Equation of State for Persistent-Flexible Liquid-Crystal Polymers. Comparison with Poly(γ-benzyl-L-glutamate) in Dimethylformamide

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ABSTRACT: Khokhlov and Semenov have proposed a theory for long persistent chains, which quite accurately describes the liquid-crystalline behavior of dilute solutions of long homogeneous bend-elastic macromolecules. In this work a simple modification of the Khokhlov–Semenov approach is used to obtain an equation of state for persistent-flexible main-chain polymers, which is valid over a wide range of polymer concentrations. Comparisons with experimental data for dimethylformamide solutions of poly(γ-benzyl-L-glutamate) yield good agreement for large polymer axial ratios, where rigid particle theories deviate strongly from the experimental results.

Introduction

It is well-known that flexibility plays an important role in the statistical thermodynamics of liquid-crystal polymers, and a number of different flexibility mechanisms have been studied in this context (cf. ref 1–3 and references therein). In particular, the concept of persistent flexibility seems to appropriately describe such frequently studied systems as poly(γ-benzyl-L-glutamate), DNA, schizophyllan,[2] and poly(hexyl isocyanate).[4] These persistent polymers are essentially rigid on a scale much shorter than the persistence length but are inadequately described by rigid particle liquid-crystal theories for longer polymer contour lengths. In a series of papers, Khokhlov and Semenov (KS) utilized an elegant perturbation scheme to obtain an expression for the free energy of a dilute system of monodisperse persistent macromolecules.[5] Their method gives a rather good description of the isotropic–nematic phase transition in a number of experimental solutions of long rodlike flexible main-chain polymers.[2-4] However, it is also interesting to consider the effects of flexibility on liquid-crystalline behavior away from the transition and at higher concentrations.

In this work, the KS approach is extended in an approximate fashion by employing Lee's[6] description of excluded-volume effects for rigid main-chain polymers based on a generalization of the Carnahan–Starling equation. A simple numerical calculation, based on the trial function method, yields the equation of state for a liquid of monodisperse persistent polymers interacting via hard-core steric repulsions. This result is used to reexamine osmotic pressure data for the poly(γ-benzyl-L-glutamate)–dimethylformamide system, which are in strong disagreement with theories for hard rigid particles at large axial ratios.[7,8] It is shown that the persistent-flexibility mechanism treated within this approximate extension of the KS theory can account for these discrepancies and indeed yields good agreement with the experimental data over an extended range of polymer concentration (i.e., up to volume fractions of ~0.4).

Hard Rigid Main-Chain Polymers

Many theories describing the liquid-crystalline behavior of rigid rodlike particles interacting solely via hard-core steric repulsions are based on a free energy expression of the form

$$F/(N_p k_B T) = \mu_o/(k_B T) + \sigma(f) + \ln c - 1 + A(v,x) + B(v,x)\,\rho(f) \quad (1)$$

(cf. ref 7). Here N_p is the number of particles contained in the volume V, k_B is the Boltzmann constant, T is the temperature, $c = N_p/V$ is the particle number density, and μ_o is the chemical potential in the standard state (ideal solution with $c = 1$). The orientational free energy is given by

$$\sigma(f) = \sigma_{rigid}(f) = \int f(\theta) \ln f(\theta)\, d\Omega \quad (2)$$

where $f(\theta)$ is the distribution function of the rod axes, normalized such that $\int f(\theta)\, d\Omega = \int d\Omega = 1$. The remaining terms represent the configurational free energy, where

$$\rho(f) = \frac{4}{\pi}\int |\sin(\Omega - \Omega')| f(\theta)\, f(\theta')\, d\Omega\, d\Omega' \quad (3)$$

and $(\Omega - \Omega')$ denotes the angle between two rods. The distinctions between the models are contained entirely in the functions $A(v,x)$ and $B(v,x)$, where v is the particle volume fraction and x is the particle axial ratio.

Onsager studied the orientational ordering transition of long hard rigid cylinders using a second-order virial expansion.[9] In this case $A(v,x)$ and $B(v,x)$ are given by

$$A(v,x) = A_0(v,x) = 0 \quad (4a)$$

and

$$B(v,x) = B_0(v,x) = xv \quad (4b)$$

where, in addition, effects due to the rod ends are neglected. Subsequently, a number of approximate methods have been devised to describe liquid-crystalline behavior at higher volume fraction ($v \gtrsim 0.1$), where the second virial approximation loses its validity. Among these theories, which are all distinguished by their specific choice of $A(v,x)$ and $B(v,x)$, are Alben's model,[10] scaled particle theory,[11,12] and, recently, Lee's model.[6] In the following, the last model is used because it may be extended to include short-range soft interactions and therefore appears more versatile than scaled particle theory. Lee has proposed a functional scaling approach that decouples orientational and translational degrees of freedom for elongated particles and therefore is very similar to

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the decoupling approximation.[13] Generalizing the Carnahan–Starling equation for hard spheres to the case of spherocylinders of total length $L + D$ (i.e., cylinder length, L, and diameter, D), he obtains a free energy of the form of eq 1, with

$$A(v,x) = A_L(v,x) = 4v\frac{1 - 3v/4}{(1-v)^2} \tag{5a}$$

and

$$B(v,x) = B_L(v,x) = v\frac{1 - 3v/4}{(1-v)^2}\frac{3x^2/2}{1 + 3x/2} \tag{5b}$$

where $x = L/D$. This approach yields good agreement with Monte Carlo simulations for short spherocylinders[6] (cf., also the numerical results in ref 14). For longer ($L/D \gtrsim 10$) isotropically distributed spherocylinders, Lee's equation of state deviates from the truncated virial expansions obtained from recent numerical results[15] (as does the scaled particle expression of ref 12). However, Lee's result still improves significantly over the second-order virial expansion. It should also be mentioned that in the L/D range of interest here ($10 \lesssim L/D \lesssim 100$), the above comparison is limited due to the insufficient convergence of the virial series. For spherocylinders constrained to be parallel, which corresponds to a well-ordered nematic phase, Lee's equation of state yields very good agreement with Monte Carlo results[16] even for long spherocylinders up to volume fractions ~ 0.5 (cf. also the recent density functional calculations of the nematic-to-smectic transition in this system[17,18]).

Persistent-Flexible Polymers

In contrast to the rigid rodlike polymers of the preceding section, persistent-flexible main-chain polymers are conceived as long cylindrical homogeneously bend-elastic filaments of persistence length P, contour length L, and diameter D. The interactions between the macromolecules are again assumed to be of purely steric nature. The liquid-crystalline phase behavior of this system at the isotropic-to-nematic transition was studied in detail by KS, using the second virial approximation.[5] Subsequently, the same authors extended their method by describing excluded-volume effects in terms of a continuum version of Flory's lattice approach to the steric part of the free energy.[19] In both cases, the free energy assumes the form of eq 1. However, the orientational free energy, σ, is no longer given by σ_{rigid} but becomes a rather complex function, σ_{flexible}, which depends on the ratio L/P. Using a theory, originally developed by Lifshitz,[20] KS derive an expression for σ_{flexible} appropriate for long ($L \gg D$) persistent polymers and arbitrary values of L/P. Unfortunately, this general expression for σ_{flexible} is too complex to be used for specific calculations, and KS proceed instead by expanding σ_{flexible} in the two limits $L/P \ll 1$, i.e., nearly rigid polymers, and $L/P \gg 1$, i.e., semiflexible or wormlike polymers. They obtain

$$\sigma(f) = \sigma_{\text{flexible}}(f) = \begin{cases} \sigma_{\text{rigid}}^{(0)}(f) + (L/P)\sigma_{\text{rigid}}^{(1)}(f) & L/P \ll 1 \\ (L/P)\sigma_{\text{semiflexible}}^{(0)}(f) + \sigma_{\text{semiflexible}}^{(1)}(f) & L/P \gg 1 \end{cases} \tag{6}$$

where

$$\sigma_{\text{rigid}}^{(0)}(f) = \int f(\theta) \ln f(\theta)\, d\Omega \tag{7a}$$

$$\sigma_{\text{rigid}}^{(1)}(f) = \frac{1}{12}\int [\partial f(\theta)/\partial\theta][\partial \ln [f(\theta)]/\partial\theta]\, d\Omega \tag{7b}$$

$$\sigma_{\text{semiflexible}}^{(0)}(f) = \frac{1}{8}\int [\partial f(\theta)/\partial\theta][\partial \ln [f(\theta)]/\partial\theta]\, d\Omega \tag{8a}$$

$$\sigma_{\text{semiflexible}}^{(1)}(f) = -2 \ln \int f(\theta)^{1/2}\, d\Omega \tag{8b}$$

Notice that in this approach to persistent flexibility, the angular distribution function, $f(\theta)$, denotes an average along the particle contour with respect to the orientational distribution of unit vectors tangential to the contour. For $L/P = 0$ one of course recovers $\sigma = \sigma_{\text{rigid}}^{(0)} = \sigma_{\text{rigid}}$, the case of rigid rods discussed in the previous section. In contrast to σ_{flexible}, which manifests itself on a length scale set by P, the steric repulsions governing the excluded volume occur on a scale $O(D)$, on which the polymer is considered well approximated as rigid cylinder. The terms in the free energy representing excluded-volume effects are therefore to a good approximation formally identical with the rigid-rod case. The phase behavior of persistent rods for $L/P \ll 1$ and $L/P \gg 1$ can thus be calculated in complete analogy to that of rigid rods if $\sigma = \sigma_{\text{flexible}}$ in eq 1, where σ_{flexible} is given by eq 6.

Using Onsager's trial function approach for $f(\theta)$ and eq 1 together with eq 4a,b and 6, KS obtained the phase boundaries and the order parameter for the isotropic liquid-crystalline phase transition. They also show that approximate results for arbitrary L/P can be obtained with good accuracy by interpolating between the results for $L/P \ll 1$ and $L/P \gg 1$.

Equation of State for Persistent-Flexible Polymers

The theory of the previous section can be used in conjunction with Lee's description of excluded-volume effects (i.e., eq 1 in conjunction with eq 5a,b and 6) to calculate an approximate equation of state for persistent macromolecules. In order to consider intermediate L/P, KS applied a simple polynomial ratio interpolation scheme to the final results obtained in the rigid and semiflexible limits. Although this procedure works well for several quantities including the order parameter at the transition, it does not work for the pressure. The equation of state calculated in this fashion near phase coexistence in the anisotropic phase generally does not continuously tie on to the pressure calculated in the biphasic regime. This difficulty can be avoided by interpolating the initial expressions for σ_{flexible} in eq 6. In analogy with ref 4, the interpolation via the ratio of two simple polynomials gives

$$\sigma(f) = \sigma_{\text{flexible}}(f) \approx \frac{\sigma_0(f) + \sigma_1(f)(L/P) + \sigma_2(f)(L/P)^2}{1 + \sigma_3(f)(L/P)} \tag{9}$$

where the coefficients σ_i ($i = 0$–3) are easily obtained by equating eq 9 with eq 6 in the limits $L \ll P$ and $L \gg P$, respectively. The results are

$$\sigma_0(f) = \sigma_{\text{rigid}}^{(0)}(f) \tag{10a}$$

$$\sigma_1(f) = s(f)\, \sigma_{\text{rigid}}^{(0)}(f) + \sigma_{\text{rigid}}^{(1)}(f) \tag{10b}$$

$$\sigma_2(f) = s(f)\, \sigma_{\text{semiflexible}}^{(0)}(f) \tag{10c}$$

$$\sigma_3(f) = s(f) \tag{10d}$$

where

$$s(f) = (\sigma_{\text{semiflexible}}^{(0)}(f) - \sigma_{\text{rigid}}^{(1)}(f))/(\sigma_{\text{rigid}}^{(0)}(f) - \sigma_{\text{semiflexible}}^{(1)}(f)) \tag{10e}$$

As before,[5] $f(\theta)$ is now approximated via Onsager's trial

function

$$f(\theta) = \frac{\alpha}{\sinh \alpha} \cosh(\alpha \cos \theta) \quad (11)$$

where α is a variational parameter.[9] Even with this relatively simple choice of $f(\theta)$, the integrations in eq 7a,b and eq 8a,b yield somewhat cumbersome expressions. It is therefore more convenient to use expansions of the integrals in terms of large α, i.e.

$$\sigma_{\text{rigid}}^{(0)}(\alpha) \approx \ln \alpha - 1 + \pi \exp(-\alpha) + O(\exp(-2\alpha)) \quad (12a)$$

$$\sigma_{\text{rigid}}^{(1)}(\alpha) \approx \frac{1}{6}(\alpha - 1) + \frac{1}{6}[\pi/2]^3[1 - [2\alpha/\pi]^2] \exp(-\alpha) + O(\alpha^2 \exp(-2\alpha)) \quad (12b)$$

$$\sigma_{\text{semiflexible}}^{(0)}(\alpha) \approx \frac{1}{4}(\alpha - 1) + \frac{1}{4}[\pi/2]^3[1 - [2\alpha/\pi]^2] \exp(-\alpha) + O(\alpha^2 \exp(-2\alpha)) \quad (13a)$$

$$\sigma_{\text{semiflexible}}^{(1)}(\alpha) \approx \ln(\alpha/4) - q \exp(-\alpha/2) + \frac{1}{4}q^2 \exp(-\alpha) + O(\exp(-3\alpha/2)) \quad (13b)$$

where $q = 2K(1/2) - 4E(1/2) = -1.694426$ and K and E are complete elliptic integrals. For the purpose of the present calculation, it is sufficient (see below) to retain the leading order terms only, and thus eq 9 becomes

$$\sigma(f) = \sigma_{\text{flexible}}(\alpha) \approx \frac{12[\ln 4 - 1][\ln \alpha - 1] + [\ln(16\alpha) - 3]z + (1/4)z^2}{12[\ln 4 - 1] + z} \quad (14)$$

where $z = (\alpha - 1)L/P$. Note that Odijk has also given a numerically very similar expression for $\sigma(f)$ for general L/P in the Gaussian limit (cf. eq IX.8 and IX.9 in ref 2). For $\rho(\alpha)$ (eq 3) the exact expression[9]

$$\rho(\alpha) = 2I_2(2\alpha)/\sinh^2 \alpha \quad (15)$$

is used, where I_2 is a modified Bessel function.

Following the argument presented in the previous section, the free energy is now approximately given given by eq 1 with $\sigma = \sigma_{\text{flexible}}$ given by eq 14 and $A = A_L$ and $B = B_L$ given by eq 5a,b. The parameter α follows from the minimization of the free energy, i.e.

$$\partial\sigma_{\text{flexible}}(\alpha)/\partial\alpha + B_L(v,x)\, \partial\rho(\alpha)/\partial\alpha = 0 \quad (16)$$

Furthermore, the chemical potential

$$\mu/(k_B T) = \mu_0/(k_B T) + \ln c + \sigma_{\text{flexible}}(\alpha) + \partial[vA_L(v,x) + vB_L(v,x)\, \rho(\alpha)]/\partial v \quad (17)$$

and the reduced pressure

$$v_0\Pi/(k_B T) = v + v^2\, \partial[A_L(v,x) + B_L(v,x)\, \rho(\alpha)]/\partial v \quad (18)$$

where v_0 is the volume of one polymer molecule. The numerical calculation of the phase diagram and the equation of state are standard and completely analogous to the case of rigid rodlike particle (cf. ref 2).

Comparison with the Poly(γ-benzyl-L-glutamate)–Dimethylformamide System

Nearly a decade ago, Kubo and Ogino[7,8] determined the osmotic pressure of poly(γ-benzyl-L-glutamate) (PBLG) in dimethylformamide (DMF), a solvent chosen to minimize polymer aggregation (i.e., polydispersity), over a wide range of polymer volume fractions. With increasing concentration, PBLG undergoes an alignment transition. Although the liquid-crystalline state of PBGL is cholesteric, rather than nematic, there is evidence that the forces giving rise to the twist are only a small perturbation.[1] Making the additional assumption that the interactions between the polymers in the solvent are identical with those of the hard particle fluid, Kubo and Ogino[7,8] compare different hard particle equations of state Π to the experimentally determined osmotic pressure, Π_{os}. The three preparations studied in detail had molecular weights of 23 800, 66 000, and 155 000 (denoted PBLG-A, -B, and -C, respectively). Of the rigid hard rod theories due to Onsager,[9] Alben,[10] Lasher,[11] and Cotter,[12] only the last provides a reasonable fit to the data for the shortest polymer, and then only if the axial ratio is replaced by a significantly (~30%) smaller effective axial ratio. For the two longer polymers, even Cotter's scaled particle theory strongly underestimates the transition volume fractions and the pressure in the anisotropic phase. In particular, the slope of the osmotic pressure as a function of polymer volume fraction changes much too drastically across the transition.[7,8] Kubo and Ogino attribute these deviations from the rigid-rod behavior mainly to the flexibility of PBLG, but, except for the above effective axial ratio, suggest no suitable theoretical description of the flexibility effects. It is therefore interesting to compare their osmotic pressure data with the equation of state for persistent-flexible macromolecules derived in the previous section.

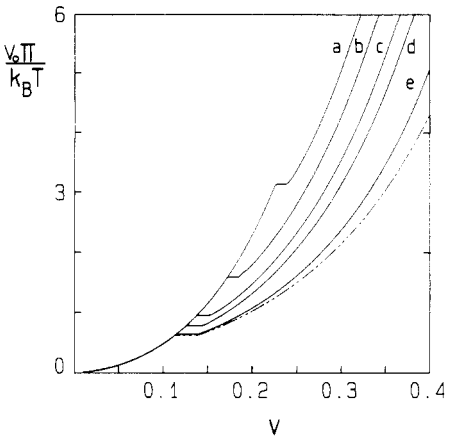

Figure 1. Equation of state for rodlike persistent-flexible polymers, $v_0\Pi/(k_BT)$, vs polymer volume fraction, v, for different persistence lengths, P, when $x = 26.2$, $D = 16$ Å, and (a) $L/P = 1$ ($P \approx 420$ Å); (b) $L/P = 0.5$ ($P \approx 840$ Å); (c) $L/P = 0.2$ ($P \approx 2100$ Å); (d) $L/P = 0.1$ ($P \approx 4200$ Å); (e) $L/P = 0.01$ ($P \approx 42000$ Å). The broken line represents $L/P = 0$ ($P = \infty$).

Using the experimentally determined molar volumes for PBLG-A to -C (cf. ref 7) and a molecular diameter of 16 Å^3 yields the axial ratios $x = L/D = 9.0$ for PBLG-A, $x = 26.2$ for PBLG-B, and $x = 62.8$ for PBLG-C. This is in close accord with the polymer axial ratios estimated in the solid state, i.e., 9.3, 27.3, and 65.8.[8] Note again that the total polymer contour length is $L + D$.

In order to compare the present results with the experimental osmotic pressure Π_{os}, one needs to know the persistence length, P. In general, the determination of P depends strongly on the solvent and on the modeling of the geometry and the dynamics of the macromolecules (cf. ref 22). The resulting uncertainties in the value of P are reflected by the wide range of persistence lengths for the PBLG–DMF system quoted in the literature (e.g., 850 Å $\lesssim P \lesssim$ 1400 Å[21]). Figure 1 illustrates the equation of state (eq 18) for different values of P using $x = 26.2$ (PBLG-B) as an example. As the polymer becomes less flexible (i.e, P is increased), the pressure in the anisotropic phase decreases, the transition is shifted to lower volume fractions, and the biphasic region widens slightly

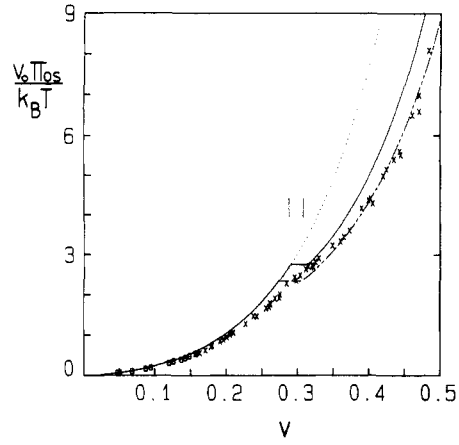

Figure 2. Reduced osmotic pressure, $v_o\Pi_{os}/(k_BT)$, vs polymer volume fraction, v, for PBLG-A (x = 9.0). The dotted line is the theoretical result for the metastable isotropic state; the solid line is the theoretical result for flexible polymers (P = 2000 Å); and the broken line is the theoretical result for hard rigid spherocylinders (P = ∞). Symbols indicate experimental data: Circles represent measurements at 30 °C tabulated in ref 7, and crosses represent data taken from Figures 2 and 4 in ref 8. Two short vertical lines indicate the position of the experimental phase boundaries, found using a polarizing microscope.[7]

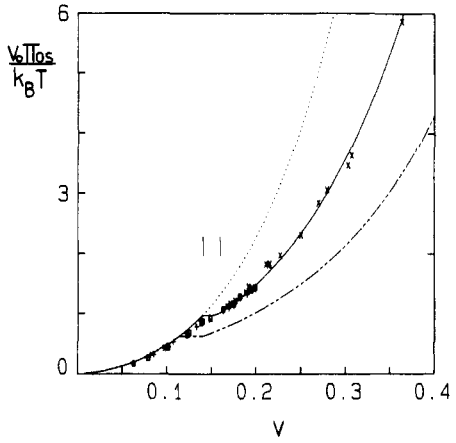

Figure 3. Same as Figure 2 but for PBLG-B (x = 26.2). The additional symbols, plusses, and stars, represent data points obtained at 15 and 45 °C, respectively, tabulated in ref 7. Here, the crosses represent data points taken from Figures 3 and 4 in ref 8.

(cf. ref 5). The approach toward the rigid-rod limit is quite slow, so that flexibility effects are strong even at small ratios of L/P (as pointed out previously in ref 5). In the following, the rigid-rod limit P = ∞ is compared to the case where P = 2000 Å, which gives the best overall agreement with the data for PBLG-B and -C.

Figures 2–4 show the comparison of the experimental reduced osmotic pressure $v_o\Pi_{os}/(k_BT)$ for PBLG-A, -B, and -C with the equation of state derived in the previous section. For PBLG-A, Lee's rigid-rod theory (P = ∞) yields rather good agreement with the data, whereas for P = 2000 Å the present theory overestimates the effects of flexibility. The softening of the transition, apparent in the data for PBLG-A, may be due to slight side-by-side association of the polymer.[8] For larger x, i.e., for PBLG-B and -C, the ridig-rod case (P = ∞) deviates strongly from the experimental values, as found previously for scaled particle theory.[7,8] Equation 18 for persistent-elastic macromolecules, however, yields good agreement with the experimental osmotic pressures for P = 2000 Å over an extended range of polymer volume fractions.

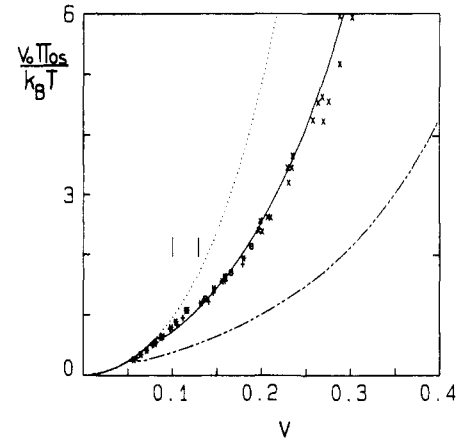

Figure 4. Same as Figure 3 but for PBLG-C (x = 62.8).

Discussion

The above results are obtained using a number of approximations, including the trial function in eq 11 and the interpolation of the free energy via eq 9 and 14. To estimate the effect of the trial function approximation, the transition concentrations for rigid rods (P = ∞) according to eq 11 were compared with the numercially exact calculations.[6] The deviations are between 2 and 5% for $10 \leq x \leq 100$. Similar values are obtained for the pressure at the transition. As mentioned, the interpolation in eq 9 gives σ_{flexible} only approximately. However, KS have argued that an interpolation of this type introduces an error smaller than the one due to the trial function. Equation 14 for σ_{flexible} represents the leading term for large variational parameter α. Including the higher order terms proportional to $\exp(-\alpha/2)$ and $\exp(-\alpha)$ (cf. eq 12a,b and 13a,b) yields results whose graphs are virtually indistinguishable from those presented in the figures. Finally, it should be noted that maintaining the excluded-volume terms in the free energy in their rigid particle form is a somewhat ad hoc approximation, whose quantitative quality is difficult to assess. The resulting overall error may be partly absorbed in the somewhat larger value of P (=2000 Å) in the flexible case.

On the experimental side, association of polymers as well as the preparation process itself give rise to some polydispersity in the particle size and shape distribution (cf. ref 7), and this effect is neglected here. It should also be mentioned that ref 8 contains osmotic pressure results for volume fractions exceeding those shown in Figures 2–4. For $v \gtrsim 0.5$, the present theoretical results increasingly overestimate the osmotic pressure. However, Kubo[8] indicates that considerable hysteresis was observed in some of the experiments at volume fractions between 0.5 and 0.7. Furthermore, at high densities ($v \gtrsim 0.6$) the local hard rod character of the PBLG polymer is no longer a good approximation, and side-chain effects apparently become important.[8]

In conclusion, the results of KS for the orientational free energy of persistent-flexible polymers combined with Lee's description of rigid particle excluded-volume effects remedy the major discrepancies between theory and experiment observed by Kubo and Ogino for $v \lesssim 0.5$. Only for small axial ratios, where the present equation of state seems to exaggerate flexibility effects, is the rigid-rod theory in somewhat better agreement with the data. The approach to flexibility utilized in this work is simple enough also to be useful in describing the liquid-crystalline behavior exhibited by self-assembling molecules. Rigid particle theories tend to overestimate the coupling between

aggregation and liquid-crystalline ordering in these systems, which leads to an anomalous behavior.[24] Efforts are underway to adapt the representation of $\sigma_{flexible}$ used in this work (cf. eq 9 and 14) and Lee's description of excluded volume to the highly disperse particle populations characteristic of solutions of reversibly polymerizing proteins[23,25,26] or surfactant micelles.[27,28]

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Registry No. γ-Benzyl-L-glutamate (SRU), 25038-53-3; γ-benzyl-L-glutamate (homopolymer), 25014-27-1.

Kinetics of Mesophase Transitions in Thermotropic Copolyesters. 3. Poly[(phenyl-*p*-phenylene terephthalate)-*co*-[(1-phenylethyl)-*p*-phenylene terephthalate]] Copolyester

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ABSTRACT: Structure formation kinetics of a copolyester consisting of *p*-benzenedicarboxylic acid (TPA), phenylhydroquinone (PHQ), and (1-phenylethyl)hydroquinone (PEHQ) with a molar ratio of 50/25/25 has been studied. This copolyester shows periodic *c*-axis order in its X-ray diffraction pattern due to equal unit lengths of the comonomers. The crystal unit cells for quenched and annealed TPA/PHQ/PEHQ copolyester are both monoclinic but with slightly different sizes. Two transition processes from its nematic to solid states can also be identified. Isothermal kinetics of the transitions indicate that the fast transition process is nucleation-controlled crystal growth. The development of the slow process is hampered by the previously grown crystals in the fast process. A higher transition temperature of the fast transition process compared with that of the slow process is attributed to a larger enthalpy change (thermodynamic effect) and melting of relatively ordered domains (kinetic effect) during this transition.

Introduction

During the last 10 years, there has been an increasing interest in the development of thermotropic liquid crystalline polyesters in both academic and industrial areas of research. From the engineering point of view, a lowering of transition temperatures of the polyesters due to the limitation of processing conditions is desirable, as well as enhancement of the anisotropic nature of their flow behavior (low viscosity above their transition temperatures) and their ultimate mechanical properties. One way to approach such goals is to copolymerize different aromatic ester monomers to disturb the regularities of the polyester crystalline structures. Basically, two different paths can be carried out. The first is the path of disturbing the regularities along the chain axis by introducing different monomer lengths, such as in the case of the Xydar copolyesters consisting of *p*-dihydroxybenzoic acid (HBA), 4,4′-dihydroxybiphenyl (HBP), and *p*-benzenedicarboxylic acid (TPA), or introducing additional solid kinks, such as in the case of the Vectra copolyesters with HBA and 6-hydroxy-2-naphthoic acid (HNA). From crystalline structural characterization by wide-an-

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