Tailored Rigid−Flexible Block Copolymers. 3. Fate of the Flexible Block within the Mesophase

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ABSTRACT: Diblock copolymers were prepared by condensation of benzoyl-terminated poly(*p*-benzamide) [PhCO(PBA)] and anilino-terminated poly(*m*-phenylene isophthalamide) [PhNH(MPD-I)]. The copolymers were freed from unreacted prepolymers and also partially fractionated by selective extraction techniques. The formation of the nematic phase was investigated for three copolymers having a similar length of the rigid PhCO(PBA) block and a fraction β of flexible segment covering a range from 0.5 to 0.7. In the *N*,*N*-dimethylacetamide (DMAc) containing 3% LiCl solvent the critical volume fraction v_2^{i} of the PhCO(PBA) prepolymer was largely unaffected by copolymerization with a similar length of the flexible PhNH(MPD-I) block. At the largest β value only a 25% increase in the critical composition of PhCO(PBA) was observed. The mesophase appears capable of admitting much longer flexible sequences than anticipated. These results are qualitatively in line with a reduced flexibility of the flexible segment due to the self-consistent orientational field of the mesophase. However, comparison of data in aggregating and nonaggregating solvents suggests that mesophase formation should be described in terms of supramolecular assemblies rather than molecularly dispersed units.

Introduction

Assemblies based on rigid macromolecules distributed within a matrix of flexible polymers are commonly found in nature (*i.e.* connective tissue, vitrous body of the eye) and also find industrial applications (*e.g.* high-performance composites).[1] In the vast majority of cases the concentration of the reinforcing element within the matrix exceeds the critical concentration at which liquid crystalline order develops. Since, as is well-known,[2] a coiling polymer cannot be accommodated within an ordered mesophase, the system should demix under equilibrium conditions even in the case of chemically compatible components.[3] While stable composites can nevertheless be assembled using suitable technology, the use of rigid−flexible copolymers is the best approach to achieve an intimate mixing of the two components under thermodynamically stable conditions.[4]

Matheson and Flory[5] suggested that a flexible segment, covalently linked to a rigid one, is admitted within the mesophase even though the degree of order is decreased, the critical concentration is increased, and the biphasic gap is narrowed. In their lattice treatment, the coil segment may be regarded as a kind of diluent of the mesophase and has a degree of flexibility unaffected by the orientational order. At variance with Matheson and Flory, Vasilenko *et al.*[6] have assumed that the self-consistent orientational field of the mesophase induces partial orientational and conformational ordering of the flexible component.

The elucidation of the organization of the flexible component within the mesophase is of great significance from both a fundamental and an applied point of view. For instance, the mechanical properties of the processed copolymers are expected to depend upon the distribution of the two components.[4,7] However, the difficulty in producing well tailored block copolymers has hindered an unambigous verification of theoretical models.[7−10]

We have recently reported the tailored synthesis of pure diblock copolymers based on segments of benzoyl-terminated poly(*p*-benzamide) [PhCO(PBA)] and anilino-terminated poly(*m*-phenylene isophthalamide) [PhNH(MPD-I)].[11] In the present article a series of these copolymers differing only in the length of the flexible PhNH(MPD-I) segment will be used to determine the critical concentration at which the mesophase forms in solutions of *N*,*N*-dimethylacetamide (DMAc) containing 3% LiCl. Data in 96% H_2SO_4 are also included. As shown by diluted solution studies presented in Parts 1[11] and 2[12] of this series, the two solvents differ in their affinity for the blocks, affording the possibility of investigating the role of supramolecular assembling on mesophase formation.

Experimental Section

1. Materials. Following the approach described in Part 1, three copolymer samples **N1P1**, **N2P2**, and **N3P3** were obtained from a one-pot, two-step scheme of Yamazaki's[13] condensation starting from benzoyl-terminated poly(*p*-benzamide) [PhCO(PBA)] (**P1**, **P2**, **P3**) and anilino-terminated poly(*m*-phenylene isophthalamide) [PhNH(MPD-I)] (**N1**, **N2**, **N3**) prepolymers. The copolymers were freed from unreacted PhNH(MPD-I) by extraction with pure DMAc, which (as assessed from solubility, ^{1}H NMR, and intrinsic viscosity) did not solubilize PhCO(PBA). These techniques are described in detail in Part 1.[11] Only traces of copolymers were soluble in pure DMAc. Fractions of copolymers were then extracted by gradual addition of LiCl to DMAc; 82% of the total copolymer produced was found to dissolve in DMAc/1% LiCl, a solvent which did not dissolve unreacted PhCO(PBA). The copolymers were thus not only purified from unreacted homopolymers but also partially fractionated due to partitioning of components with extreme values of the rigid−flexible ratio in the residue of the DMAc/1% LiCl extraction or in a solution of pure DMAc. Traces of triblock molecules (rigid−flexible−rigid type) are likewise expected to concentrate in the former residue. DMAc (Fluka) was freshly distilled over calcium hydride. LiCl (Aldrich) was dried over P_2O_5 under reduced pressure at 150 °C for 6 h. H_2SO_4 (96%; Fluka) was used as received.

Solutions of PhCO(PBA) and of copolymers were prepared in DMAc/3% LiCl and 96% H_2SO_4 by adding diluent to the weighed polymer under stirring. Concentration (C_p) is given as weight of polymer per 100 mL of solvent and as polymer volume fraction v_2. The v_2 values for PBA were calculated using the previously determined[14] partial specific volume

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Table 1. Viscosity Data for Prepolymers and Copolymers[a]

PhNH(MPD-I)				PhCO(PBA)				copolymers		
	H_2SO_4	DMAc/3% LiCl			DMAc/3% LiCl	H_2SO_4			H_2SO_4	DMAc/3% LiCl
sample	$[\eta]$	$[\eta]$	M_v		$[\eta]$	$[\eta]$	M_v	sample	$[\eta]$	$[\eta]$
N1	0.35	0.40	13 500	**P1**	2.86	1.56	11 800	**N1P1**	1.35	2.30
N2	0.49	0.60	23 000	**P2**	3.00	1.75	12 600	**N2P2**	1.20	1.90
N3	0.60	0.70	28 200	**P3**	3.20	1.80	12 800	**N3P3**	0.90	1.35

[a] $[\eta]$ in dL/g at 25.0 ± 0.1 °C.

(0.7542 mL/g) in DMAc/3% LiCl. The v_2 values for the diblock were obtained by using, for the partial specific volume of poly(*m*-phenylene isophthalamide) in DMAc/3% LiCl, the value 0.7087 mL/g, which we determined pycnometrically at 25 °C. Additivity of partial specific volumes of rigid and flexible block was assumed.

2. Critical Compositions. Solutions were optically examined under a POLYVAR polarizing microscope at room temperature. Solutions were extinguishing and isotropic for values of concentration $C_p \leq 5$ g/dL but showed liquid crystalline droplets at larger concentrations. In order to assess the critical concentration at which the mesophase appears, concentrated solutions in the biphasic region were gradually diluted with the solvent until the faintest sign of liquid cristallinity could be detected. The critical composition was then confirmed (±0.1 g/100 mL) by increasing polymer concentration starting from isotropic solutions in the pretransition zone. The conjugated composition was determined by increasing the polymer concentration of the biphasic systems until the last sign of isotropic material was detected. It is worth noting that it is extremely difficult to determine the point at which the last isotropic fraction disappears in the bright field produced when the predominantly anisotropic phase is viewed in polarized light. As a consequence the conjugated composition values might be affected by an underestimation on the order of 5%.

3. Viscosity and Light Scattering. Molecular weights of PhCO(PBA) prepolymers were assessed from intrinsic viscosity measured in 96% H_2SO_4 (a nonaggregating solvent) as described in Part 2.[12] The relationship reported by Schaefgen *et al.*[15] was used ($M_w/M_v \approx 0.99$)[12]

$$[\eta] = (1.9 \times 10^{-7}) M_w^{\ 1.7}$$

For PhNH(MPD-I) no aggregation is shown in both H_2SO_4 and DMAc/3% LiCl.[12] For the determination of the molecular weight, we used the equation

$$[\eta] = (2.9 \times 10^{-4}) M_v^{\ 0.76}$$

which we had determined from light-scattering analysis in DMAc/3% LiCl.[12] The intrinsic viscosity of block copolymers was determined in both 96% H_2SO_4 and DMAc/3% LiCl.[11,12] All viscosity data were obtained at 25.0 ± 0.1°C.

Light scattering for PhCO(PBA) solutions was performed using a WYATT DAWN F apparatus operating at 633 nm. Solutions were clarified by centrifugation for 1 h at 18 000*g* and by filtration using 0.45 and 0.2 μm Altech filters for 96% H_2SO_4 and DMAc/3% LiCl, respectively. Four different dilutions in the range 0.5−1.0% were prepared from a stock solution by solvent addition. The effective concentration of solutions was confirmed, after light-scattering measurements, using a UV−vis BECKMAN DU-640 spectrophotometer. The refractive index increment of PBA in DMAc/3% LiCl, measured using a CHROMATIX KMX-16 differential refractometer operating at 633 nm, was found to be 0.274 mL/g. The value of d*n*/d*c* in 96% H_2SO_4 (0.320 mL/g) was obtained from the literature.[16]

Results

Relevant intrinsic viscosity and molecular weight data for the prepolymers are included in Table 1. It is seen that the molecular lengths of the three PhCO(PBA) samples are nearly the same, amounting to ≈100 *para*-repeating residues ($M_0 = 119$). Assuming isodiametrical units, this is also the axial ratio X_R of the rigid block.

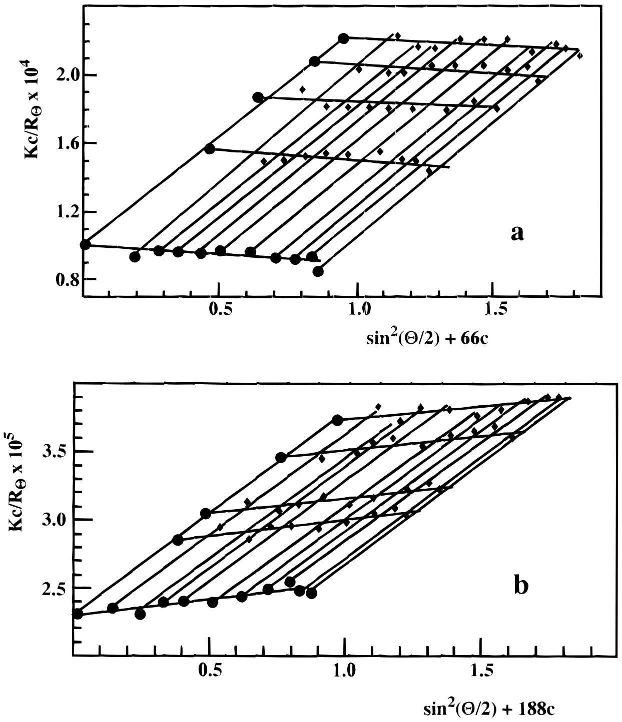

Figure 1. Zimm Plot of PhCO(PBA) sample **P1** in 96% H_2SO_4 (a) and in DMAc/3% LiCl (b).

The molecular length of the three PhNH(MPD-I) prepolymers changes instead in a significant range from $X_F \approx 110$ to ≈240 *meta*-repeating residues ($M_0 = 119$). Therefore, the block copolymers are characterized by a nearly constant axial ratio of the rigid block and variable lengths of the flexible segments.

As discussed in more detail in Parts 1[11] and 2,[12] the values of $[\eta]$ for PhCO(PBA) and for the copolymers are larger in DMAc/3% LiCl than in H_2SO_4. This indicates an aggregation of PhCO(PBA) in DMAc/3% LiCl which is confirmed by the light-scattering results reported in Figure 1, showing that the apparent molecular weight of PhCO(PBA) is about a factor 5 larger in the organic solvent (actual values of M_v are 44 000 in DMAc/3% LiCl and 10 000 in H_2SO_4). Aggregation of PhCO(PBA) in DMAc/3% LiCl was also detected through light scattering by Schaefgen *et al.*[15] and by Ying and Chu.[17] The former authors report even larger aggregation factors (up to 12) than the value observed here. The latter authors claim instead molecular dispersion when polymer concentration is below 0.2%, but the details of the synthesis of their PBA samples are unclear. On the other hand our data reveal that the aggregate is stable in the relatively high concentration range used for the light-scattering determination and also in the lower range (C_p from 0.05 to 0.1) used for the viscosity measurements.[12]

Table 2. Critical Composition in DMAc/3% LiCl

PhCO(PBA)					copolymers					
sample	$C_p^{i\ a}$	v_2^i	v_2^a	v_2^a/v_2^i	sample	β^b	$C_p^{i\ a}$	v_2^i	v_2^a	v_2^a/v_2^i
P1	6.1	0.044	0.071	1.6	**N1P1**	0.53	6.2	0.043		
P2	5.7	0.041	0.066	1.6	**N2P2**	0.65	6.8	0.047	0.062	1.3
P3	5.7	0.041	0.066	1.6	**N3P3**	0.69	7.4	0.051	0.065	1.3

[a] Grams of polymer in 100 mL of solvent. [b] Fraction of flexible segments in the copolymer.

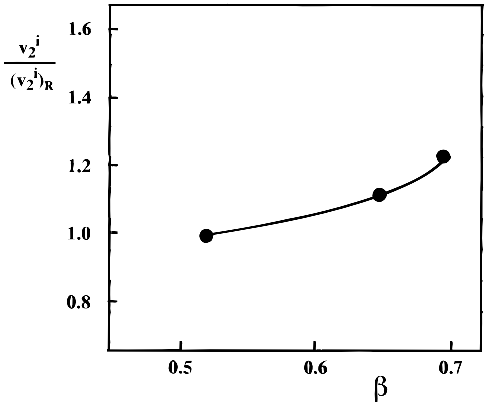

Figure 2. Critical volume fraction for copolymers referred to the corresponding value for the rigid block plotted against the fraction of flexible segment β. Data in DMAc/3% LiCl.

The data in Table 1 exhibit a decrease in $[\eta]$ when the length of the flexible block is increased. It was shown in Part 2 that the occurrence of this effect in nonaggregating solvents is consistent with the hydrodynamic behavior theoretically expected for rigid−flexible diblock molecules.[12]

The fraction of flexible segments in the copolymer is

$$\beta = \frac{X_F}{X_F + X_R}$$

$X_F + X_R$ representing the extended length. Values of β for the three copolymers are collected in Table 2. Also included in Table 2 are the critical composition data measured for the PhCO(PBA) prepolymers and for the three copolymers. The values of the composition at which the anisotropic phase appears, v_2^i, and its conjugated value, v_2^a, observed for the PhCO(PBA) samples are in line with the extensive data in the literature for the PBA homopolymer in the DMAc/3% LiCl solvent.[3,18]

The critical concentration in DMAc/3% LiCl for the copolymers with lowest β (0.53) is nearly the same as that of the corresponding rigid block. For the other two copolymers v_2^i appears to increase, with respect to the value for PhCO(PBA), but the effect is a rather small one, as evidenced in Figure 2 by the ratio of the v_2^i values for the copolymers to the corresponding v_2^i values of the rigid block.

The width of the biphasic region is characterized by v_2^a/v_2^i values of ≈1.6 for PhCO(PBA) which are reduced to ≈1.3 for the copolymers. The latter conclusion is not altered by the possible underestimation of v_2^a (*cf.* Experimental Section), which affects both the prepolymer and the copolymer solutions.

Under the polarizing microscope a difference was noticed between the nematic droplets of the homopolymers and the copolymers. The former exhibited larger dimensions and reverted more quickly than the latter to the original shape when deformed by application of pressure on the cover slide.

Solutions of PhCO(PBA) and of the copolymers in 96% H_2SO_4 failed to show liquid crystallinity and remained isotropic up to the solubility limit ($v_2 \approx 0.2$). We were initially surprised by this finding, but we confirmed that no degradation had occurred, as previously shown by the results reported in Part 2.[12] The unexpected finding is however in line with the pioneering work by Kwoleck *et al.*,[19] who did not report data in H_2SO_4 but showed that critical concentrations were much larger in inorganic acids than in the DMAc/3% LiCl solvent.

Discussion

1. Molecular Theory. In the case of the Matheson and Flory[5] treatment, the flexible segment is forced to enter the mesophase because it is covalently bound to the rigid one but it is not orientationally altered. The expected increase in the critical composition with the size of the flexible segment is therefore a rather large one. For instance, the v_2^i value for a rigid homopolymer with 50 isodiametrical units is increased by a factor of *ca.* 2.3 in the case of a block copolymer composed of 50 rigid and 50 flexible units (for details see Figure 2 of ref 5 and Figure 6 of ref 9). Likewise, the critical axial ratio X^c, which stabilizes the undiluted mesophase (predicted to be 6.7 for rigid rods in the lattice treatment[20]), is increased by a factor of *ca.* 4.8 when a fraction $\beta = 0.5$ of flexible segments is part of the block copolymer sequence (for details see Figure 2 of ref 6). Factors appear to be larger in the undiluted systems but definitively not in line with the modest values of $v_2^i/(v_2^i)_R$ (less than 1.3) reported in Figure 2.

The theory of Matheson and Flory[5] further predicts a strong reduction of the width of the narrow biphasic region. This effect is only qualitatively in line with the modest decrease in v_2^a/v_2^i observed with our copolymers. As pointed out elsewhere,[18] the width of the biphasic region for a polydisperse homopolymer is generally found to be narrower than predicted and close to the width expected for a monodisperse system. The origin of this deviation from theory has not been adequately explained.

In the case of the Vasilenko *et al.* treatment,[6] where straightening of the flexible segment is postulated, a less pronounced increase in the critical parameters v_2^i and X^c with β is expected, since the flexible block contributes to the overall molecular asymmetry. The detailed predictions by Vasilenko *et al.* are dependent not only upon the fraction β of flexible segments but also upon flexibility parameters characterizing the fraction of chain links in the bent conformation, expected to differ in the isotropic (f_o) and anisotropic phases (f).

For a block copolymer composed of an equal number of rigid and flexible units ($\beta = 0.5$), the critical axial ratio X^c (defined by the sum $X_F + X_R$) is predicted to increase[6] by the factors 3.6, 2.8, 1.4, and 1.0, corresponding to the stiffness parameters $f_o = 0.8$, 0.7, 0.6, and 0.4, respectively (for details see Figure 3 of ref 6). These factors are considerably reduced (increased) at smaller (larger) values of β. Quantitative comparison of the present data with the theory of Vasilenko *et al.*

requires an evaluation of the flexibility parameter for PhNH(MPD-I). However the comparison cannot be expected to be a rigorous one, since the calculation refers to an undiluted system of multiblock chains where each $X_F + X_R$ sequence is decoupled by a freely rotating bond.

The above theory further predicts that, for relatively large values of β, inversely related to f_0, two nematic phases with different order parameters should exist. This is justified by the trend of the order parameter S_F of the flexible segment, which shows a steep increase at relatively small β. Since the present data were centered around the biphasic isotropic–nematic region, we could not verify this prediction.

2. Flexibility Parameter. The flexibility parameter is controlled by the conformational energy for internal rotation ϵ according to the equation[21]

$$f_0 = \frac{(z-2)\exp(-\epsilon/KT)}{1 + (z-2)\exp(-\epsilon/KT)} \tag{1}$$

where z is the lattice coordination number. For the freely rotating chain, $\epsilon = 0$, and in the case of the cubic lattice, $f_0 = 0.8$. Semiflexible chains with $\epsilon > 0$ and $f_0 < 0.63$ were predicted to attain spontaneous ordering in the melt by an earlier (now abandoned) Flory's theory.[21] A free homopolymer with $f_0 > 0.63$ is too flexible to spontaneously form a mesophase in terms of the early Flory's theory.[20] Moreover, it would not even be admitted to the mesophase of another rigid homopolymer.[2,3] The key feature of the Vasilenko *et al.* treatment is, in fact, the recognition that once the flexible segment is forced to enter the mesophase of the rigid block to which it is chemically linked, the self-consistent field promotes additional stiffening (an analogy may be made with the nematic field induced coil → helix transition[22]).

The flexibility parameter can be calculated from the ratio of the unperturbed mean-square end-to-end distance $\langle R_0^2\rangle$ to the contour length $R_{MAX} = X_F L_0$[21]

$$f_0 = \frac{2L_0}{\langle R_0^{\,2}\rangle / R_{MAX} + L_0} \tag{2}$$

where L_0, the length of the repeating unit corresponding to $M_0 = 119$, can be taken equal to 6.1 Å for PhNH(MPD-I) on the basis of geometrical consideration. The Kuhn segment $\langle R_0^2\rangle/R_{MAX}$ is related to the persistence length q by the relation[23]

$$2q = \frac{\langle R_0^{\,2}\rangle}{R_{MAX}} \tag{3}$$

The unperturbed mean-square end-to-end distance can be calculated using the well-known equations[23]

$$[\eta] = KM^{1/2}\alpha^3$$

$$[\eta]_\theta = KM^{1/2}$$

$$K = \Phi_0\left(\frac{\langle R_0^{\,2}\rangle}{M}\right)^{3/2} \tag{4}$$

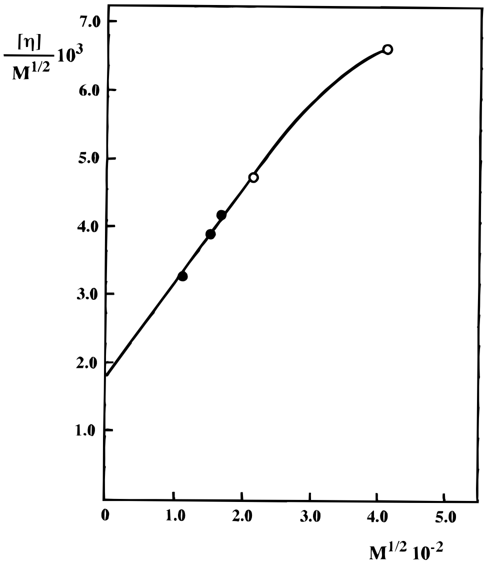

Figure 3. Stockmayer–Fixmann plot allowing the calculation of K (eqs 4 and 5) from the intercept. Data: ●, from Table 1 of the present paper; ○, from Table 1 of ref 12.

Table 3. Flexibility Parameter for PhNH(MPD-I)

sample	X_F[a]	$\langle R_0^2\rangle$ (Å^2)	R_{max} (Å)	q (Å)	f_0
N1	113	12 850	689	9	0.51
N2	193	21 940	1177	9	0.51
N3	237	26 890	1446	9	0.51

[a] Degree of polymerization referred to a unit with $M_0 = 119$ and $L_0 = 6.1$ Å.

where α is the expansion factor, $[\eta]_\theta$ is the viscosity in a θ-solvent, and $\Phi_0 = 2.1 \times 10^{21}$ mol^{-1}.[24] The value of K can be calculated using the Stockmayer–Fixmann equation[23]

$$[\eta]/M^{1/2} = K + 0.51\Phi_0 BM^{1/2} \tag{5}$$

from a plot of $[\eta]/M^{1/2}$ *vs* $M^{1/2}$, such as that in Figure 3, yielding $K = 1.95 \times 10^{-3}$. Data used are collected in Table 3, along with the values of $\langle R_0^2\rangle$, f_0, and persistence length q, which turns out to be ≈9 Å. Alternative analysis of the viscosity and light-scattering[12] data using the semiempirical method proposed by Krigbaum[23] gave similar results for f_0 and q. We note that Tsvetkov and co-workers[25,26] reported values of q as low as 8 Å and as large as 22 Å for the same polymer from hydrodynamic data.

The observed values of K and q, though somewhat larger than those of typical flexible polymers (for polystyrene and polyisobutylene, $K = 0.8 \times 10^{-4}$ and 1.08×10^{-4}, respectively, at 25 °C),[27] are definitively much smaller than those reported for semirigid polymers which show liquid crystalline behavior.[28] The latter are characterized by values of $q \geq 100$ Å. The polyterephthalamide of *p*-aminobenzhydrazide, which is a borderline case (being able to show liquid crystalline behavior only under a flow field),[27] exhibited q values between 50 and 80 Å.[28]

The flexibility parameter f_0 appears smaller than the critical 0.63 value, below which a spontaneous ordering in the melt is predicted by the abandoned Flory's theory mentioned above. Even in terms of the Vasilenko *et al.* treatment, a value of $f_0 = 0.50$ leads to the expectation of significant ordering in the melt and hence to a small effect of the flexible segment on $v_2^{\,i}$. However, the flexibility parameter (eq 1) is based on a model too crude for application to real semiflexible chains. Moreover, its limited range of reliability (from 0.8 to 0.63) results in a strong influence of any indetermination on q and, particularly, L_0. On the basis of the more reliable value of q, which reveals a considerable flexibility, and of the relatively large values of β, the dependence of $v_2{}^i$ upon β shown in Figure 2 appears surprisingly small and at the present time can only be qualitatively correlated with the induced orientation and conformational ordering postulated by Vasilenko *et al.* Data for other copolymers appear desirable for a definite assessment of the issue. In the next section we shall consider alternative contributions based on the aggregation of PhCO(PBA) occurring in DMAc/3% LiCl.

3. Supramolecular Assemblies. Molecular dispersion was assumed in the vast majority of studies in which the measured critical concentration was compared with theoretical predictions.[3] However, the present light-scattering data reveal that PhCO(PBA) is molecularly dispersed at relatively high concentration only in H_2SO_4. Supramolecular entities composed of at least five single molecules appear instead to be stable in DMAc/3% LiCl in the concentration range 0.5−1.0% and can therefore be assumed to persist at the still larger concentration at which the mesophase appears.

It is therefore necessary to reconsider the kind of agreement which has often been found between experimental and theoretical values of $v_2{}^i$ for a variety of homopolymers, and for PBA in DMAc/3% LiCl in particular. Calculated $v_2{}^i$ values were based on well-known equations of the type

$$v_2{}^i \approx \frac{\text{const}}{X} \tag{6}$$

where the constant may vary according to different theories[30] between ≈4 and ≈10. The axial ratio X was calculated using the contour length/diameter ratio for rods or the $2q/d$ ratio based on the persistence length for long semirigid chains.

Our **P1** sample has a molecular weight of 11 800, corresponding to 100 repeating units each of length 6.6 Å and diameter 5 Å. The axial ratio of single dispersed molecules is therefore 132. The latter yields a calculated $v_2{}^i \approx 0.048$ (Flory's 6.4 value for the constant was used), which is consistent with the experimental value of 0.044. However, since molecular dispersion is obviously not occurring, this agreement with theory must be a fortuitous one. Due to the general nature of the theoretical model, it is nevertheless possible to use eq 6 to calculate a value of X using the experimentally determined $v_2{}^i$. The value of X so derived may reflect the axial ratio of a supramolecular entity and should be consistent with the size and shape of the assembly.

To exemplify the above concept, we present in Figure 4a a simple (admittedly arbitrary) model based on seven rodlike particles having the axial ratio 100 (*e.g.*, 100 repeating units each with length = diameter equals 10 Å) and a side-by-side shift of $^1/_4$th of the length along the main axis. The total length of the assembly is 1000 + 250 × 6 = 2500 Å while the diameter is between 20 and 30 Å. Averaging the latter value, the axial ratio X of the aggregated particle is 104. In this case, rather close values of X characterize the geometry of single rods and of supramolecular particles. This illustrates how the present and the reported[3] agreement between experiment and molecular parameters for PBA in DMAc/3% LiCl can be a fortuitous one. Supramolecular effects in homopolymers should also be considered for other unexplained effects such as the smaller than expected width of the biphasic region and large critical concentrations observed in nonaggregating solvents.

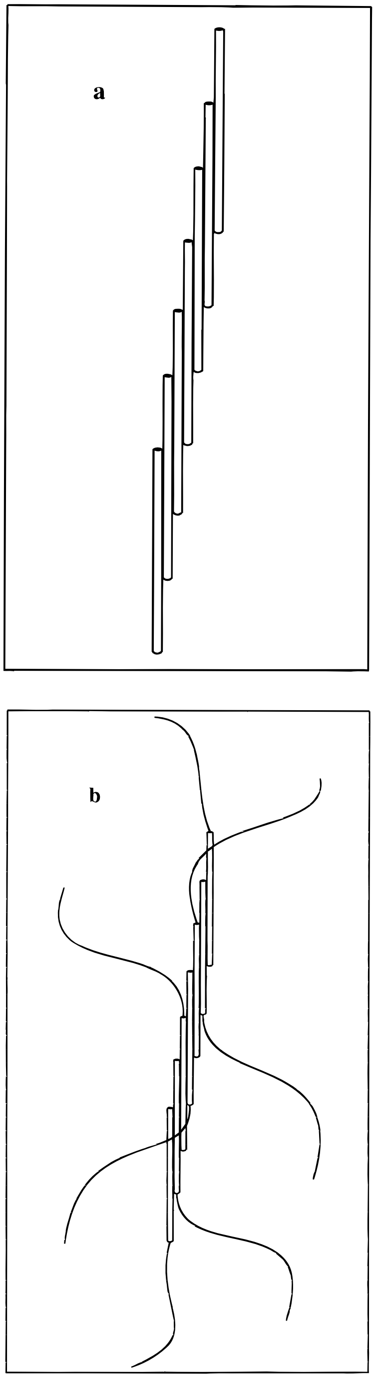

Figure 4. Schematic representation of a nematic aggregation of assemblies involving seven molecules each with a side-by-side shift of $^1/_4$th of the length and alternating orientations: (a) PhCO(PBA) homopolymer; (b) copolymer.

The above considerations refer to the PhCO(PBA) homopolymer in DMAc/3% LiCl. The viscosity data in Table 2 and our previous results[11,12] reveal that the aggregation of PhCO(PBA) segments persists even in the case of copolymers. However, it is not easy to assess if the shape and degree of aggregation are altered by the flexible segment. Even for the homopolymeric assembly, we only know that it should have an axial ratio of ≈130 and at least five single molecules. A variety of models could conform with these requirements. Therefore any conclusion concerning the organization of the flexible segments within the mesophase is unwarranted for the present system.

In Figure 4b we extend the same scheme of Figure 4a to the case of a rigid−flexible block copolymer with no alteration of the aggregation pattern of the rigid homopolymer. In the case of this arbitrary model, one can see that only the two flexible segments at the extremity of the assembly might contribute to the asymmetry along the main axis. The contribution of the remaining flexible chains is felt mostly along the diameter of the assembly. Even this crude model does show the difficulty in attributing the modest increase in the critical concentration of the copolymer solely to conformational ordering.

The model of a quasi-micellar organization sketched in Figure 4b should be of considerable interest for further study of mesophase formation by supramolecular assemblies[1,31] and for the properties expected for the corresponding composite materials. It is worth noticing that the present results suggest that rather long sequences of flexible units are admitted in the mesophase. This effect might have important implications for materials for which an efficient reinforcement of the flexible component is desired.

Further work on other types of tailored copolymers including different block sequences, and an extended range of β and q values is in progress and will be reported at a later date. Of special interest appear to be the systems for which true micelles are the precursors of the mesophase.[1,31] On the other hand, verification of the theoretical models discussed above should be sought in nonaggregating solvents.

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