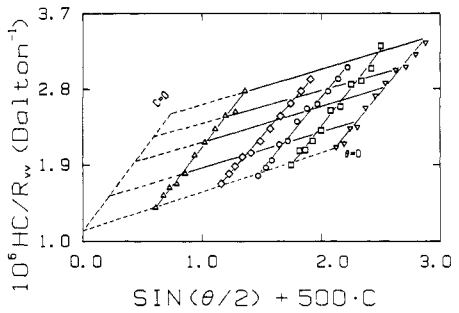

Figure 1. Zimm plot of PETFE in diisobutyl adipate at 240 °C. Hollow triangles denote 1.22×10^{-3} g/mL; hollow diamonds, 2.32×10^{-3} g/mL; hollow circles, 2.94×10^{-3} g/mL; hollow squares, 3.50×10^{-3} g/mL; and inverted hollow triangles, 4.25×10^{-3} g/mL. $M_w \simeq 9.0 \times 10^5$.

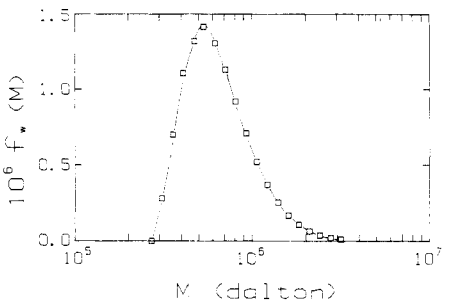

Figure 2. Molecular weight distribution $f(M)$ of a PETFE sample. $M_w = 9.0 \times 10^5$, $M_w/M_n \approx 1.35$.

value approach developed by McWhirter and Pike.[10,11] It differs from our earlier histogram method,[12] which is nonlinear. MSVD has been tested by using simulated time correlation functions and experiments involving dilute solutions of polystyrene, poly(methyl methacrylate),[13] and polyethylene.[2]

(b) Method of Regularization Based on Tikhonov and Miller As Used by Abbiss et al.[14] The regularization technique considered the ill-posed problem carefully and was shown to yield results comparable to those from MSVD for unimodal distribution functions under realistic experimental conditions. In particular, we compared the two Laplace inversion approaches (a) and (b) in our studies of PPTA in concentrated sulfuric acid[5] and PMMA in methyl methacrylate.[15]

(c) CONTIN. This regularization algorithm was kindly provided by Provencher,[16] who introduced Fisher's statistic test for determining the optimum solution in the inversion procedure. CONTIN has the ability to resolve multimodal $G(\Gamma)$ under favorable conditions.

Laplace inversion of the time correlation function must be handled with a great deal of caution because of its ill-posed nature. We tried to accomplish this step (3) using three different tested schemes: the singular value decomposition technique with discrete multiexponentials to approximate $G(\Gamma)$, a method of regularization whereby a linearized smoothing operator was used, and CONTIN, which had been distributed widely by Provencher throughout the world. It was gratifying to confirm that the three schemes yielded comparable results for $G(\Gamma)$ in our data analysis, with the variance agreeing to within 10%.

For a PETFE polymer in diisobutyl adipate, we were able to dissolve the polymer, clarify the solution, and perform the dilution at 250 °C under nitrogen. Static and dynamic light scattering measurements as well as differential refractometry measurements were performed at 240 (±0.02) °C and λ_0 = 488 nm using an argon ion laser (Spectra Physics Model 2020-03) operating at ~100 mW. Figure 1 shows a Zimm plot whereby we determined the weight-average molecular weight $M_w = 9.0 \times 10^5$. By combining static and dynamic properties with the Laplace inversion of $|g^{(1)}(\tau)|$, we were able to determine, for the first time, an estimate of the molecular weight distribution (MWD) of an alternating copolymer of ethylene and tetrafluoroethylene, as shown in Figure 2. The molecular weight distribution was surprisingly narrow, as $G(\Gamma)$ yielded a variance $\mu_2/\bar{\Gamma}^2$ of only ~0.10, where $\bar{\Gamma} = \int \Gamma G(\Gamma)\, d\Gamma$ and $\mu_2 = \int (\Gamma - \bar{\Gamma})^2 G(\Gamma)\, d\Gamma$. In the transform from $G(\Gamma)$ to MWD, we determined the scaling relation between the translational diffusion coefficient and the molecular weight using polymers of different molecular weights, each individually characterized. A detailed characterization is under way.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation, Polymers Program (Grant DMR 8314193).

Registry No. PETFE, 25038-71-5.

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Received November 21, 1985;
Revised Manuscript Received February 11, 1986

A Comment on the Stability of Orientational Order in Homopolymer Melts[1]

It is now widely known that rigidly rodlike chain molecules will spontaneously adopt a nematic order whenever sufficiently concentrated. Theory[2,3] indicates that attractive interchain forces are not necessary for support of

this order, although for rods of small aspect ratio such forces assume greater importance.[4] Some 30 years ago, Flory[2] discussed the approximate level of chain flexibility that could be permitted while preserving the stability of such entropically stabilized, orientation order in the melt. More recent work[5] can now be used to reexamine this topic. The present communication demonstrates that a slightly generalized form of Flory's seminal result is obtained and that it is useful.

The basic approach is that of the familiar lattice model construction.[6] The particular chains of interest are semirigid in the two-state sense epitomized by a helix–coil internal equilibrium. Reference 5 details the model assumptions and formal development of the statistical thermodynamics of the corresponding isotropic–nematic phase equilibrium. Equation 36 of that paper displays the corresponding chemical potential, μ_p, for an isotropic (unprimed) phase in the form

$$(\mu_p - \mu_p^\circ)/RT = \ln v_p + x\{v_p(1 - 1/x) + \chi v_s^2 + m \ln [1 - \rho/(1 - \theta)]\} \quad (1)$$

Equation 40 of ref 5 gives the chemical potential of a chain in the nematic (primed) state in the form

$$(\mu_p' - \mu_p^\circ)/RT = \ln v_p' + (x - 1)v_p' + x\chi' v_s'^2 - x[\ln (1 - Q) + Q] - \ln (y/x)^2 - mx \ln s - \ln \sigma \quad (2)$$

The superscript zero corresponds to the appropriate reference state, R is the gas constant, T is the absolute temperature, v_p is the volume fraction of polymer, x represents the aspect ratio of its fully extended (helical) form, χ is the Flory–Huggins solvation parameter, $v_s = 1 - v_p$, y is the lattice-model order parameter, s and σ are the Zimm–Bragg parameters[7] that characterize the conformational equilibrium, θ is the fraction of conformational units in the rigid or helical configuration, ρ is the number of sequences of such units, and the quantity m denotes the number of conformational units that are required to sequentially adopt this same helical configuration in order to generate a chain section with unit axial ratio. The quantity Q has the general form

$$Q = v_p'(\theta' - ym\rho') \quad (3a)$$

but as previously reported,[5] for homopolymers that must support a nematic order without additional fields or constraints, the stable condition is found to be $\theta' = 1$ and $\rho' = 1/mx$ so that

$$Q = v_p'(1 - y/x) \quad (3b)$$

for the situation in hand. Equation 33 of ref 5 gives

$$\sigma = \rho^2/[(\theta - \rho)(1 - \theta - \rho)] \quad (4)$$

as the relation between σ, ρ, and θ.

Attention is to be focused on neat fluids. Thus, equality of the chemical potentials from eq 1 and 3 defines the condition of equilibrium between nematic and isotropic phases. Equations 2 and 4 may be introduced to eliminate Q and ρ, thereby expressing the equilibrium condition in terms of the variables v_p, v_p', y, x, θ, σ, m, and s, i.e., in terms of the concentration, order, size, and conformation of the chain molecules. The underlying physical principles of the order/disorder equilibrium can be highlighted by taking limits of these variables. Let $v_p = v_p' = 1$. This corresponds to neglecting differences in the free volume between phases and between a phase and the reference state. We shall let $y = 1$, which is the lattice-model condition for perfect orientational order. Letting x become large is appropriate for such units concatenated in very long chains. It is usually the case for synthetic chain molecules that the factors contributing to conformational preferences are of fairly short range. Thus, there is very little general tendency for units to "cooperate" in the helix–coil sense.[7] Formally, we set $\sigma = 1$ to signify this independent or "uncooperative" situation. As an attendant implication of $\sigma = 1$, we also acquire the relation (cf. eq 32 and 33 of ref 5)

$$s = \theta/(1 - \theta) \quad (5)$$

so that only m and θ remain. Performing the indicated limits and some algebra yields

$$\ln \theta_c = -1/m \quad (6)$$

as the condition for ideally nematic–isotropic equilibrium between isopycnic phases of long, uncooperative chains. The subscript c denotes the critical value of θ which ensures equilibrium. A noteworthy feature of the selected limits is that without exception they tend to lower θ_c. Consequently, eq 6 gives an unambiguous lower bound to the critical value of θ to be associated with any particular chain geometry (m).

Flory[2] deduced an expression for the critical stiffness in the form

$$\ln (1 - f_c) = -1 \quad (7)$$

where f_c is the critical fraction of bent units. In our notation $1 - f_c = \theta_c^m$, which corresponds to the physical statement that a fundamental "unit" is bent if even one monomeric component is nonrigid.

It is possible to relate θ to the observable characteristic ratio, C_∞, in a manner that is consistent with the two-state conformational model used so far. Explicitly[2]

$$C_\infty = (1 + \theta)/(1 - \theta) \quad (8)$$

It is also possible to obtain m, although not as cleanly. By hypothesis, there are only rigid and random coil configurational states available, and m is essentially a measure of the average width of the rigid sequences. If only one or several very similar rectilinear geometries are available, then m is easily obtained from crystallographic data or models. For example, in the case of polyethylene, the crystalline all-trans form (orthorhombic) has two chains per unit cell[8] of dimension $7.4 \times 4.9 \times 2.54$ Å.[3] The chain axis lies in the c direction, so that the diameter corresponding to a circle with area equal to one-half the area normal to this direction is 4.8 Å. Thus, the c-axis projection of 1.27 Å per methylene unit implies that $m = 4.8/1.27 = 3.8$ for the all-trans conformation that we take as representative of "the" rigid state. In more complex cases detailed knowledge of the conformational properties is required. Thus, both θ_c and m can be obtained either from experiment or from conformational calculations.

It is of some interest to compare the observed values of C_∞ for common polymers with the critical value obtained from 6 and 8 once an estimate of m is in hand. Let us assume that m is always identical with that found in the crystalline solid for each polymer. Data are tabulated in ref 8. For polyethylene, m is 3.8 so that the critical characteristic ratio is 7.6, in contrast to the 6.7 value observed at 138 °C.[9] Thus, polyethylene is reliably predicted to exhibit isotropic behavior in the melt. On the other hand, poly(*p*-phenyleneterephthalamide) has $m = 1.6$, a critical characteristic ratio of 3.3, and an observed[10] value of $C_\infty = 20$. Clearly, if a melt of high molecular weight PPDT could be prepared it would be ordered. A third type of example is afforded by poly(tetrafluoroethylene), for which $m = 4.5$; i.e., its critical characteristic is 9.0, and calculated estimates of C_∞ at the normal melting point range above 11.[11] Although this value is in excess of the

critical value $C_\infty = 9$, and the more elaborate theory of Ronca and Yoon[12] also predicts order in the PTFE melt, it would be imprudent to conclude that PTFE must be ordered in the melt. Recall that all of the approximations that underpin eq 6 conspire to underestimate θ_c. Thus, while the inequality C_∞ (observed) $< C_\infty^{(c)}$ (critical) represents an unambiguous prediction of isotropy in the melt, the condition C_∞ (observed) $\gtrsim C_\infty^{(c)}$ (critical) is not immune from equivocation. Certainly, when their difference is on the order of only 20% caution is suggested both in interpreting existing data and in performing new experiments.

Thus, the lattice-model description of neat, semirigid chains yields a simple criterion for stable orientation order. The lower limit of chain stiffness can be compactly rendered as

$$C_\infty^{(c)} = [1 + \exp(-1/m)]/[1 - \exp(-1/m)] \quad (9)$$

by combining eq 6 and 8. This reduces to the result Flory[2] obtained some 30 years ago in the limit $m = 1$. The predictions of this relationship seem to be in good accord with observations. It can be most fruitfully employed to sort any homopolymer melt into isotropic ($C_\infty < C_\infty^{(c)}$), orientationally ordered ($C_\infty \gg C_\infty^{(c)}$), or borderline ($C_\infty \gtrsim C_\infty^{(c)}$) classes.

Registry No. Polyethylene, 9002-88-4; (*p*-phenylenediamine)·(terephthalic acid) (copolymer), 25035-37-4; (*p*-polyphenylene)·(terephthalamide) (SRU), 24938-64-5; poly(tetrafluoroethylene), 9002-84-0.

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(1) This communication recapitulates an address delivered at the Symposium in honor of the late Professor P. J. Flory's 75th birthday at Stanford University in June 1985, some 2 months before his death. It is respectfully dedicated to his inspiring and celebrated contributions to the study of macromolecules.
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Received October 29, 1985

Sharpness of the Functionality Induced Structural Transition in Poly(styrene–isoprene) Star Block Copolymers

In a recent publication,[1] we reported on the solid-state morphology of poly(styrene–isoprene) star block copolymers having 30 wt % polystyrene outer blocks. The method of synthesis employed[2,3] enabled well-defined materials to be produced so that a systematic study of the effect of functionality (number of diblock arms) and arm molecular weight on the microstructure could be made. The most striking finding of this study was the discovery of a transition in equilibrium domain morphology from the normally observed cylindrical morphology (for this composition) to an ordered bicontinuous (OB) structure upon increasing the functionality of the star molecules. In addition, the functionality required to obtain the OB structure was found to decrease as the molecular weight of the diblock arm increased. For the samples having 10^4 molecular weight (outer) polystyrene blocks, 2- and 4-arm stars exhibited the morphology of hexagonally packed polystyrene cylinders in a polyisoprene matrix while 8-, 12-, and 18-arm stars exhibited the OB structure. In the OB morphology the polystyrene forms two distinct three-dimensional networks of short rods which are mutually interwoven but unconnected.[4]

The purpose of this work is to investigate the sharpness of this structural transition with functionality by studying the corresponding 5- and 6-arm-star copolymers. The experimental techniques utilized were transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and dynamic mechanical thermal analysis (DMTA). It was found that the 5-arm star exhibited exclusively cylindrical morphology while the 6-arm star was predominantly OB.

The star block copolymers were prepared by using the chlorosilane linking method which has been described in detail previously.[2,3] The chlorosilanes used for the linking reactions were 1-(methyldichlorosilyl)-2-(trichlorosilyl)ethane and 1,2-bis(trichlorosilyl)ethane. The pentafunctional material was synthesized from vinyltrichlorosilane and methyldichlorosilane following the procedures outlined elsewhere.[2,3] The hexafunctional linking agent was obtained from Petrarch Systems, Inc. The linking reactions were facilitated by the addition of tirethylamine following the polymerization of the isoprene segment of the diblock. It has been found[5] that the addition of amines or ethers, which are known[6] to cause disruption of poly(isoprenyllithium) aggregates, facilitates the linking event leading to the formation of star-shaped polymers.

The size exclusion chromatography measurements were done with the Waters 150C instrument with tetrahydrofuran as the mobile phase at 30 °C. The number-average molecular weights were determined in toluene at 38 °C with the Wescan membrane osmometer. The nomenclature used to describe the samples is as follows: SI 5/30/10 is a 5-armed poly(styrene–isoprene) star containing 30 wt % polystyrene outer blocks with molecular weights of 10^4. The same diblock precursor was used to prepare both the 5- and 6-arm stars for which the functionalities achieved were 4.9 and 6.0, respectively. The characterization results are given in Table I.

The details of the experimental methods used for TEM, SAXS, and DMTA have been given elsewhere.[1] Briefly, the 1-mm-thick samples were prepared by slow casting from a 3 wt % solution in toluene, a nonpreferential solvent for polystyrene and polyisoprene,[7] over a period of 1 week followed by 120 °C annealing under high vacuum for 1 week. This sample preparation technique was used in order to obtain, as nearly as possible, thermodynamic equilibrium structures. Thin sections for TEM were obtained by cryoultramicrotomy at −110 °C followed by osmium tetraoxide vapor staining. SAXS patterns were obtained with a Kratky camera equipped with a Braun one-dimensional position-sensitive detector. The SAXS data were corrected for sample absorption, wire sensitivity, and parasitic scattering. Slit-length desmearing was done by using Vonk's FFSAXS Version 3 program.[8] Mechanical analysis was performed with a Polymer Labs DMTA in the single-cantilever mode at a frequency of 1 Hz and a scan rate of 5 °C/min.

The electron micrograph in Figure 1a shows that sample 5/30/10 has the domain morphology of polystyrene cylinders in a polyisoprene matrix as evidenced by the axial and longitudinal cylindrical projections seen to the right

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