Rigid backbone polymers, XVII: Solution viscosity of polydisperse systems

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When plotted against concentration v_2^0, the viscosity η^0 curve of isotropic solutions of lyotropic nematic mesomorphic polymers increases according to:

$$\eta^0=\eta_0[[\eta]v_2^0+(\pi/4)[\eta]^2(v_2^0)^2+K_2(\ln\bar{x})^2[\eta]^3(v_2^0)^3+\ldots]$$

in which η_0 is the solvent viscosity, K_2 a numerical constant, $\bar{x}$ is the average molecular axial ratio and $[\eta]$ the intrinsic viscosity as defined by:

$$[\eta]=\frac{2\bar{x}^2}{45}\quad\frac{1}{\ln 2\bar{x}-1.84}+\frac{3}{\ln 2\bar{x}-0.61}\left(+\frac{14}{15}\right)$$

At the concentration v_2^* an anisotropic phase appears and the viscosity curve shows a decrease in slope followed by a change in direction at a peak viscosity η^p at v_2^p. Upon further increase in v_2^0 the system undergoes a phase inversion and finally turns fully anisotropic at v_2^A. In the biphasic interval the viscosity is described by:

$$\eta^0=\eta_{\mathrm{mat}}\quad 1+\frac{(5\lambda+2)}{2(\lambda+1)}\,v_{\mathrm{inc}}$$

where $\lambda=\eta_{\mathrm{inc}}/\eta_{\mathrm{mat}}$, the ratio of the inclusions viscosity to the matrix viscosity, and v_{inc} the volume fraction of the inclusions in the system. It must be emphasized that the molecular weight of the polymer in both phases changes continuously with concentration, resulting in commensurate changes in η_{ince}, η_{mat} and their ratio λ. In the anisotropic region the viscosity first decreases moderately and then increases precipitously with v_2^0, according to:

$$\eta^0=\eta_0\left[\frac{2\bar{x}^2}{90S}\left(\frac{5}{\ln 2\bar{x}-1.8}+\frac{6}{\ln 2\bar{x}-0.61}\right)+2\right]^{\frac{v_2^0}{1-\frac{V_{25^\circ}}{V_E}}}$$

in which S is an order parameter and V_{25°, V_E are volumes swept by the orbits of the flowing rodlike macromolecules. The equations give results in good qualitative and fair quantitative agreement with experimental data in the literature.

INTRODUCTION

High molecular weight rigid backbone polymers may exhibit in solution the unique property of lyotropic nematic mesomorphicity (liquid crystallinity) once they surpass a certain critical volume concentration v_2^*. In the concentration interval $0<v_2^0<v_2^*$ the solution is completely isotropic and the total concentration v_2^0 equals the concentration of the isotropic phase v_2.

When a solid polymer capable of lyotropic mesomorphicity is gradually diluted, it first passes into a single anisotropic (oriented) liquid crystalline phase of concentration v_2'. The point where isotropic inclusions in the anisotropic matrix appear upon dilution or disappear upon concentration, is characterized by a polymer concentration v_2^A. Above it, $v_2^0=v_2'$. In the concentration interval $v_2^*\leqslant v_2^0\leqslant v_2^A$ there exist two phases, isotropic and anisotropic. If allowed a period of days or weeks the phases will separate into two layers, but when first appeared and during viscosity measurements the phases are microscopically intermingled, are not at a state of true equilibrium, and may be identified by such means as cross-polarized light microscopy. The spontaneous phase transitions at v_2^* and v_2^A were observed by many workers. Theoretical treatments of the phase transitions, based on thermodynamics[1-15] and molecular dynamics[5] were reasonably successful in explaining the phenomena. In the treatment of Flory[3,4,6-13], the parameters required for the prediction of phase transitions were experimentally measurable, a fact that contributed to the wide acceptance of his work.

A characteristic feature of the systems is that the total viscosity η^0 of the system containing one or two liquid phases, passes through a pronounced maximum when plotted as a function of the concentration v_2^0. Following Hermans[16] it became customary to identify the peak in viscosity with the concentration v_2^*; that is, the solution was assumed to be fully isotropic in the concentration interval $0<v_2<v_2^*$ and then abruptly change to anisotropic in the range $v_2'>v_2^*$. As will be shown in this work,

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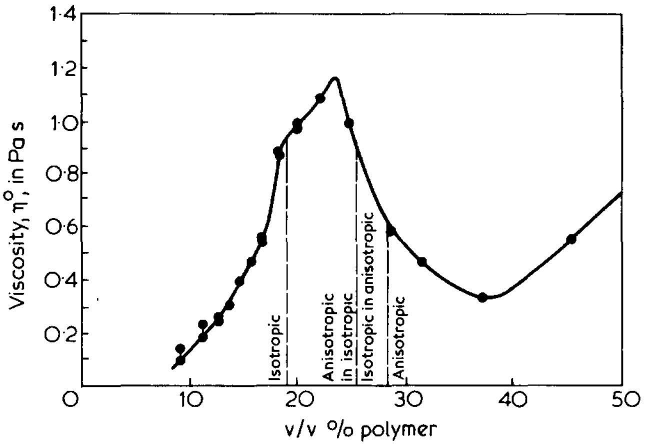

Figure 1 Viscosity as a function of polymer concentration for the system poly (50% n-hexyl + 50% n-propyl) isocyanate of M_W = 41 000 in toluene at 25°C

the identification of the peak in the viscosity curve with v_2^* is implausible. Furthermore, our observations[17–21] on the systems poly(n-alklisocyanate)/solvent and poly(n-alkyl + aralkyl)isocyanate/solvent indicated that the point v_2^* occurs at a concentration lower than v_2^p, the concentration associated with the viscosity peak, η^p. Similar observations were reported by Iizuka[22] and Kiss and Porter[23] on solutions of poly(γ-benzyl-L-glutamate) (PBLG) in several solvents. Our observations indicate further[20,21] that the solution does not become fully ansiotropic once v_2^p is surpassed, the point v_2^A is reached only after a substantial reduction in η^o, from η^p to η^A. A similar observation was mentioned by Iizuka[22]. The experimental observations indicate that $0 \ll v_2^* < v_2^p < v_2^A < 1.0$, and that the corresponding viscosities follow the relationship $0 < \eta^* < \eta^p > \eta^A \ll \eta^s$, η^s being the viscosity of the polymeric system in the gel or solid state. The data were determined by two techniques: measurements of the total viscosity η^o of the system as a function of v_2^o, and microscopic observations in cross-polarized light.

In *Figure* 1 a plot of the viscosity η^0 vs. concentration v_2^0 for poly(50% n-hexyl + 50% n-propyl)isocyanate in toluene is shown[20,21]. The weight average molecular weight of the polymer was $M_w = 41\,000$. In the figure the concentrations at which phase transitions were observed by means of cross-polarized light microscopy are also shown. The figure is typical of several other polyisocyanate/solvent systems[21].

The curve in *Figure* 1 has four important features: (1) The rate of increase of viscosity with concentration becomes smaller once the anisotropic phase makes its first appearance at v_2^*, and a shoulder develops on the curve. (2) The peak in the curve is at a concentration v_2^p substantially above v_2^*. (3) The point of phase inversion is between v_2^p and v_2^A. (4) The point v_2^A occurs at a concentration smaller than the concentration associated with η_{min} the viscosity minimum on the high concentration side of the viscosity peak. The shoulder observed by us in many polyisocyanate/solvent systems[21] in the close vicinity of v_2^* was observed by Iizuka[22] and Kiss and Porter[23] on the low concentration slope of the viscosity curves of PBLG/SOLVENT systems.

Our microscopic observations on lyotropic liquid crystalline polyisocyanides[24] and polyisocyanates[17–19] indicated that the anisotropic phase in the concentration interval $v_2^* < v_2^0 < v_2^p$ preferentially adopts the form of spherical droplets supended in an isotropic matrix. Similar observations were reported by Robinson[25] on PBLG in several solvents. However, polymers such as cellulose derivatives and aromatic homo- and copolyamides do not exhibit well-defined droplets of the anisotropic phase suspended in the isotropic matrix. In these cases, the preferred appearance under the cross-polarized light microscope is in the form of ill-defined highly birefringent blotches of the anisotropic phase fading at their boundaries into the isotropic non-birefringent matrix. With increased concentration, the fraction of the area in the field of vision that exhibits birefringence increases until it becomes the major phase, carrying the isotropic phase as poorly defined inclusions in an anisotropic matrix. Beyond v_2^A, the system becomes fully anisotropic and the last vestiges of isotropy disappear. In only very few instances were we able to observe anisotropic droplets, in cellulose derivatives or aromatic polyamide systems, similar to the few shown in *Figure* 10 of Morgan's paper[26]. Our conclusion is that the anisotropic phase of polyisocyanides, polyisocyanates and PBLG makes its initial appearance preferentially in the form of well-defined droplets, while the anisotropic phases of aromatic polyamides and cellulose derivatives appear preferentially as ill-defined birefringent blotches. Literature data[26,27] indicate the viscosity curves of such polymers to be rather smooth in the $v_2^0 < v_2^p$ range and to exhibit no shoulders. In our laboratories, attempts to detect the shoulder on a viscosity curve of a mesomorphic aromatic copolyamide have failed. The above observations lead us to conclude that the appearance of a shoulder on the viscosity curve at about v_2^* is associated with the appearance of the anisotropic phase in the form of well-defined spherical droplets, floating in the isotropic matrix. Therefore, the following treatment of the biphasic interval, $v_2^* < v_2^0 < v_2^A$, will be limited to systems in which the anisotropic phase makes its first appearance in the form of spherical droplets. The gross conclusions obtained from such a treatment are most likely to be applicable to systems in which the anisotropic phase adopts an ill-defined blotchy form. One should not expect, however, that this treatment will be applicable in every detail.

In the following sections the isotropic regime, the biphasic interval and the anisotropic region will be treated. The approach will be based upon experimental observations. At the same time physical and rheological arguments will be invoked in order to explain and predict the viscosity behaviour of the system.

THE ISOTROPIC REGIME

In the limit of zero shear, let η denote the viscosity of a dilute isotropic suspension of macromolecules in a solvent whose viscosity is η_0. Then $(\eta - \eta_0)/\eta_0 = (\eta/\eta_0) - 1 = \eta_{sp}$ the specific viscosity. Letting c denote the concentrations of the suspended matter and noticing that it may be replaceable by the volume fraction v_2^0, η_{sp}/c defines the reduced viscosity, and its limiting value at $c = 0$ is the intrinsic viscosity $(\eta_{sp}/c)_{c=0} = [\eta]$.

It was shown by Huggins[28] and Simha[29] that η_{sp} can be written as a power series of the type

$$\eta_{sp} = [\eta]c + a_2c^2 + a_3c^3 + \dots \qquad (1)$$

that the coefficients a_i are related to each other as

$$a_2 = k_1[\eta]^2,\ a_3 = k_2[\eta]^3, \ldots$$

and that η_{sp} can therefore be written as

$$\eta_{sp} = [\eta]c + k_1[\eta]^2c^2 + k_2[\eta]^3c^3 \ldots \qquad (2)$$

where the constants k_i are numerical constants independent of the shape of the molecules. The magnitude of the intrinsic viscosity depends on the shape of the suspended (solute) particles. For a dilute suspension of monodisperse solid spheres, $[\eta] = 2.5$[30,31] and is known as the Einstein coefficient.

For a suspension of non-spherical molecules, modelled by dumb-bells or rods, Simha[29] derived:

$$\eta_{sp} = [\eta]c + k_1[\eta]^2c^2 + \ldots \qquad (3)$$

where $k_1 = 0.77$ and

$$[\eta] = (3/2)(L^2/d^2) = (3/2)x^2 \qquad (4)$$

with x being the axial ratio of the particle length L to its diameter d. Riseman and Ullman[32] obtained $k_1 = 0.73$, indicating that a measure of variability around $k_1 = 0.77$ is possible. In fact, a value of $k_1 = 0.75$ was experimentally obtained by Hermans[16] from dilute solutions of PBLG in the highly viscous solvent *m*-cresol at low shear stresses.

An intrinsic viscosity value was derived by Eisenschitz[33] for long prolate ellipsoids of axial ratio f in the absence of Brownian motion:

$$[\eta] \approx \frac{f^2}{15(\ln 2f - 1.5)} \qquad (5)$$

where $f = a_1/a_2$ with a_1 being the major axis and a_2 the minor axis of the ellipsoid. This derivation was predicated on an assumption that the particles are distributed isotropically before the onset of motion and that subsequently each particle moves in a fixed orbit[34]. Simha[35] derived the intrinsic viscosity of prolate ellipsoids of $f \gg 1$, accounting for the influence of Brownian motion, and obtained:

$$[\eta] = \frac{f^2}{15(\ln 2f - 1.5)} + \frac{f^2}{5(\ln 2f - 0.5)} + \frac{14}{15} \qquad (6)$$

As the volume of an ellipsoid of axes a_1, a_2 is not the same as that of a cylinder of the same length and diameter, a correction factor of

$$x = f(2/3)^{-1/2} \qquad (7)$$

determined by Tanford[36], may be introduced into equations (5) and (6) with the following results:

$$[\eta] \approx \frac{2x^2}{45}\left(\frac{1}{\ln 2x - 1.84}\right) \qquad (8)$$

and

$$[\eta] = \frac{2x^2}{45}\left(\frac{1}{\ln 2x - 1.84} + \frac{3}{\ln 2x - 0.61}\right) + \frac{14}{15} \qquad (9)$$

For prolate ellipsoids $[\eta] > 2.5$ in all cases. For $x = 10$, equation (8) yields $[\eta] = 3.85$ and equation (9) yields $[\eta] = 10.37$. Also, $[\eta]$ increases with x. The reasonable agreement between the experimental data of rodlike PBLG[16] and equation (3), and through it equation (4), indicates that in relatively dilute solutions under low shear stresses the hydrodynamic behaviour of rodlike particles is very close to that of long and thin prolate ellipsoids, or that the experimental techniques are not refined enough to differentiate between them.

The effects of increased concentration on viscosity may be visualized in terms of excluded volume. Thus, in very dilute solutions there is no overlap of the excluded volume of all the solute particles and equation (2) reduces to $\eta_{sp}/c \simeq [\eta]$. With increased concentration the excluded volumes of pairs of solute particles start overlapping each other. At this point the second term in the righthand side of equation (2) becomes important. It was shown by Onsager[1] that the exact magnitude of the 'covolume' of two cylinders, i.e. the overlapped part of the excluded volume, is a product of the axial ratios, of the angle of approach between one another, and of a constant independent of particle shape or angle. The value of the constant, $\pi/4$, is 0.785, reasonably close to the value determined by Simha[29] for k_1, namely 0.77. As the particle concentration further increases, three particle collisions gain in importance and their effects become measurable. In this case the 'covolume' of the excluded volume of three rods was shown by Onsager[1] to be a product of an independent constant, of ($\ln x$) and of a factor depending on d and L to the third power. When the definition of equation (4) is inserted into equation (2), then the cubic term shows a dependence on x^6. Therefore, it appears that k_2 in the third term on the righthand of equation (2) should be replaced by a product of a new constant and $(\ln x)^2$:

$$k_2 = K_2(\ln x)^2 \qquad (10)$$

which brings the power series of the specific viscosity, equation (2), and the excluded volume approaches to show the same sixth power dependence of x in the third term of the expansion.

Assembling the above into a single equation, one obtains:

$$\eta_{sp} = [\eta]c + (\pi/4)[\eta]^2c^2 + K_2(\ln x)^2[\eta]^3c^3 + \ldots \qquad (11)$$

where $[\eta]$ for rigid backbone macromolecules adopting a rodlike conformation is defined by equation (9). Equation (11) is almost the same as one obtained by Matheson[37] by considering the treatments of Simha[29,35] and Doi[38]. The numerical value of K_2 and its independence from x are not known yet, but may be evaluated from the fit of experimental results to equation (11).

In the range of interest, the polymer concentration is relatively high. This leads to high values of the viscosity η that are larger than the solvent viscosity η_0, usually by an order of 10^3. Therefore, one can approximate the specific viscosity by $\eta_{sp} \approx \eta/\eta_0$. Also, because of the magnitude of η and the large ratio of η/η_0, it appears that in the concentration range of interest, where the three terms of equation (11) are evident, the solution viscosity and the specific viscosity may be of the same order of magnitude. Observations on isotropic solutions of high η or high η_{sp} lead to the same conclusions.

When η or η_{sp} are plotted on log–log paper against c or against the molecular weight M, then a linear dependence of the viscosity on c or M is observed. Experimental observations[27,39,40] indicate that in the limit of zero shear, the viscosity within the isotropic regime is related to c as:

$$\eta \propto c^{\beta} \text{ with } 5.3 \leqslant \beta \geqslant 3.5 \qquad (12)$$

For the same set of data[27,39,40] the dependence of η on M showed the proportionality of:

$$\eta \propto M^{\alpha} \text{ with } 8 > \alpha \geqslant 5.25 \qquad (13)$$

In all cases of rigid backbone polymers, the ratio of α/β was larger than unity. The data from ref 40, for example, give $\beta = 4.05$ and $\alpha = 6.35$, $\alpha/\beta = 1.57$. The relationship between α and β may be explained as follows: from equation (2) one may represent the solution viscosity by:

$$\eta \propto ([\eta]c)^{\beta} \qquad (14)$$

In the limit of zero concentration the intrinsic viscosity follows the Mark–Houwink relationship

$$[\eta] = KM^{a} \qquad (15)$$

where K is a characteristic constant. It follows from equation (14) and (15) that[41]:

$$\eta \propto c^{\beta} M^{a\beta} \qquad (16)$$

with

$$a = \alpha/\beta \qquad (17)$$

Ridgid backbone polymers follow a dependence of $a > 1$ in their Mark–Houwink relationship. Therefore $\alpha/\beta > 1$ as observed[27,39,40]. In the case of flexible polymers $a < 1$. Here the exponent β in equation (12) will be larger than the exponent α in equation (13)[27,40–44]. The fact that for rigid backbone polymers with $a > 1$, $\alpha > \beta$ helps in understanding the changes in the viscosity within the biphasic interval.

The above discussion applies to monodisperse polymers where the number average molecular weight, M_n, equals the weight average molecular weight, M_w. In the reality of rigid backbone polymers the polymers are polydisperse with $M_w > M_n$. In the case of condensation polymers prepared under equilibrium conditions, such as poly-*p*-benzamide (PBA) or poly-*p*-phenyleneterephthalamide (PPTPA), the ratio of M_w/M_n is ~ 2. The anionically prepared polyisocyanates exhibit $1 < M_w/M_n < 2$. For flexible polymers, the relationship

$$\eta = M^{3.4} \qquad (18)$$

appears to be valid when $M = M_w$[45] and not when $M = M_n$. The solution viscosity of flexible polymers follows the same exponential dependences on (cM) when $M = M_w$[45]:

$$\eta = (cM)^{3.4} \qquad (19)$$

From the work of Papkov *et al.*[27] and Baird and Ballman[40], the relationships in equations (12) and (13) for rigid backbone polymers follow a dependence on M_w and not on M_n, as for flexible polymers.

The viscosity of an isotropic solution of a polydisperse polymer may be visualized as arising from the summation of the viscosities of all the contributing molecular weight species in the polymer:

$$\eta \propto \Sigma c_i^{\beta} M_i^{\alpha\beta} \qquad (20)$$

where $\Sigma c_i = c$ and the molecular weight of the species M_i is measured in terms of M_w. In the case of phase separation, where the polymer partitions into two coexisting solutions in a manner such that the concentration and molecular weight distribtuion (*MWD*) are not the same in both phases, then the effects of *MWD* on their viscosities is expected to be profound. The concentration where the phase separation of monodisperse polymers takes place was approximated by Flory[4] to be at

$$v_2^* \simeq (8/x)(1 - 2/x) \qquad (21)$$

which for large x may be simplified further to give

$$v_2^* \simeq 8/x \qquad (22)$$

For polydisperse systems x should be replaced by its number average value $\bar{x}_n^0$, averaged over all molecular weight species in the polymer. In terms of weight average molecular weights, equation (22) may be rewritten as

$$v_2^* \approx \frac{8(M_w/M_n)}{\bar{x}_w^0} \qquad (23)$$

The average axial ratio $\bar{x}_n^0$ of the polymer in *Figure* 1 was determined as ~ 40. Equation (21) yields $v_2^* = 0.19$ for $\bar{x}_n^0 = 40$. As is shown in the figure, microscopic observations indicated $v_2^* \simeq 0.19$. Several other polyisocyanate systems in ref 21 also gave very good agreement between the calculated and observed v_2^*. It was gratifying to find that equations (21) and (22) hold for polydisperse systems when x was replaced by $\bar{x}_n^0$.

THE BIPHASIC INTERVAL

When observed through the cross-polarized light microscope, the anisotropic phase of polyisocyanates and several other polymers first appears as minute birefringent droplets, as is shown in *Figure* 3D of ref 17. As the concentration of the polymer increases, the number of the anisotropic entities increases as is shown in the upper left photograph of *Figure* 1 or the lower left photograph of *Figure* 4 of the same reference. With the increase in the number of birefringent droplets, increases in their average size and their size distribution become clear (*Figure* 1*a* in ref 46). When a low level of shear is applied to the biphasic system by means, say, of a slight movement of the coverglass of the sample on the microscope stage, then the anistropic droplets start flowing in the currents in the isotropic matrix without the droplets being deformed. Because of the high fluidity of the isotropic matrix and the speed of motion of the spherical anisotropic inclusions, no photo-micrographs were obtained, but the motion of underformed anisotropic droplets across many lengths of the microscopic field of vision was observed in sheared solutions of concentrations slightly above v_2^*. The resistance of the minute droplets to deformation indicates that their viscosity may be higher than that of the suspending matrix when present in small amounts. The droplets are microscopic yet far greater than molecular sizes. Because of this, molecular scale treatments of uniform isotropic solutions cannot hold for this case. The approach of Taylor[47] in the determination of the viscosity of colloidal spherical inclusions was adopted. Corrections were made due to the fact that in the biphasic interval of polydisperse polymer solution the average molecular weight in each phase changes continuously over the range of $v_2^* < v_2^0 < v^A$.

It was shown by Taylor[47,48] that the viscosity of a suspension of spherical inclusions is

$$\eta^0 = \eta_{mat}\left(1 + \frac{(5\lambda + 2)}{2(\lambda + 1)} \cdot V_{inc}\right) \tag{24}$$

where η_{mat} is the viscosity of the suspending matrix, V_{inc} is the volume fraction of the inclusions and

$$\lambda = (\eta_{inc}/\eta_{mat}) \tag{25}$$

η_{inc} being the viscosity of the inclusions. From equation (24) the intrinsic viscosity of the system is obtained

$$[\eta] = \frac{5\lambda + 2}{2(\lambda + 1)} \tag{26}$$

which varies between the limits of 2.5 for solid spheres with $\lambda = \infty$, as calculated by Einstein[30], and 1 for $\lambda = 0$.

Flory and co-workers[6-10] showed that when a solution of a polydisperse polymer separates into isotropic and anisotropic phases, the concentration of the polymer in the ansiotropic phase v'_2 is larger than the concentration in the isotropic phase v_2:

$$v'_2 > v_2^0 > v_2 \tag{27}$$

and the average molecular weight, or average axial ratio in the anisotropic phase $\bar{x}'_n$ is larger than in the isotropic phase $\bar{x}_n$:

$$\bar{x}'_n > \bar{x}_n^0 > \bar{x}_n \tag{28}$$

The numerical evaluation of the detailed parameters for a most probably[9] or a Poisson[10] distribution is cumbersome, but the evolving picture may be summarized: Upon the appearance of minute quantities of anisotropic spheres at v_2^*, they preferentially contain the highest molecular weight species existing in the system. Since these are taken from the initial $\bar{x}_n^0$ average, and encompass a very small fraction of the polymer, the value of $\bar{x}_n$ in the isotropic matrix will be only slightly reduced. As the volume fraction V' of the anisotropic phase increases at the expense of the volume fraction V of the isotropic phase, larger and larger quantities of the higher M fractions partition into the anisotropic phase. Since the highest M species were used up first, species with decreasing M end up in the anisotropic phase, gradually bringing the value of $\bar{x}'_n$ down. At the same time, the species remaining in the isotropic phase, being depleted of ever increasing amounts of the higher M fractions, also decrease their $\bar{x}_n$ value. Finally, at the point v_2^A, $\bar{x}'_n$ equals $\bar{x}_n^0$ and the isotropic phase vanishes. Schematic descriptions of the above for moderate $\bar{x}_n^0$ starting at microscopically observable V', are present in *Figures* 4 and 8 of ref 9. From this reference, for $\bar{x}_n^0 \gg 20$, the value of $\bar{x}_n$ upon approaching v^A is far smaller than $\bar{x}_n^0/4$ and the value of x'_n upon approaching v^* is much larger than $5\bar{x}_n^0$.

From equations (12) and (13) we recall that the dependence of the viscosity on M is much more pronounced than its dependence on the concentration. The total increase of v_2^0 over the biphasic region is 1.5 times its value at v_2^*. Therefore, even if v_2 will increase from v_2^* to v_2^A, the large drop in $\bar{x}_n$ over the same concentration interval will sharply decrease the viscosity of the isotropic phase within the biphasic interval. In fact, because most of the polymer added in the biphasic interval ends up in the growing and more concentrated anisotropic phase, changes in v_2 within this interval are expected to be small. This may reinforce the dependence of η on the dropping M. Thus, at the point v_2^A the viscosity of the isotropic phase whose $\bar{x}_n < \bar{x}_n^0/4$, may be of the order of only 10% of the viscosity of the isotropic phase at the point v_2^*.

To determine the viscosity of the anisotropic inclusions several facts must be recognized:

(1) From the observations on several polyisocyanate systems[20,21], as well as Iizuka[22] and Kiss and Porter[23] on PBLG systems, it appears that the viscosity[20,21,23] or the reduced viscosity[22] at the point v_2^A is about 20% of the corresponding values at v_2^*. Moreover, the viscosity values at v_2^A are substantial in size.

(2) The viscosity η^P at the point v_2^P is about 1.6 times the magnitude of η^{*}[20-23].

(3) The phase inversion from anisotropic inclusions in an isotropic matrix to isotropic inclusions in an anisotropic matrix occurs between v_2^P and v_2^A, at a point where microscopy shows the volume of the anisotropic inclusions to be about $V' = 0.7$[20,21].

(4) The change in the concentration v_2^0 over the biphasic interval is limited and is dependent on the concentration v_2 at the point v_2^*. According to Flory[4] the concentration at v_2^A should be

$$v_2^A = v'_2 \simeq 1.56 v_2 \simeq 12.5/\bar{x}_n \tag{29}$$

with v_2 and $\bar{x}_n$ corresponding to their values in the isotropic phase at v_2^*. A later treatment[13] led to

$$v_2^A = v'_2 \simeq 11.6/\bar{x}_n \simeq 1.45(8/\bar{x}_n)(1 - 2/\bar{x}_n) \tag{30}$$

in which the numerical value of 1.45 is closer to the value of 1.34 deduced by Onsager[1]. Equation (30) was tested on several polyisocyanate systems and was found to be correct within the experimental margin of error.

Based on the above facts, and recalling that right near v_2^* the anisotropic inclusions indicated that $\eta_{inc} > \eta_{mat}$ may be valid, several trial calculations following equation (24) were performed. They were based on the following numerical values: at v_2^*, $\eta^0 = \eta_{mat} = 1000$; at v_2^A, $\eta^0 = \eta_{mat} = 200$; the viscosity of the isotropic phase right before vanishing at v_2^A is $\eta_{inc} = 150$. The calculations were performed under two assumptions: (1) the viscosity of both phases drops linearly from the values at v_2^* to the corresponding values at v_2^A, and (2) the viscosity of both phases shows a non-linear convex drop over the biphasic interval, reflecting the high dependence of η^0 on M.

Table 1 Viscosity of biphasic system, η^0, from equation (24), convex change assumed

V_{inc}	η_{inc}	η_{mat}	λ	η^0
0.00	1500	1000	1.500	1000
0.05	1487	983	1.513	1077
0.10	1473	970	1.519	1155
0.20	1436	933	1.539	1290
0.30	1392	890	1.564	1401
0.40	1333	838	1.591	1482
0.50	1261	772	1.633	1517
0.60	1166	693	1.683	1500
0.70	1030	595	1.731	1407
0.80	850	470	1.809	1209
0.50	772	1261	0.612	2250
0.40	693	1166	0.594	1893
0.30	595	1030	0.578	1557
0.20	470	850	0.553	1111
0.10	320	580	0.552	669
0.05	230	400	0.575	431
0.00	150	200	0.750	200

Table 2 Viscosity of biphasic system, η^0, from eq. (24), linear change assumed

V_{inc}	η_{inc}	η_{mat}	λ	η^0
0.00	1500	1000	1.500	1000
0.05	1435	957	1.499	1048
0.10	1370	915	1.497	1089
0.20	1240	830	1.494	1145
0.30	1110	745	1.490	1169
0.40	980	660	1.485	1161
0.50	850	575	1.478	1120
0.60	720	490	1.469	1046
0.70	590	405	1.457	941
0.80	460	320	1.438	802
0.40	490	720	0.681	1183
0.30	405	590	0.686	875
0.20	320	460	0.696	609
0.10	235	330	0.712	384
0.05	193	265	0.728	287
0.00	150	200	0.750	200

Several values of η_{inc} at v_2^* were tried, namely $\eta_{inc}=1000$, $\eta_{inc}=1200$ and $\eta_{inc}=1500$. The numerical data for two such sets of calculations for convex and linear decrease in viscosity starting with $\eta_{mat}=1000$ and $\eta_{inc}=1500$, are presented in *Tables* 1 and 2, respectively. The results are plotted in *Figure* 2, in which the viscosity η^0 in the isotropic range shows a concentration dependence of about 4 powers, approximating experimental observations on rigid backbone polymers.

Within the biphasic interval the peak η^p of the curve describing the linearly changing viscosity, is closer to v_2^* than v_2^A. It is also much smaller than the value of η^p associated with the convexly decreasing viscosity. The latter peak appears to be very similar to experimental data[20–23] with respect to both position and magnitude. It is of interest to note that when a concave drop in viscosity was considered, the viscosity peak moved to the left making the viscosity η^* merge with the peak viscosity η^p. Both curves in *Figure* 2 are typical of similar viscosity changes down to initial inclusions viscosity of less than half the initial matrix viscosity at v_2^*, $\eta_{inc}<\eta_{mat}/2$.

At very high values of V', the matrix is the anisotropic phase and the inclusions are isotropic. In *Tables* 1 and 2 η^0 values calculated according to equation (24) covering anisotropic inclusions in an isotropic matrix and *vice versa* are presented, respectively, above and below the lines in each *Table*. When plotted, the η^0 values appear to intersect at about $V'=0.70$. The fact that the observed phase inversion occurs at about this value of V' seems to indicate that an equivalence of the viscosities plus packing considerations may play a role in the process of phase inversion. The phase inversion itself may be visualized as resulting from the impingement upon one another or droplets closely packed in space. It is known that monodisperse spheres packed in hexagonal close packing occupy 74% of the total volume of the system. A more realistic approach is to estimate the packing density under the assumption of random packing. In this case monodisperse spheres packed in dense random packing occupy 63.5% of the overall volume and when packed in loose random packing they occupy 61% of the volume[49]. We recall that upon appearance, the anisotropic droplets are not uniform in size. *Figure* 4C of ref 19 shows that this non-uniformity remains until the point where the droplets merge to become a part of the anisotropic matrix. The figure is typical of many such figures obtained close to the phase inversion boundary. The gradation in size tends to increase the volume fraction occupied by the anisotropic droplets[31]. Therefore, one may conclude that $V'=0.7$ is a reasonable estimate for the phase inversion as obtained from packing considerations, and in agreement with experiment. The phase inversion does not take place at the same time throughout the volume of the system. The

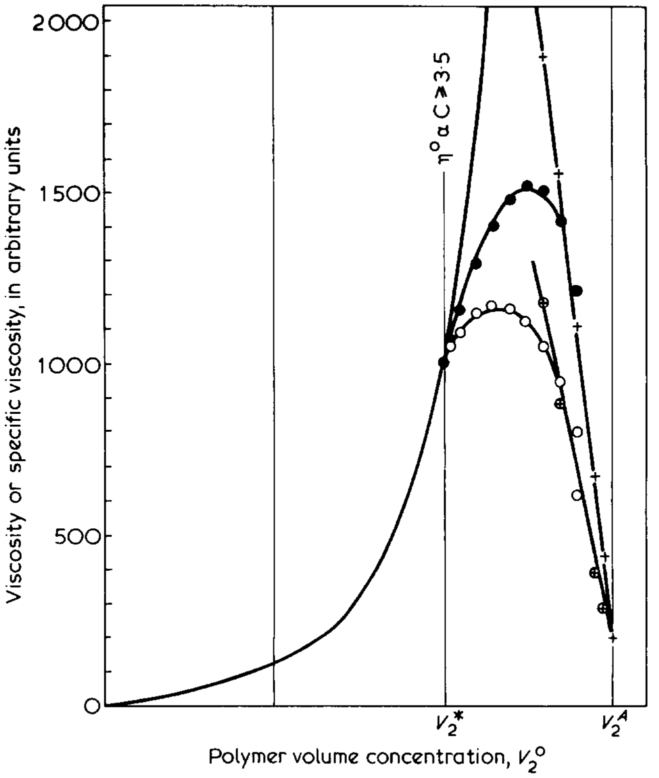

Figure 2 Viscosity as a function of concentration in the isotropic regime and the biphasic interval. Viscosity at v_2^* is 1000 and v_2^A, 200. For convex change: ●, anisotropic inclusions in isotropic matrix and + stands for isotropic inclusions in anisotropic matrix. For linear change; ○, anisotropic inclusions in isotropic matrix and ⊕, isotropic inclusions in anisotropic matrix

gradation of transition will tend to smooth the viscosity curve in the neighborhood of the phase inversion.

The viscosity curve in the biphasic interval can be approximated by the use of Taylor's[47] equation (24) in which the values of η_{mat}, η_{inc} and λ change across the interval as a consequence of the changes in $\bar{x}_n'$ and $\bar{x}_n$ in accordance with Flory's treatment of polydisperse systems[6,7,9,10].

THE ANISOTROPIC REGIME

Once the concentration of rigid backbone macromolecules in a solution surpasses v_2^A, then the equilibrium structure of the solution is that of a nematic liquid crystal. During a steady flow viscosity measurement, the preferred direction of the rigid backbones is the direction of the flow.

Even though no adequate theory is available at present for describing the viscosity behaviour of anisotropic nematic solutions containing polymers such as the polyisocyanates or the aromatic polyamides, we believe that a treatment similar to that of Simha[29,35] is applicable. Starting with suspensions containing relatively large particles, in which Brownian motion is insignificant, the intrinsic viscosity of prolate ellipsoid particles maintaining the direction of their major axis perpendicular to the direction of flow (Z-axis), was shown by Jeffery[50] and Guth[51,52] to be the following:

$$[\eta]=\frac{f}{(2\ln 2f-3)}+2 \tag{31}$$

When the suspension of such particles is isotropic before and during flow, and when the thickness of the particles is neglected, equation (32) holds[53-55]:

$$[\eta]=\frac{2f}{3\pi(\ln 2f-1.8)} \tag{32}$$

For rodlike particles whose major axis is fixed during flow at given angles θ and φ relative to the Z-axis, the intrinsic viscosity was determined by Burgers[55] to be

$$[\eta]=\langle g\rangle F(x) \tag{33}$$

where the particle shape factor is defined by

$$F(x)=\frac{x^2}{6(\ln 2x-1.8)} \tag{34}$$

and the orientation factor is

$$\langle g\rangle=\sin^4\theta\sin^2\varphi \tag{35}$$

It was demonstrated that the intrinsic viscosity of suspensions of rodlike particles is closer to the value calculated from equation (33) than to the value calculated from equation (32)[53].

In the flow of rodlike macromolecules Brownian motion plays a very significant role and cannot be disregarded. Following Simha, these effects may be accounted for through a modification of equation (33):

$$[\eta]=\langle g\rangle\left(\frac{f^2}{6(\ln 2f-1.5)}+\frac{f^2}{5(\ln 2f-0.5)}\right)+\frac{14}{15} \tag{36}$$

which, when converted from prolate ellipsoids of axial ratio f to cylindrical rods of axial x, changes to

$$[\eta]=\frac{2x^2\langle g\rangle}{90}\left(\frac{5}{\ln 2x-1.8}+\frac{6}{\ln 2x-0.61}\right)+\frac{14}{15} \tag{37}$$

leading to

$$\eta_{sp}=\left[\frac{2x^2\langle g\rangle}{90}\left(\frac{5}{\ln 2x-1.8}+\frac{6}{\ln 2x-0.61}\right)+\frac{14}{15}\right]v_2^0 \tag{38}$$

and, recalling that $\eta_{sp}=\eta/\eta_0-1$, we obtain for polydisperse polymers

$$\eta^0\simeq\eta_0\left[\frac{2\bar{x}^2\langle g\rangle}{90}\left(\frac{5}{\ln 2\bar{x}-1.8}+\frac{6}{\ln 2\bar{x}-0.61}\right)+2\right]v_2^0 \tag{39}$$

where $\bar{x}$ is the average axial ratio. In line with the above discussion, this average axial ratio is the weight average $\bar{x}_w^0$ one.

The orientation factor $\langle g\rangle$ attains values only within the range $1\geqslant\langle g\rangle\geqslant 0$[54]. Upon perfect alignment in the direction of flow $\langle g\rangle=0$. At this point $\eta_{sp}=(14/15)v_2^0$ and $\eta^0\simeq 2\eta_0\bar{v}_2^0$ are obtained. Recalling that the observed minimum viscosities at the $v_2^0>v_2^A$ range are of the order of several hundred times the viscosities of the corresponding solvents[20,21,23], the η_{sp} and η^0 values obtained above under the condition of $\langle g\rangle=0$ are far too low to be acceptable.

In the literature dealing with conventional low-M liquid crystalline substances, there exist parameters other than $\langle g\rangle$ to define the average orientation of rodlike particles[56]. Prominent among them is the order parameter S defined by Tsvetkov[57] as

$$S=(1/2)\langle 3\cos^2\theta-1\rangle=\langle p_2(\cos\theta)\rangle \tag{40}$$

where θ is the average angle between the molecular axis and the direction of flow (Z-axis), $P_2(\cos\theta)$ is the second Lengendre polynomial, and the brackets indicate an average[58]. If the orientation of the rodlike particles was entirely random, one would have $\langle\cos^2\theta\rangle=1/3$ and $S=0$. If, however, the particles were all aligned parallel to each other in the direction of flow, then $\cos\theta=\pm 1$ and $S=1.0$. Thus S is a measure of the particle alignment[59]. S can be experimentally determined by techniques such as nuclear magnetic resonance[56,58,59], Raman spectroscopy[56,59], optical birefringence measurements[59,60] and X-ray diffractometry[61].

At the transition point from the isotropic to the mesomorphic nematic phase of low-M mesogenic substances, the magnitude of the order parameter is about $S\simeq 0.42$[62]. Upon cooling from that point, the value of S increases across the mesomorphic range reaching values of $S\simeq 0.7$ upon solidification[62]. From isothermal dilution experiments on low-M liquid crystal formers resulting in a loss of mesogenicity beyond a characteristic concentration, it is obvious that the value of S decreases with increased dilution[63] within the nematic state. Physical considerations indicate that the same behaviour must prevail also in rodlike molecules of high molecular weight. This means that at the point v_2^A the fully anisotropic solution is less ordered than at higher v_2^0 and that S at v_2^A is smaller than at higher concentrations. Adopting the values of S of low-M materials as plausible values for polymeric substances, equation (37) can be rewritten as:

$$[\eta]=\frac{2x^2}{90S}\left(\frac{5}{\ln 2x-1.8}+\frac{6}{\ln 2x-0.61}\right)+\frac{14}{15} \qquad (41)$$

with $S\simeq 0.42$ at v_2^A and $S\simeq 0.70$ at $v_2^0=1.0$. Equations (38) and (39) may be corrected accordingly. Equation (41) indicates that the viscosity of the anisotropic solution is highest at v_2^A and gradually decreases towards $v_2^0=1.0$. We know, however, that this is not the case and that after gradually decreasing from η^A the viscosity passes through a minimum, η_{min}, and then increases steeply. This increase is due, we believe, to crowding effects discussed below. At present we are interested in discussing the viscosity curve in the interval η^A to η_{min}. Inserting in equation (38) the value of $x=40$ yields a η_{sp} value of $\sim 130v_2^0$ for $\langle g\rangle=1.0$ and $(14/15)v_2^0$ for $\langle g\rangle=0$. This indicates that when the rodlike molecules are fully aligned in the direction of flow the viscosity practically vanishes and that left is independent of x. Substituting $\langle g\rangle$ by $1/S$ in equation (38) with $x=40$, yields $\eta_{sp}=310v_2^0$ for $S=0.42$ and $\eta_{sp}=182v_0^2$ for $S=0.70$. Recalling that the observed values of η_{sp} at the point of η_{min} were usually over 200 (except for cases of highly viscous solvents), it is our impression that the viscosities obtained from equation (38) with substitution of $\langle g\rangle$ by $1/S$ are in far better agreement with experiment than without substitution.

It is well known that in concentrated suspensions particle crowding increases the viscosity of the system. The case for spherical particles was treated by Mooney[64]. We do not believe, however, that rodlike particles can or should be treated in the same manner as spherical particles.

The increased polymer concentration in the anisotropic phase tends to increase S and decrease the solution viscosity. However, the very same increase in concentration increases the crowding of the rigid macromolecules, leading to an eventual sharp increase in the viscosity. When a dilute suspension of rigid rods flows, the volume of the solvent swept by the orbit of each rod is closely approximated by a cylinder having an elliptical cross section whose shape is determined by the angles the rigid rod makes with the direction of flow (Z-axis) of the solution[53]. Letting φ_2 be the angle in the direction of the major axis of the ellipse and φ_3 be the angle in the direction of the minor axis, then for a large x ($L\gg d$) the volume swept by the rodlike particle, V_E, is approximated by

$$V_E=\frac{2\pi L^3\tan\varphi_2\tan\varphi_3}{(1+\tan^2\varphi_3)(1+\tan^2\varphi_2)^{1/2}} \qquad (42)$$

At relatively high concentrations the average values of φ_2 and φ_3 are expected to be small, to become close to one another, and to be comparable to the angle θ in equation (40). Therefore, equation (42) may be replaced by its approximation

$$V_E=\frac{2\pi L^3\tan^2\theta}{1+\tan^2\theta} \qquad (43)$$

in which θ can be experimentally determined as discussed above. In the limit of perfect alignment in the flow direction, the volume swept by the rodlike particle equals only its own volume and V_E reduces to

$$V_P=\tfrac{1}{2}\pi Ld^2 \qquad (44)$$

When the concentration of rod-like molecules in a flowing anisotropic solution has increased to a level such that each molecule cannot describe the orbit approximated by equation (42), impingement on and friction of one molecule with others interfere with the flow of the solution causing its viscosity to increase. The rate of increase of the viscosity may be described by the rate in which V_E approaches V_P. Incorporation into the corrected equations for viscosity yields equations for $[\eta]$, η_{sp} and η^0 in the fully anisotropic phase, of which the following is typical:

$$\eta^0\simeq\eta_0\left[\frac{2\bar{x}^2}{90S}\left(\frac{5}{\ln 2\bar{x}-1.8}+\frac{6}{\ln 2\bar{x}-0.61}\right)+2\right]\frac{v_2^0}{1-\frac{V_P}{V_E}} \qquad (45)$$

The value of $S\simeq 0.7$ upon solidification indicates that at that point $\theta\approx 25°$. Therefore, to achieve a better agreement with reality, V_P in equation (45) should be replaced by the volume of V_E calculated according to equation (43) for $\theta\approx 25°$. It must be recalled that the value of S varies from $S\simeq 0.42$ to $S\simeq 0.7$ as v_2^0 changes from v_2^A to 1.0.

The resulting viscosity equations for the fully anisotropic solution of a polydisperse polymer, then, are:

$$[\eta]=\left[\frac{2\bar{x}^2}{90S}\left(\frac{5}{\ln 2\bar{x}-1.8}+\frac{6}{\ln 2\bar{x}-0.61}\right)+\frac{14}{15}\right]\frac{1}{1-\frac{V_{25°}}{V_E}} \qquad (46)$$

$$\eta_{sp}=\left[\frac{2\bar{x}^2}{90S}\left(\frac{5}{\ln 2\bar{x}-1.8}+\frac{6}{\ln 2\bar{x}-0.61}\right)+\frac{14}{15}\right]\frac{v_2^0}{1-\frac{V_{25°}}{V_E}} \qquad (47)$$

and

$$\eta^0\simeq\eta_0\left[\frac{2\bar{x}^2}{90S}\left(\frac{5}{\ln 2\bar{x}-1.8}+\frac{6}{\ln 2\bar{x}-0.61}\right)+2\right]\frac{v_2^0}{1-\frac{V_{25°}}{V_E}} \qquad (48)$$

Experimental difficulties such as very high viscosity and/or gellation impede measurements in the region of very high v_2^0, therefore attempts to reach higher levels of accuracy in the equations above, are not warranted at present.

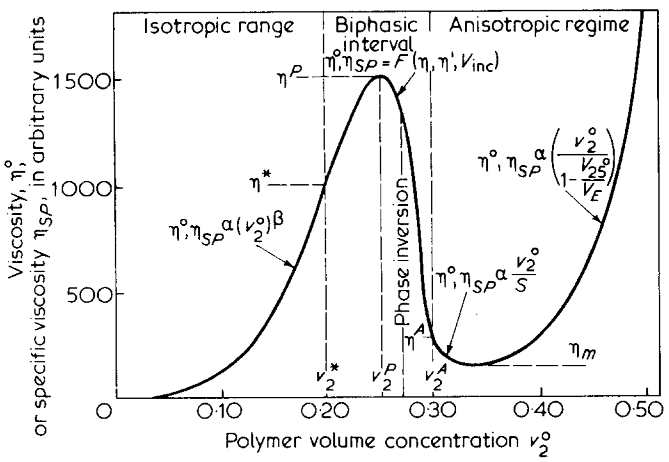

Figure 3 Viscosity vs concentration curve of a mesogenic polymer whose anisotropic phase makes its first appearance in the form of minute spherical droplets suspended in an isotropic matrix. Parameters affecting the behaviour of the solution at different concentration levels, are indicated

In the anisotropic region the viscosity curve decreases moderately with increased concentration. At η_{min} it reaches its minimal value and the crowding effects of the rodlike particles become increasingly noticeable. With further increase in concentration the viscosity increases at an accelerated pace such that it goes to infinity at the point of solidification, where $S \simeq 0.7$ and $V_E \approx V_{25°}$. A sample calculation according to equation (47), assuming $L = 400$ and $\bar{x} = 40$, yielded $\eta_{sp} = 690 v_2^0$ for $\theta = 30°$ and $\eta_{sp} = 1000 v_2^0$ for $\theta = 28°$, indicating that in the region of low $\theta (\theta < 30°)$ the viscosity increases at an extremely fast rate upon approaching $\theta \simeq 25°$. The initial decrease and subsequent rapid increase of the viscosity are in agreement with experimental observations.

DISCUSSION

The description and explanation of the viscosity behaviour of rigid backbone polymer solutions was discussed above.

In several works on the solution properties of PBA[27,66] and of PPTPA[67] it is indicated that the molecular weights determined from η^p by means of equation (21) were always substantially smaller than the corresponding molecular weights obtained by other techniques. We believe this discrepancy is an indication that v_2^p is not v_2^* and that $v_2^* < v_2^p$. When the correct values of $\bar{x}$, to be determined at v_2^*, will be inserted in equation (21) then the molecular weights so obtained will be in far better agreement with the results obtained by other methods.

The recent theory of Doi[38] concerning, among other variables, the viscosity of concentrated solutions of rodlike molecules (in the $v_2^0 < v_2^*$ region) appears to be conceptually similar to the Goldsmith and Mason[53] treatment of crowding effects by cylindrical particles. In his presentation, Doi indicates a viscosity dependence on c^3 and on M^6, in a reasonable agreement with the experimental data given in equations (12) and (13), respectively. However, the dependence of the coefficient of rotational diffusion, D_r, on molecular weight (average rod length), is far off the mark when compared with experiment. According to Doi[38], $D_r \propto 1/L^9$ while Tsvetkov and coworkers[68] obtained $D_r \propto 1/M^{2.7}$ for the rodlike PBA. In Doi's theory[38], the crowding effects are described through their effects on the radius of a cylinder in space defined by the tip of a rodlike particle. This is akin to our elliptical cross-section of the particle's orbit in space[53]. Doi maintains that the radius of the cylinder becomes comparable to the diameter of the rod when $c = 1/dL^2$, and that its magnitude is $\sim 1/cL^2$. This indicates that for any decent particle lenth, the radius of the cylinder describing the orbit of the particle is extremely small, already at exceedingly dilute solutions, $c \ll 1/L^3$. The spatial disposition of the rodlike particles and their cylindrical orbits relative to the direction of flow are assumed to be isotropic in Doi's theory. From a comparison of equation (5) with equations (33), (34) and (35) one finds, in agreement with experimental results, that in concentrated or moderately concentrated solutions the average direction of the suspended rodlike particles is not isotropic but at an average angle θ relative to the flow direction. It should also be recalled that the onset of anisotropy in polymeric systems is estimated to occur at a point where the order parameter S is 0.42, more or less. This corresponds to an average angle θ of 38.4°, indicating that a significant level of preferred orientation exists in the isotropic solution right below v_2^*. This fact prevents one from carrying Doi's theory into the isotropic concentration region close to v_2^*, and of course not into the anisotropic state. Thus, Doi's[38] theory may be applicable to dilute isotropic solutions under zero shear where, theoretically, there exists no flow.

The theoretical treatment of the solution viscosity by Matheson[37], is limited to monodisperse systems only. The biphasic interval is assumed to contain two phases whose viscosities remain constant throughout the range. Phase inversion is assumed to occur midway between v_2^* and v_2^A and to be associated with the point η^p. These assumptions are invalid in systems where polydispersity exists. Therefore, while the theoretical treatment of Matheson[37] may not hold for polydisperse systems, it may be perfectly suitable for the description of the viscosity behaviour of suspensions of viruses or colloidal droplets[69] where the molecular weight of the substances in each phase do not change with concentration.

CONCLUSIONS

A viscosity vs concentration curve covering the three concentration ranges described in this work, is shown in *Figure* 3. In it, arbitrary units were used so that the figure may serve to demonstrate the variations in both η^0 and η_{sp}.

The equations describing the viscosity behaviour in the three ranges may be summarized by

$$\eta^0 = \eta_0[[\eta]c + (\pi/4)[\eta]^2 c^2 + K_2(\ln \bar{x})^2[\eta]^3 c^3 + \ldots] \tag{49}$$

for the isotropic region where $[\eta]$ is defined by equation (9) and c is replaceable by v_2,

$$\eta^0 = \eta_{mat}\left(1 + \frac{(5\lambda + 2)}{2(\lambda + 1)} \cdot V_{inc}\right) \tag{50}$$

for the biphasic interval, recalling that η_{mat}, η_{inc} and λ change with M in both phases across the concentration interval, and

$$\eta^0 = \eta_0 \left[\frac{2\bar{x}^2}{90S} \left(\frac{5}{\ln 2\bar{x} - 1.8} + \frac{6}{\ln 2\bar{x} - 0.61} \right) + 2 \right] \frac{v_2^0}{1 - \frac{V_{25^\circ}}{V_E}} \qquad (51)$$

for the anisotropic range where S and V_E change with v_2^0.

The equations are in qualitative and in reasonable quantitative agreement with experimental data in the literature.

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