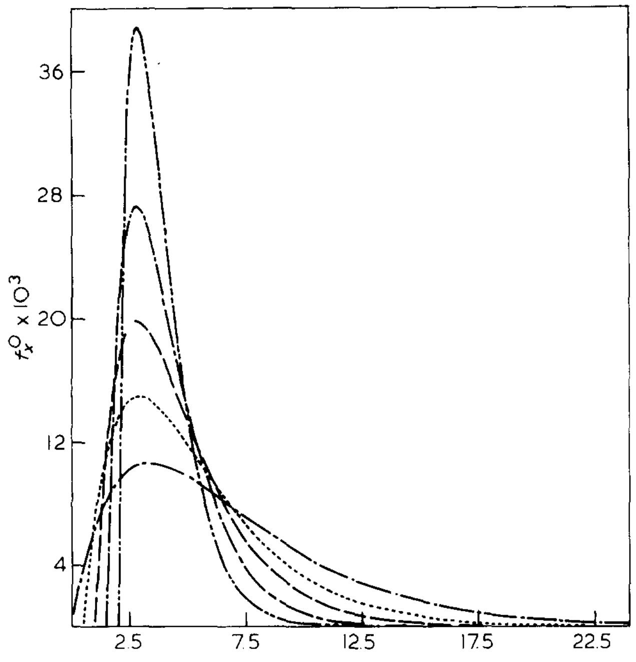

Figure 2 f_x^0 against x for the most probable distribution and for a m.p.d. empirically-shifted from the origin (see equation (2)). The notation is the same as that for the curves in *Figure 1*

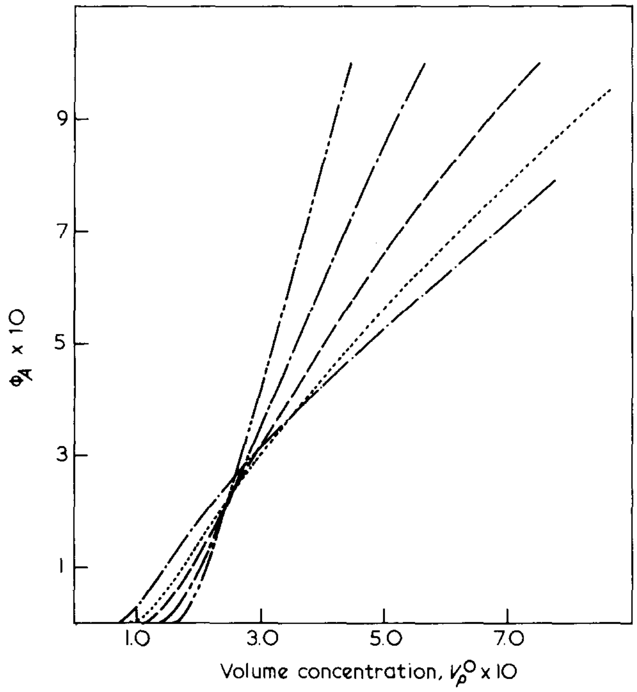

Figure 3 ϕ_A against v_p^0 for the distributions of *Figure 1*. The notation is the same as that for *Figures 1* and *2*. e.g. (— · — · —) is for m.p.d. with p = 0.9714

that normally found experimentally[9–16]. We note that a Poisson[23] or Gaussian[29,30] distribution may give a short range of existence for the biphasic system. For example Frost and Flory[23] gave results for a Poisson distribution with $\bar{x}=6$ which have $v_p^{0*}=0.22$ and $v_p^{0**}=0.41$ (see their Figure 6). Here v_p^{0**} is the volume fraction of polymer at which the wholly-anisotropic phase (i.e. $\Phi_A \simeq 1.0$) is formed. Thus in that case the biphasic range is characterized by $0.22 \leqslant v_p^0 \leqslant 0.41$. Moscicki and Williams[29,30] calculated v_p^{0*} and v_p^{0**} for a Gaussian distribution over a range of x_0 and $\Delta_{\frac{1}{2}}$ values. In general the biphasic range was rather narrow but was increased if x_0 was decreased and $\Delta_{\frac{1}{2}}$ was increased. For $x_0=30$ and $\Delta_{\frac{1}{2}}=20$, it was found[30] that the biphasic range was $0.225 \leqslant v_p^0 \leqslant 0.52$, this being an example of small x_0 and large $\Delta_{1/2}$. Flory and Frost[22] gave results for a m.p.d. with $p=0.875$ (i.e. $\bar{x}=8.00$) and $p=0.950$ (i.e. $\bar{x}=20.0$). Their results for Φ_A (see their Table 1 and Figures 4 and 6) were as follows. For $p=0.875$, $v_p^{0*}=0.15$ and Φ_A increases approximately quadratically with respect to the variable v_p^0 reaching $\Phi_A=0.78$ for $v_p^0 \rightarrow 1.0$. So for chains of such a short average length and having a m.p.d. the wholly-

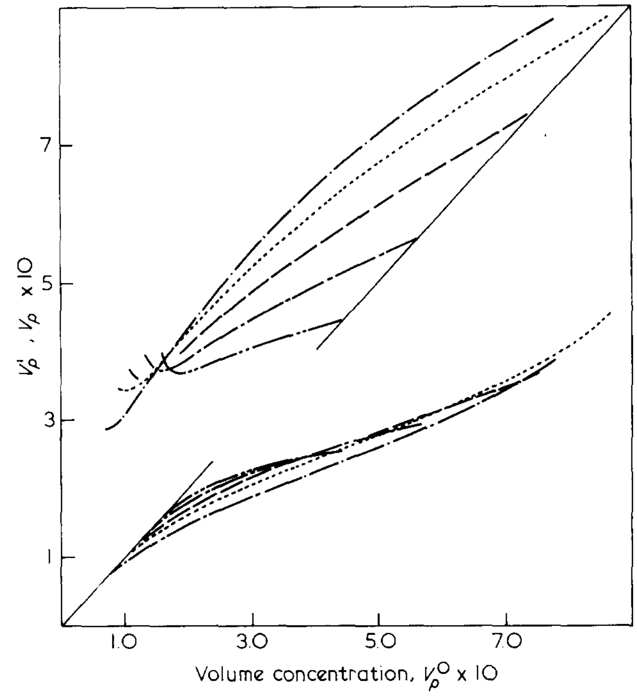

Figure 4 v_p (lower curves) and v_p' (upper curves) against v_p^0 for the distributions of *Figure 1*. The notation is the same as that for *Figures 1–3*. e.g. (· · · ·) is for an empirically-modified m.p.d. with $C_0 = 5$

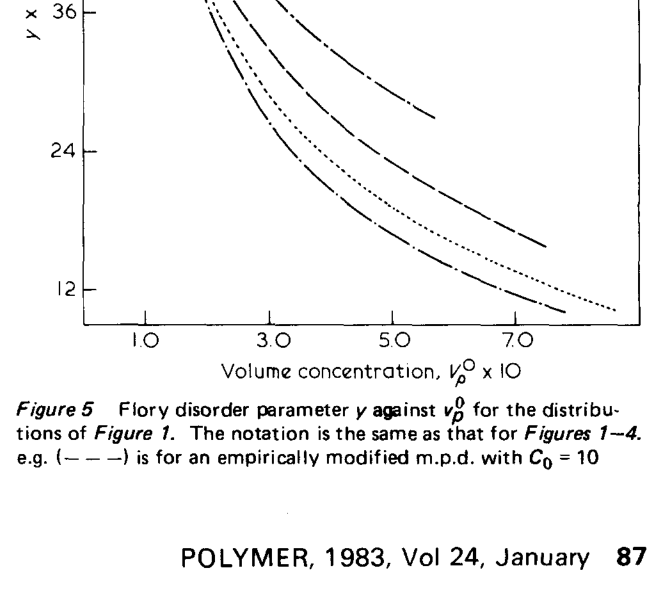

Figure 5 Flory disorder parameter y against v_p^0 for the distributions of *Figure 1*. The notation is the same as that for *Figures 1–4*. e.g. (— — —) is for an empirically modified m.p.d. with $C_0 = 10$

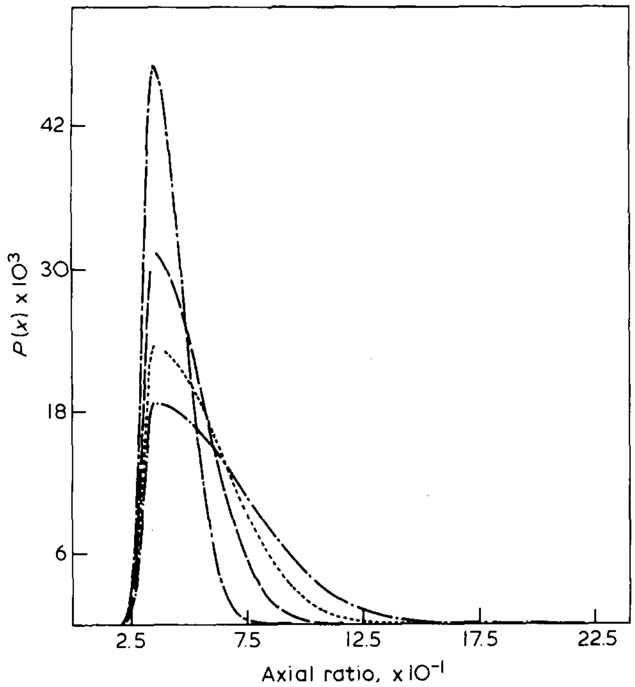

Figure 6 $P(x)$ for asymmetric Gaussian distributions. Curves denoted as (—.—.—), (. . . .), (— — —) and (— - — -) all correspond to a lower-half-width equal to 10 and with upper half-width equal to 90, 70, 50 and 30 respectively

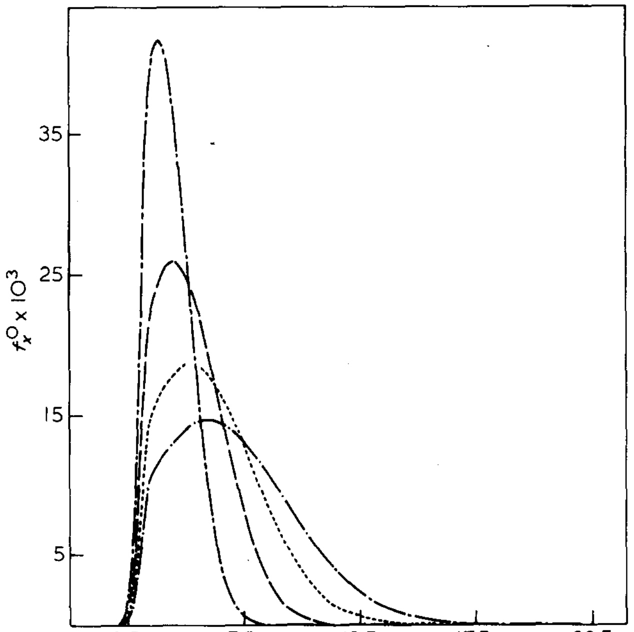

Figure 7 f_x^0 for the asymmetric Gaussian functions of *Figure 6*. The notation is the same as in *Figure 6*

anisotropic phase is not attained. For $p=0.950$, $v_p^{0*}=0.13$ and Φ_A increases approximately linearly with increasing v_p^0, reaching unity at $v_p^0=1.0$. This is quite similar to the behaviour shown in *Figure 3* for $p=0.9714$. From these results we conclude that the m.p.d. appears to always give a very broad biphasic range, and that this is far broader than is normally observed experimentally[9-16].

Figure 4 shows plots of v_p and v'_p for the m.p.d. with $p=0.9714$. For $v_p^0<v_p^{0*}$ we have $v_p=v_p^0$ and $v'_p=0$ (isotopic behaviour). For $v_p^0>v_p^{0**}$ we would have $v'_p=v_p^0$ and $v_p=0$ (wholly-anisotropic behaviour), but since v_p^{0**} is closed to unity, this is not evident in our results. Note that in the biphasic range v_p and v'_p increase steadily with icreasing v_p^0 giving v'_p/v_p in the range 3 to 2.7 as v_p^0 is increased to unity. For completeness, *Figure 5* shows y against v_p^0 for the m.p.d. having $p=0.9714$. y falls steadily with increasing v_p^0, reaching values close to unity. We have also calculated the quantities[22,23] $f_x=(1-\Phi_A)v_p/v_p^0$ and $f'_x=\Phi_A v'_p/v_p^0$ which gives the amounts of x-meric species in isotropic and anisotropic phases, respectively, and hence give information on the partitioning of the species between the two phases. These results will not be given here but they are entirely consistent with the behaviour already fully described for the m.p.d. by Flory and Frost[22].

EMPIRICAL MODIFICATIONS OF THE MOST PROBABLE DISTRIBUTION

Cotts and Berry[36] showed (their Figure 7) that the molecular weight distribution curve determined for the condensation polymer poly([benzo 1,2-d:5,4-d′)bisoxazole-2,6 diyl]-1,4-phenylene) was qualitatively different from that calculated for a most-probable distribution. It was found that, relative to a m.p.d., there was a depletion of components of very low and high molecular weight. As a first approximation to the form of the observed distribution we have empirically; modified the m.p.d. (to give the net depletions) as follows.

We write

$$f_x^0=C_0+x(1-p)^{-2}p^{x-1} \qquad (2)$$

The second term is recognized from equation (1) and C_0 is a displacement factor. We have made calculations for different values of C_0 in the range 5 to 20, choosing p in each case so as to retain $\bar{x}=35$. *Figure 2* shows the curves for f_x^0 whilst *Figure 1* shows the curves for $P(x)$. A comparison of the curves in *Figure 2* shows that low and high molecular length species are depleted, and the asymmetry of the successive curves decreases, as C_0 is increased. We note that the model curve for $C_0=15$ (---) is a fair representation of the experimental curve of Cotts and Berry[36]. *Figure 3* shows that as C_0 is increased (i) v_p^{0*} *increases*, due to depletion of high molecular length species, (ii) v_p^{0**} *decreases*, due to depletion of low molecular length species. Thus the biphasic range $v_p^{0*}\leqslant v_p^0\leqslant v_p^{0**}$ is markedly decreased as C_0 is increased. It is clear from these calculations, and those to be given in the following section, that the m.p.d. gives too large a biphasic range principally because the low molecular length species in this distribution prevent v_p^{0**} occurring at reasonably low values. *Figure 4* shows v_p and v'_p against v_p^0 for different values of C_0. v_p increases with increasing v_p^0 but at a rate which is far smaller than that in the isotropic phase (where $v_p=v_p^0$). As C_0 is increased the successive curves for v_p become closer, appearing to tend to a limiting behaviour. The curves for v'_p go to progressively lower levels as C_0 is increased. The qualitative interpretation is that, for a given value of v_p^0 in the biphasic range, as C_0 is decreased (see *Figure 2*) v'_p has to increase in order to maintain the stable anisotropic phase in the presence of an increasing amount of *low* molecular length species. Such an interpretation is also obtained for calculations based on a Gaussian distribution (see ref. 30, Figures 5 and 12) and for the asymmetric Gaussian function (following section). The Flory parameter y increases markedly as C_0 is increased (*Figure 5*).

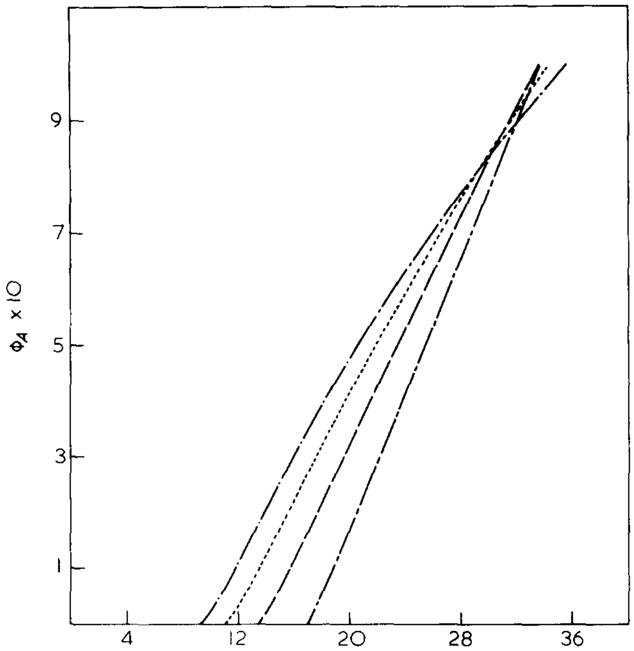

Figure 8 Φ_A against v_p^0 for the distributions of *Figure 6*. The notation is the same as that for *Figures 6* and *7*

ASYMMETRIC GAUSSIAN DISTRIBUTION FUNCTION

In order to see how the phase behaviour is changed on changing the relative amounts of high and low molecular length species whilst maintaining a fixed value of $\bar{x}$, we have made calculations using an asymmetric Gaussian function $P_L^H(x)$ which takes on different Gaussian forms below and above x_0. The Gaussian function itself may be conveniently written as [29,30]

$$P(x)=\frac{n_x}{n_p^0}=\exp\left(-\left[4\ln 2\left(\frac{x-x_0}{\Delta_{\frac{1}{2}}}\right)^2\right]\right) \qquad (3)$$

Figure 6 shows the 'piece-wise' $P_L^H(x)$ for $x_0=35$ and for the lower-half-width (L) equal to 10 and for the upper-half-width (H) equal to 30, 50, 70 and 90. The corresponding curves for f_x^0 are shown in *Figure 7*. The main qualitative difference between the curves of *Figure 7* is that the high molecular length 'tail' is being markedly increased as H is increased. The results are shown in *Figures 8–10*. As H is increased v_p^{0*} steadily decreases from 0.17 to 0.095, but v_p^{0**} is hardly changed. This shows that the high molecular length species effectively determine the value of v_p^{0*} (an important observation) *and* that the low molecular length species determine v_p^{0**}. Note that the absence of low molecular length species (c.f. the m.p.d.) in these calculations allows v_p^{0**} to occur as reasonably low values and hence allows the biphasic range to be narrow. *Figure 9* shows v_p and v_p' against v_p^0 and we see that as H increases the v_p curves move to lower values in a parallel manner whilst the v_p' curves become increasingly separated as v_p^0 is decreased. As for the results in the previous section, v_p' curves displace to higher values as the distribution becomes relatively richer in low molecular length species in order to sustain a stable anisotropic phase: i.e. the greater the proportion of short chains in the distribution the higher must v_p' become. *Figure 10* shows curves for the parameter y and we see that the values are substantially above unity in all cases (c.f. the m.p.d. curve in *Figure 5*).

DISCUSSION

It is clear from the above that the most probable distribution predicts an extremely broad biphasic range such that $v_p^{0*}<0.1$ and $v_p^{0**}\sim 1$. The main difficulty arises from the low molecular length species present in this distribution which lead to large values of v_p^{0**}. The empirical modification of the m.p.d., which gives depletions of both low and high molecular length species, leads to a marked decrease in v_p^{0**} (hence markedly decreasing the biphasic range) and to a less-marked, but clearly seen, increase in v_p^{0*}. These results are more in accord with actual systems[9–16] for which the biphasic range typically occurs for $0.15<v_p^0<0.35$. The calculations for the asymmetric Gaussian reinforce the idea that low molecular weight species effectively determine v_p^{0**}, and thus effectively determine the extent of the biphasic range, and that high molecular weight species effectively determine v_p^{0*}. The constancy of v_p^{0**} in *Figure 8* is due to the constancy of the distribution of $P(x)$ on the low molecular length side of the peak (*Figure 7*) and this is very good evidence that v_p^{0*} is effectively determined by the low molecular length species in the distribution.

Our dielectric studies[26–28] had shown that the dielectric increment $\Delta\varepsilon$ and maximum loss factor ε_m'' increased nearly linearly through v_p^{0*} for a poly(n-hexylisocyanate) and reached their maxima well-within the biphasic range before sharply decreasing as v_p^0 was increased towards v_p^{0**}. Given the observation that the curves for v_p against v_p^0 show a marked decrease in slope at v_p^{0*} (*Figures 4* and *9*) and that the high molecular length species partially fractionate into the anisotropic phase for $v_p^0>v_p^{0*}$, it is not possible to obtain $\Delta\varepsilon$(calc.), using the

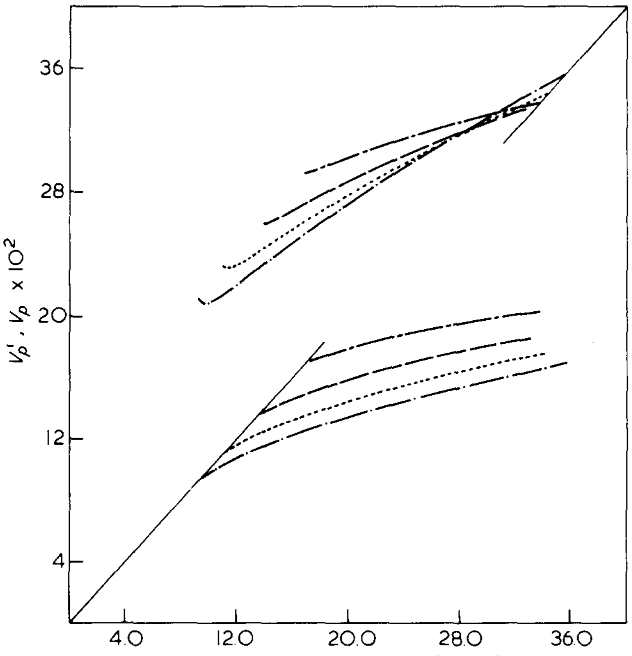

Figure 9 v_p (lower curves) and v_p' (upper curves) against v_p^0 for the distributions of *Figure 6*. The notation is the same as that in *Figures 6–8*

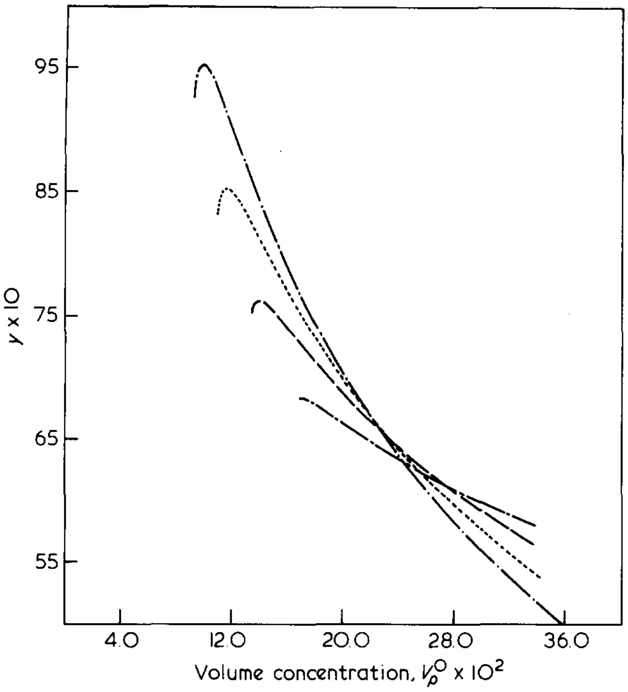

Figure 10 Flory disorder parameter *y* against v_p^0 for the distributions of *Figure 6*. The notation is the same as that in *Figures 6–9*

present distributions, which increases nearly linearly through v_p^{0*} as for the experimental result. Neither is this possible using the Gaussian[29,30] or Poisson[23] distributions considered earlier. This reinforces our conclusion[33] that such experimental behaviour may result if a small high molecular weight 'tail' is present which acts as a perturbation on the behaviour of the system as a whole but gives a very significant decrease in v_p^{0*} (by as much as a factor of two) since the high molecular weight tail is largely responsible for the formation of the anisotropic phase just above v_p^{0*}. Calculations of the dielectric behaviour assuming such a tail[33,34] give a good simulation of the experimental results.

It is apparent that the viscosity behaviour of poly(alkylisocyanates)[11–16] and aromatic polyamides[5–10] varied from sample to sample, as was indicated above. The present calculations show that v_p^{0*}, v_p^{0**}, Φ_A, v_p and v_p' are strongly dependent on the form of the distribution. It seems likely that the variations from sample to sample reflect variations in the high molecular weight portions of the distribution. The occurrence of η_m well within the biphasic range may arise primarily since v_p^{0*} is determined by a small high molecular weight tail in the distribution so η_m really gives information on the condition when the main part of the distribution function enters the anisotropic phase—which leads, at slightly higher values of v_p^0, to the phase inversion 'anisotropic in isotropic'→isotropic in anisotropic'. If these ideas are correct we would predict that the viscosity of the isotropic component of the biphasic system would show a marked increase in viscosity with increasing v_p^0 for $v_0^0 < (v_p^0)_m$, where the latter is the volume fraction for which $\eta = \eta_m$ for the biphasic system.

The present and earlier model calculations[18–25,29,30] serve as a useful predictor of the variation in phase behaviour of rod-like molecules in solution as the molecular weight and its distribution are systematically varied. Our calculations[29,30,33] are based on entropy considerations alone and do not include the effect of temperature-dependent specific interactions between molecules. Such interactions are important and have been investigated by Flory and coworkers for certain systems[18–25]. Temperature does have an effect on v_p^{0*} and the dielectric relaxation behaviour of poly(n-hexylisocyanate) in concentrated solution[26,28]. Whilst this may be interpreted as being due to the variation in the specific interactions between molecules with temperature, it seems likely that the departures of the molecules from rod-like behaviour, with a tendency to form multiple broken rods at high temperature, is also an important factor which needs to be included in further model calculations for such systems.

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