tinue to change at the trailing edge, even for stars with very long arms.

Conclusions

We have shown that the terminal relaxation spectrum for linear chains approaches a limiting form at high molecular weights and concentrations ($M/M_e \gg 1$). The limiting form at the long-time end appears to be attained rather quickly ($M/M_e \approx 5$), but values of $M/M_e \approx 100$ seem necessary to resolve the part at short times. An estimate of reduced dynamic moduli for the fully resolved terminal spectrum was made. Values of the universal constants $J_e^0 G_N^0 = 2.4$, $G_N^0/G_m'' = 3.56$, and $\eta_0\omega_m/G_N^0 = 0.97$ were derived from the limiting curves and found to be in good agreement with the values for different species and concentrations. The modulus shift factor varies with concentration as $b \propto \phi^k$, where k is somewhat greater than 2. The behavior of stars differs substantially. Dynamic moduli for stars at different concentrations can be superposed, but the modulus shift factor has a much weaker concentration dependence: $b \propto \phi$. Assuming $G_N^0 \propto \phi^k$ for both linear and star polymers, $J_e^0 G_N^0$ for stars is a function of concentration, molecular weight, and polymer species. Thus, the terminal spectrum for star polymers appears not to approach constant limiting form, at least in the range of compositions investigated here.

Acknowledgment. This work was supported by the National Science Foundation (Grant ENG 77-15683-A01 to Northwestern University and Grant DMR-79-08299 to the University of Akron). We thank the Northwestern University Materials Research Center for use of its facilities. We are also grateful to Mr. Jeffrey Gotro of Northwestern University and Dr. Jacques Roovers of the National Research Council of Canada for permission to use their data.

References and Notes

(1) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(2) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(3) Marin, G.; Menezes, E. V.; Raju, V. R.; Graessley, W. W. *Rheol. Acta* **1980**, *19*, 462.
(4) Rochefort, W. E.; Smith, G. G.; Rachapudy, H.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Part A-2* **1979**, *17*, 1197.
(5) Raju, V. R.; Rachapudy, H.; Graessley, W. W. *J. Polym. Sci., Part A-2* **1979**, *17*, 1223.
(6) Graessley, W. W.; Roovers, J. *Macromolecules* **1979**, *12*, 959.
(7) Gotro, J., private communication.
(8) Raju, V. R.; Smith, G. G.; Marin, G.; Knox, J. R.; Graessley, W. W. *J. Polym. Sci., Part A-2* **1979**, *17*, 1183.
(9) Vrentas, C. M.; Rochefort, W. E.; Smith, G. G.; Graessley, W. W. *Polym. Eng. Sci.* **1981**, *21*, 285.
(10) Markovitz, H. *J. Polym. Sci., Polym. Symp.* **1975**, *50*, 431. Plazek, D. J.; Riande, E.; Markovitz, H. Raghupathi, N. *J. Polym. Sci., Part A-2* **1979**, *17*, 2189.
(11) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818.
(12) Isono, Y.; Fujimoto, T.; Takeno, N.; Kajiura, H.; Nagasawa, M. *Macromolecules* **1978**, *11*, 888.
(13) Riande, E.; Markovitz, H.; Plazek, D. J.; Raghupathi, N. *J. Polym. Sci., Polym. Symp.* **1975**, *50*, 405.
(14) Graessley, W. W., manuscript in preparation.
(15) Orbon, S. J.; Plazek, D. J. *J. Polym. Sci., Part A-2* **1979**, *17*, 1871.
(16) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.
(17) Isono, Y.; Nagasawa, M. *Macromolecules* **1980**, *13*, 862.
(18) Dossin, L. M.; Graessley, W. W. *Macromolecules* **1979**, *12*, 123.
(19) Dossin, L. M. Ph.D. Thesis, Materials Science and Engineering Department, Northwestern University, Evanston, Ill., 1978.
(20) Rouse, P. E. *J. Chem. Phys.* **1973**, *21*, 272. Ham, J. S. *Ibid.* **1957**, *26*, 625.

Influence of Flow on the Isotropic–Nematic Transition in Polymer Solutions: A Thermodynamic Approach

T. J. Sluckin*

Department of Mathematics, University of Bristol, University Walk, Bristol BS8 1TW, United Kingdom. *Received February 26, 1981*

ABSTRACT: The effect of an elongational flow field on the concentration dependence of the isotropy–anisotropy transition in dilute polymers is investigated by a quasi-thermodynamic method. It is found that in such flow fields the transition is shifted toward the low-concentration regime. The shift depends on a number of experimentally accessible quantities in the bulk phases. The resulting equations have a Clausius–Clapeyron-like form.

Introduction

Polymers which consist of rigid rodlike sections can, under some circumstances, in sufficiently concentrated solutions, exist in an anistropic nematic phase. This can be important in achieving high-modulus properties. In general, at low concentrations the nematic phase does not form. However, at some critical polymer mole fraction c_I a nematic phase at polymer mole fraction $c_N > c_I$ can be in equilibrium with the isotropic phase at mole fraction c_I. Homogeneous solutions with polymer mole fraction c, where $c_I < c < c_N$, cannot exist; rather the solution separates into two homogeneous phases with different polymer mole fractions c_I and c_N. A basic statistical mechanical theory of this phenomenon was developed by Flory.[1]

In view of the possible technological significance of these anisotropic solutions, it is of interest to ask what circumstances might favor the formation of the anisotropic phase. One such circumstance is to place the polymer solution in an extensional flow field. It has been known for some time[2,3] that flow fields can have significant orientation effects. Marrucci and Sarti[4] investigated the effect of elongational flow on the isotropy–anisotropy transition. They used a quasi-equilibrium statistical mechanical approach, assuming irrotational flow and, thus, that the velocity field was describable in terms of a potential, and they modeled the polymer in solution by a freely jointed

* Present address: Faculty of Mathematical Studies, University of Southampton, Highfield, Southampton, SO9 5NH, United Kingdom.

0024-9297/81/2214-1676$01.25/0

chain made up of a large number of equal rigid links. They were then able to study how the boundaries of the two-phase region change as a function of elongational strain rate and to calculate the critical strain rate required in order to stabilize the nematic phase in an arbitrarily dilute solution. The problem has also been studied with a dynamic mean field method.[8]

In this paper we adopt a quasi-equilibrium thermodynamic approach to understanding the effect of a strain rate field on the isotropy–anisotropy transition in polymer solutions. This approach is less specific than the precise model studied by Marrucci and Sarti; as a consequence we are not able to predict in detail the critical strain rate for nematic stabilization in weak solutions. However, we can show that some of the results implicit in the work of Marrucci and Sarti are model independent. We derive a Clausius–Clapeyron-like equation which connects the shift in the critical polymer mole fractions c_I and c_N to the applied strain rate and which depends only on experimentally accessible quantities.

Model

We shall suppose that there are N_1 moles of solvent and N_2 moles of solute present in the samples; the polymer mole fraction is then given by

$$c = N_2/(N_1 + N_2) \tag{1}$$

The degree of anisotropy of the solution is given by the (symmetric) Saupe ordering matrix q_{ij}.[5] Rather roughly, we may suppose that

$$q_{ij} = \tfrac{1}{2}\int n(\Omega)[3\hat{n}_i(\Omega)\hat{n}_j(\Omega) - \delta_{ij}]\, d\Omega \tag{2}$$

where $n(\Omega)$ is the orientational distribution function as a function of solid angle for polymer links and $\hat{\mathbf{n}}(\Omega)$ is a unit vector in the direction Ω. Clearly $q_{ij} = 0$ for an isotropic solution. Then in unaxial nematics, we have the relation

$$q_{ij} = \tfrac{1}{2}q[3\hat{n}_i\hat{n}_j - \delta_{ij}] \tag{3}$$

The parameter q is then the magnitude of the nematic order parameter, and $\hat{\mathbf{n}}$ is the *director* of the nematic.

In a stationary homogeneous liquid we suppose that there exists a Gibbs free energy functional $G_0[N_1,N_2,q_{ij}] = G_0[N_1,N_2,q]$. G is also a function of pressure and temperature, which we shall keep constant. The stable values of q are determined by the implicit equation

$$\left(\frac{\partial G_0}{\partial q}\right)_{N_1,N_2} = 0 \tag{4}$$

In general, there will be two solutions: $q = 0$, corresponding to the isotropic state, and $q = q_0(N_1,N_2)$, corresponding to the nematic state. We may also specify the chemical potentials of the solute and the solvent

$$\mu_1 = \left(\frac{\partial G_0}{\partial N_1}\right)_{N_2,p} \qquad \mu_2 = \left(\frac{\partial G_0}{\partial N_2}\right)_{N_1,p} \tag{5}$$

At this stage we note the following two general thermodynamic results.[6] First, we have

$$\left(\frac{\partial \mu_1}{\partial c}\right)_{p,T} = -v_1\frac{dP^1}{dc} \tag{6}$$

where v_1 is the partial molar volume of the solvent, and $P^1(c)$ is the osmotic pressure of the solvent. Second, we have the Duhem–Margules condition

$$(1 - c)(\partial\mu_1/\partial c)_{p,T} + c(\partial\mu_2/\partial c)_{p,T} = 0 \tag{7}$$

This follows directly from the Maxwell relation

$$\partial^2 G/\partial N_1\,\partial N_2 = \partial\mu_1/\partial N_2 = \partial\mu_2/\partial N_1 \tag{8}$$

Effect of a Velocity Field

In the presence of a nonuniform velocity field $\mathbf{v}(\mathbf{x})$, we can define the strain rate tensor $\dot{e}_{ij}$, which is symmetric, by

$$\dot{e}_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) \tag{9}$$

and the (antisymmetric) rotation tensor ω_{ij}

$$\omega_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i}\right) \tag{10}$$

In general, we may suppose the flow to be incompressible (or almost so); in this case

$$\dot{e}_{kk} = 0 \tag{11}$$

As a result we can suppose that

$$\dot{e}_{ij} = \tfrac{1}{2}\dot{e}[3\hat{n}_i'\hat{n}_j' - \delta_{ij}] \tag{12}$$

where $\dot{e}$ is the magnitude of the strain rate tensor and $\hat{\mathbf{n}}'$ is its director.

We now *conjecture* that the behavior of the polymer solution may still be described by a (modified) Gibbs free energy functional G, where

$$G[N_1,N_2,q_{ij}] = G_0 - \lambda N_2 q_{ij}\dot{e}_{ij} \tag{13}$$

$$= G_0 - \tfrac{1}{4}\lambda N_2 q\dot{e}[3(\hat{\mathbf{n}}\cdot\hat{\mathbf{n}}')^2 + 1] \tag{14}$$

where λ is a (as yet unspecified) parameter. The stable values of q_{ij} (and thus of q and $\hat{\mathbf{n}}$) are given by

$$\partial G/\partial q_{ij} = 0 \tag{15}$$

Hence

$$\partial G/\partial(\hat{\mathbf{n}}\cdot\hat{\mathbf{n}}') = 0 \tag{16a}$$

$$\partial G/\partial q = 0 \tag{16b}$$

However, eq 16a immediately leads to the result $\hat{\mathbf{n}} = \hat{\mathbf{n}}'$, as might be expected, and hence eq 14 reduces to the functional

$$G = G_0 - \lambda N_2 q\dot{e} \tag{17}$$

We note that on symmetry grounds G can contain no terms like $q_{ij}\omega_{ij}$; if there is some tensor conjugate to ω_{ij} it must be antisymmetric and in some way express the "handedness" of a molecular twist. In any case, we shall not be concerned with such molecular behavior. There are, however, interactions between $(\nabla \times \hat{\mathbf{n}})$ and ω_{ij}; they are described by the equations of nematodynamics;[5] we shall not be interested in the director so much as in the magnitude of q.

Experimental Specification of the Order Parameter. de Gennes[5] points out that the magnetic susceptibility tensor $\chi_{\alpha\beta}$ can be used to define the liquid crystal order parameter. Then

$$\chi_{\alpha\beta} = \chi^I\delta_{\alpha\beta} + \chi^A[3\hat{n}_\alpha\hat{n}_\beta - \delta_{\alpha\beta}] \tag{18}$$

where χ^I and χ^A are, respectively, the isotropic and anisotropic parts of the magnetic susceptibility. Then because the magnetic couplings between neighboring molecules are rather small, $\chi_A \propto q$. However, it will be more convenient to use the dynamic magnetic susceptibility, $\chi_{\alpha\beta}^D$, where the frequency is taken so as to be high with respect to typical structural changes in the liquid but low with respect to electronic rearrangement times within the molecule. Then

$$\chi_{\alpha\beta}^D = \left(\frac{\partial M_\alpha}{\partial H_\beta}\right)_q \tag{19}$$

whereas the static magnetic susceptibility is given by

$$\chi_{\alpha\beta}^{S} = \left(\frac{\partial M_\alpha}{\partial H_\beta}\right)_{N_1,N_2} \tag{20}$$

where **M** is induced molar magnetic moment. We may now generalize the Gibbs free energy functional (17) to include the presence of a magnetic field; we have

$$G = G_0 - \lambda N_2 q\dot{e} - \tfrac{1}{2}N_1\chi_{1\alpha\beta}{}^{D}H_\alpha H_\beta - \tfrac{1}{2}N_2\chi_{2\alpha\beta}{}^{D}H_\alpha H_\beta \tag{21}$$

where a summation convention is assumed over repeated indices. We assume that the magnetic susceptibility tensor of the solvent is always isotropic. Then eq 21 reduces to

$$G = G_0 - \lambda N_2 q\dot{e} - \tfrac{1}{2}(N_1\chi_1{}^{DI} + N_2\chi_2{}^{DI})H^2 - \tfrac{1}{2}N_2\chi^{DA}[3(\mathbf{H}\cdot\hat{\mathbf{n}})^2 - H^2] \tag{22}$$

and $\chi^{DA} = \nu q$.

We suppose that a flow field and a magnetic field are applied to a sample in such a way that there is no liquid crystal response. This may be checked by, for instance, a birefringence experiment. Then

$$\partial G/\partial q = 0 = \partial G_0/\partial q \tag{23}$$

Hence

$$\lambda = -\nu(\partial H^2/\partial\dot{e})_{q=0} \tag{24}$$

Then if q_0 is the magnitude of the liquid crystal order parameter and $\chi_0{}^{DA}$ is the value of the anisotropic dynamic magnetic susceptibility in the stable anisotropic phase, we have

$$\chi_0{}^{DA} = \nu q_0 \tag{25}$$

and hence, using (24)

$$\lambda q_0 = -\chi_0{}^{DA}(\partial H^2/\partial\dot{e})_{q=0} \tag{26}$$

We shall need this crucial result in the next section. We return to the question of the measurement of $(\partial H^2/\partial\dot{e})$ in the Discussion.

Boundaries of the Two-Phase Region

We now suppose that a strain rate of magnitude $\Delta\dot{e}$ is applied to the polymer solution. The Gibbs free energy is then given by eq 17. Then we suppose for given N_1 and N_2 the chemical potentials μ_1 and μ_2 change to μ_1' and μ_2'. Then in the linear-response regime

$$\mu_1' = \left(\frac{\partial G}{\partial N_1}\right)_{N_2,p} = \left(\frac{\partial G_0}{\partial N_1}\right)_{N_2,p} = \mu_1 \tag{27}$$

$$\mu_2' = \left(\frac{\partial G}{\partial N_2}\right)_{N_1,p} = \left(\frac{\partial G_0}{\partial N_1}\right)_{N_2,p} - \lambda\dot{e}q = \mu_2 - \lambda q\Delta\dot{e} \tag{28}$$

We note that the response of the solvent chemical potential μ_1 to the imposed strain rate $\Delta\dot{e}$ is proportional to $(\Delta\dot{e})^2$ and thus may be ignored in the linear-response regime. Hence

$$\left(\frac{\partial\mu_1}{\partial\dot{e}}\right)_{p,c} = 0 \qquad \left(\frac{\partial\mu_2}{\partial\dot{e}}\right)_{p,c} = -\lambda q \tag{29}$$

Now in the absence of an applied strain rate field there will be, for given p and T, a situation when the isotropic phase at concentration c_I and the nematic phase at concentration c_N can coexist. When this occurs

$$\mu_{1I} = \mu_{1N} \qquad \mu_{2I} = \mu_{2N} \tag{30}$$

When there is an applied strain rate, these concentrations will change to $c_I + \Delta c_I$ and $c_N + \Delta c_N$, and the chemical potentials will still be equal, though different

$$\mu_{1I}' = \mu_{1N}' \qquad \mu_{2I}' = \mu_{2N}' \tag{31}$$

Hence

$$\Delta\mu_{1I} = \Delta\mu_{1N} \qquad \Delta\mu_{2I} = \Delta\mu_{2N} \tag{32}$$

where $\Delta\mu$ is the change in chemical potential. Hence

$$\left(\frac{\partial\mu_{1I}}{\partial c}\right)_{p,\dot{e}}\Delta c_I + \left(\frac{\partial\mu_{1I}}{\partial\dot{e}}\right)_{p,c}\Delta\dot{e} = \left(\frac{\partial\mu_{1N}}{\partial c}\right)_{p,\dot{e}}\Delta c_N + \left(\frac{\partial\mu_{1N}}{\partial\dot{e}}\right)_{p,c}\Delta\dot{e} \tag{33}$$

$$\left(\frac{\partial\mu_{2I}}{\partial c}\right)_{p,\dot{e}}\Delta c_I + \left(\frac{\partial\mu_{2I}}{\partial\dot{e}}\right)_{p,c}\Delta\dot{e} = \left(\frac{\partial\mu_{2N}}{\partial c}\right)_{p,\dot{e}}\Delta c_N + \left(\frac{\partial\mu_{2N}}{\partial\dot{e}}\right)_{p,c}\Delta\dot{e} \tag{34}$$

Substitution from eq 29 into eq 33 and 34 yields

$$\left(\frac{\partial\mu_{1I}}{\partial c}\right)_{p,\dot{e}}\Delta c_I = \left(\frac{\partial\mu_{1N}}{\partial c}\right)_{p,\dot{e}}\Delta c_N \tag{35}$$

$$\left(\frac{\partial\mu_{2I}}{\partial c}\right)_{p,\dot{e}}\Delta c_I = \left(\frac{\partial\mu_{2N}}{\partial c}\right)_{p,\dot{e}}\Delta c_N - \lambda q_0\Delta\dot{e} \tag{36}$$

It is now straightforward, using eq 6, 7, 35, and 36, to derive equations for the shift in the critical concentrations c_I and c_N as a function of applied strain rate; we use eq 26 to evaluate λq_0.

$$\frac{\Delta c_I}{\Delta\dot{e}} = \frac{-\chi_0{}^{DA}(\partial H^2/\partial\dot{e})_{q=0}}{\upsilon_{1I}(dP_I{}^1/dc)(c_N{}^{-1} - c_I{}^{-1})} \tag{37}$$

$$\frac{\Delta c_N}{\Delta\dot{e}} = \frac{-\chi_0{}^{DA}(\partial H^2/\partial\dot{e})_{q=0}}{\upsilon_{1N}(dP_N{}^1/dc)(c_N{}^{-1} - c_I{}^{-1})} \tag{38}$$

Equations 37 and 38 are our principal results. This result is analogous to the Clausius–Clapeyron equation;[7] it connects changes in external parameters along a phase coexistence line.

Finally, we can use this result to estimate, in a rough and ready way, the critical strain rate for the isotropic–nematic transition to occur at infinite dilution. In such a case, of course, the linear theory calculated in eq 37 and 38 does not apply. If we do apply it nevertheless, the criterion for the critical strain rate is

$$\Delta c_I/c_I = -1 \tag{39}$$

or

$$\dot{e}_c \cong \frac{\upsilon_{1I}(dP_I{}^1/dc)(c_N{}^{-1} - c_I{}^{-1})}{\chi_0{}^{DA}(\partial H^2/\partial\dot{e})_{q=0}} \tag{40}$$

We note that in the dilute-concentration limit we have the van't Hoff formula[7]

$$\upsilon(dP^1/dc) = k_B T \tag{41}$$

which enables eq 37, 38, and 40 to be rather readily simplified.

Discussion

There are, unfortunately, a number of factors which may limit the applicability of the theory. We now discuss these factors.

First, there is no general theory which tells us when it is feasible to use quasi-equilibrium thermodynamics in an inherently nonequilibrium, dissipative situation. Under certain circumstances, for instance, in Kelvin's derivation of the equations of thermoelectricity, this procedure has

been justified inasmuch as it is possible to derive by this method results which can be more correctly derived by nonequilibrium thermodynamics. But, in general, use of quasi-equilibrium thermodynamics (or indeed statistical mechanics, as in ref 4) is not valid in a nonequilibrium situation; it may be approximately valid, but the precise conditions of validity are not known.

Second, even if the dissipative effects which we have neglected are not important, it is not clear that one order parameter (in our case q) is sufficient to describe the polymer liquid crystal order. The simplest kind of liquid crystal is made from rigid rodlike molecules. Indeed our treatment is probably most applicable to these nonpolymeric liquid crystals. Even in such a liquid crystal there are, in principle, an infinite number of order parameters, corresponding to spherical harmonics of $n(\Omega)$ of all even orders $l \geq 2$. Under favorable circumstances it will be possible to truncate the spherical harmonic expansion of $n(\Omega)$ at the $l = 2$ terms; this corresponds to supposing that there is indeed only one order parameter. A convenient representation of this order parameter is q_{ij}, defined in eq 3. It seems that in most rigid rodlike liquid crystals, this is the case,[5] but, in principle, at least it is possible to have a liquid crystal, with $q_{ij} \equiv 0$, in which the director can only be identified from the $l = 4$ spherical harmonics. In a polymer the situation becomes even more complicated. The actual state of the polymer clearly depends not only on the spherical harmonics of $n(\Omega)$—the orientation of a typical link in the chain—but also on the relative conformation of links in the chain. It is thus possible to have nontrivially different average polymer conformations with the same q_{ij}. We may, however, hope that for "small" orientation effects, this will not be too important. We note that the "one order parameter approximation" is also adopted in ref 4, although with a language different from ours, and there is a further discussion of this point in this paper. It would presumably be possible to invent more order parameters, which might describe chain extension as well as link orientation, at the expense of complicating our analysis.

Third, it is not clear to what extent an experiment which involves the orientational response of a polymer solution to an applied magnetic field is practicable. In this connection we make two major points.

(a) It may be more feasible to use an electric field rather than a magnetic field as an orienting agent. If this is the case, eq 26 may be rewritten as

$$\lambda q_0 = \chi_0^{DA}(\partial E^2/\partial \dot{e})_{q=0} \tag{42}$$

if χ_0^{DA} is now taken to be a dynamic electrical susceptibility in the anisotropic phase and E is the electric field intensity. As de Gennes points out,[5] in some respects the magnetic susceptibility is to be preferred as a measure of the liquid crystal order parameter in that the magnetic response of each unit within the liquid is less affected by many-body effects. However, it may be the case that the liquid response to an applied electric field would be greater than to an applied magnetic field for precisely this reason. More formally, the parameter ν introduced in eq 22 and 24 is independent of N_1, N_2, and q for magnetic fields; for electric fields this will not hold so rigorously.

(b) It is easily shown, using simple partial differentiation, that

$$(\partial H^2/\partial \dot{e})_{q=0} = -(\partial q/\partial \dot{e})_{H=0}/(\partial q/\partial H^2)_{\dot{e}=0} \tag{43}$$

It may be altogether more practicable to measure the quantities on the right-hand side of eq 43. In order that the "one order parameter approximation", outlined above, be valid, it is important that all possible measures of anisotropy (e.g., magnetic susceptibility, electric susceptibility, birefringence) show consistent results. For our purpose, birefringence is probably the best measure. In this case one measures $\Delta n = n_{\parallel} - n_{\perp}$, where $n_{\parallel}$ and $n_{\perp}$ are the refractive indices measured, respectively, along the director and perpendicular to it. Thus we may rewrite eq 43 as

$$(\partial H^2/\partial \dot{e})_{q=0} = -(\partial \Delta n/\partial \dot{e})_{H=0}/(\partial \Delta n/\partial H^2)_{\dot{e}=0} \tag{44}$$

or an analogous equation with E replacing H. In general, in the isotropic fluid, both the numerator and the denominator of the right-hand side of eq 44 are likely to be small. However, the weakly first-order nature of the isotropic–nematic transition increases the susceptibility of the liquid crystal order parameter to ordering fields such as $\dot{e}$ or H; these are so-called pretransitional effects. In nonpolymeric materials the existence of a nonzero $(\partial \Delta n/\partial H^2)$ is known as the Cotton–Mouton effect; the analogous electrical phenomenon is the Kerr effect. In nonpolymeric materials the Cotton–Mouton effect is generally observed above the clearing point. It is now clear that the practicability of measuring $(\partial H^2/\partial \dot{e})_{q=0}$ turns on the existence of a measurable Cotton–Mouton effect in the isotropic polymer solution near the isotropic–nematic transition point, which is now a function of polymer mole fraction rather than of temperature. As far as we know such an effect has not yet been observed in polymer solutions. It is possible to make a rather rough estimate of the size of the effect. In MBBA, $(\partial \Delta n/\partial H^2) \sim 0.5 \times 10^{-14}$ G^{-2} near the clearing point.[5] If we suppose that the nematic–isotropic phase transition is no more strongly first order as a function of polymer concentration than the MBBA transition is as a function of temperature, we are led to expect typical values of $(\partial \Delta n/\partial H^2) \sim 0.2 \times 10^{-15}$ G^{-2}. A good experiment to determine such a value would probably require rather larger magnetic fields ($\sim$100 kG) and large samples; however, these values may not be entirely outside experimental reach. Evaluation of $(\partial \Delta n/\partial \dot{e})$ should not present so much problem as $(\partial \Delta n/\partial H^2)$; this is the well-known flow birefringence effect.[9]

Finally, we discuss what kind of experiment is possible to check the predictions of the theory: eq 37, 38, and 40. One must be able to produce a region where $\dot{e}_{ij}$ is roughly constant, and this region should be large enough for a liquid crystal transition to take place while the liquid remains in it. Presumably the critical strain rate $\dot{e}_i$ for the infinitely dilute solution should be the easiest to observe, but eq 40 only yields a rough guide to this. It should also not be too difficult to discover the shift Δc_N predicted in eq 38 by preparing a solution which is in the two-phase region outside a region of elongational flow and observing how large a stream rate is necessary in order that a homogeneous liquid crystal phase emerges from the apparatus. In order to discover the shift Δc_I it will probably be necessary to observe how large a change in concentration of polymer it is necessary to make, for a given strain rate, in order to *avoid* phase separation within the flowing solution. The phase-separated regions will suffer distortion under an elongational flow, ending up as thin strands of coiled or stretched material. These thin strands will have anomalous birefringence properties and enhanced light scatttering properties.

Despite the reservations expressed above, we believe that the experiments involved in checking the theory are worth doing and that any theory which involves only one order parameter and attempts either a thermodynamic or equilibrium statistical mechanical approach to the problem will suffer similar drawbacks to our theory.

Summary

Under some circumstances polymers in solutions can separate out into an isotropic phase at concentration c_I and a nematic phase at concentration c_N. In the presence of an elongational flow field, these concentrations change somewhat. We have derived a quasi-static thermodynamic theory connecting the change in the concentrations c_N and c_I to the applied strain rate. The formulas only include quantities which are, at any rate in principle, experimentally accessible. These quantities are the rate of change of osmotic pressure with respect to concentration in each phase, the partial molar volumes in each phase, the anisotropic part of the dynamic magnetic susceptibility in the nematic phase, and the quantity $(\partial H^2/\partial \dot{e})_{q=0}$, which is most easily determined experimentally by the ratio of the magnitude of the flow birefringence response to that of the Cotton–Mouton effect at the transition point (eq 44). The theory is analogous to the well-known Clausius–Clapeyron results. It is the differential form of the equation of state along a two-phase boundary. These results complement the statistical mechanical study of the same problem in ref 4.

Acknowledgment. I am grateful to A. Keller for suggesting the problem to me. F. C. Frank read a preliminary version of the paper and made me aware of some major pitfalls. I acknowledge useful discussions with J. Odell, M. J. Miles, and D. H. Peregrine.

References and Notes

(1) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 73.
(2) Kramers, H. A. *J. Chem. Phys.* **1946**, *14*, 415.
(3) Bird, R. B.; Armstrong, R. C.; Hassager, O. "Dynamics of Polymeric Liquids"; Wiley: New York, 1977; Vol. I. Bird, R. B.; Hassager, O.; Armstrong, R. C.; Curtiss, C. F. *Ibid.*, Vol. II.
(4) Marrucci, G.; Sarti, G. C. In "Ultra-High Modulus Polymers"; Giferri, A., Ward, I. M., Eds.; Applied Science Publishers: London, 1977.
(5) de Gennes, P. G. "The Physics of Liquid Crystals"; Oxford University Press: London, 1975.
(6) Beeby, J. L. *J. Phys. C* **1973**, *6*, 2262.
(7) See, for example: Landau, L. D.; Lifshitz, E. M. "Statistical Physics"; Pergamon Press: London, 1958; Chapter 8.
(8) Doi, M. *J. Phys. (Paris)* **1975**, *36*, 607. Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 540, 918. Auvray, L. *J. Phys. (Paris)* **1981**, *42*, 79.
(9) A discussion of magnetic birefringence (the Cotton–Mouton effect) is given in ref 5, pp 50–1. A discussion of flow birefringence occurs in ref 5, pp 211–2.

Triplet Energy Migration in Poly(acrylophenone): Dependence on Polymeric Tacticity

T. Kilp*

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

J. E. Guillet

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada.
Received April 15, 1981

ABSTRACT: Although the quantum yield of chain scission in poly(acrylophenone) (PAP) is about 0.40 and is independent of polymeric tacticity, the rates of other photoprocesses are not. Intramolecular quenching of the Norrish type II process by photoproducts is more efficient in i-PAP than in a-PAP. The reverse is true for intermolecular quenching of the carbonyl triplets by naphthalene in fluid solution at 30 °C. Stern–Volmer quenching constants are 70.1 and 15.2 M^{-1} in this case for the atactic and isotactic polymers, respectively. This difference is shown to arise as a result of the shorter triplet-state lifetime of the carbonyls in the isotactic polymer. For the atactic polymer an energy migration coefficient of 1.8×10^{-5} cm^2 s^{-1} was calculated, corresponding to a frequency of energy migration of 4.3×10^{10} s^{-1}. The root-mean-square migration length of 90 Å is less than the estimated coil dimension of about 200 Å. The quenching of phosphorescence intensity in 77 K solid solutions was found to be well described by the Perrin model. Active spheres of quenching were calculated to be 22.5 and 20.3 Å for the isotactic and atactic polymers, respectively.

Introduction

The photochemistry of poly(acrylophenone), also referred to as poly(phenyl vinyl ketone), has been extensively studied in the past decade. This polymer represents a particularly good model to determine the differences to be expected between small-molecule and macromolecular ketones containing a regularly recurring sequence of chromophores. Because of rapid intersystem crossing from the first excited singlet to the triplet, most of the observed photoprocesses can be considered as arising from the latter state, thus simplifying the interpretation of experimental results.

It has recently become apparent that the stereoregularity of a polymer chain can significantly affect the photoprocesses undergone by chromophores attached to it. For example, excimer formation has been shown[1-5] to be more efficient in isotactic polystyrene than in its atactic analogue, both in fluid solutions and in 77 K solid matrices. Tanaka and Otsu[6] have reported that poly(*tert*-butyl vinyl ketone) undergoes photodegradation more readily in the atactic than in the isotactic form. However, Kilp et al.[7] have shown that the quantum yield of the main-chain scission in poly(acrylophenone) is of the order of 0.40 and is independent of tacticity. In view of the differences which have been cited above, it was felt that a further investigation of the photoprocesses involved would prove to be of interest.

Experimental Section

Details of polymer synthesis and degradation techniques have previously been described.[7] Inhibition of chain scission was accomplished by the addition of naphthalene (purified by vacuum sublimation) to the polymer solutions.

The solvent used to form low-temperature glasses was in all cases α-methyltetrahydrofuran (α-MTHF) from Matheson

0024-9297/81/2214-1680$01.25/0