(13) P. H. Hermans and A. Weidinger, *J. Appl. Phys.*, **19**, 491 (1948).
(14) H. P. Klug and L. E. Alexander, "X-ray Diffraction Procedures", Wiley-Interscience, New York, 1974, pp 114–116.
(15) H. P. Rockwell, Jr., in "The Encyclopedia of Photography" Vol. 5, National Educational Alliance, N.Y., 1949, pp 1609 and 1610.
(16) J. N. Harman, Jr., in "The Encyclopedia of Photography", Vol. 5, National Educational Alliance, N.Y., 1949, p 1899 ff.
(17) G. H. Stout and E. H. Jensen, "X-ray Structure Determination", Macmillan, London, 1968, pp 165–177 and 200–211.
(18) C. Tanford, "Physical Chemistry of Macromolecules", Wiley, New York, 1961, p 178.
(19) F. P. Warner, W. J. MacKnight, and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 2113 (1977).
(20) C. J. Aloisio, S. Matsuoka, and B. Maxwell, *J. Polym. Sci., Part A-2*, **4**, 113 (1966).
(21) W. W. Graessley, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **13** (1), 35 (1972).
(22) S. M. Aharoni, *J. Macromol. Sci., Phys.*, **13**, 159 (1977).

Rigid Backbone Polymers. 4. Solution Properties of Two Lyotropic Mesomorphic Poly(isocyanates)

Shaul M. Aharoni* and Eugene K. Walsh

Corporate Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960.
Received October 24, 1978

ABSTRACT: Solution properties of poly(hexyl isocyanate) (PHIC) and poly(50% butyl + 50% *p*-anisole-3-propyl isocyanate) (PBAPIC) polymers were evaluated by M_w, M_n, viscosity, and microscopic techniques. The results show: (a) both polymers form liquid crystals above a certain critical concentration; and (b) both polymers partition into more concentrated anisotropic and more dilute isotropic phases (the anisotropic phase is composed of the higher molecular weight fraction of the polymer and the isotropic phase contains the lower molecular weight portions of the polymer). Microscopic observations of isotropic inclusions in the anisotropic solution phase of PHIC reveal the former to possess angular shapes. The development of this angularity is explained as resulting from the growth of the isotropic inclusions.

A statistical thermodynamic theory applicable to concentrated solutions of polydisperse rigid polymers was recently put forth by Professor Flory.[1] Accordingly, in the event that a concentrated solution of rigid polymer molecules separates into a disordered, isotropic phase and an ordered, anisotropic phase, the higher molecular weight, M, fractions would preferentially partition into the anisotropic phase, and the lower M fractions would concentrate in the isotropic phase. Furthermore, the theory shows that the concentration, c, of the polymer in the anisotropic phase will be substantially higher[2] than in the isotropic phase.

We have recently discovered[3,4] that many poly(isocyanate) polymers exhibit lyotropic and thermotropic mesomorphic behavior. The poly(isocyanates) capable of forming liquid crystals may be divided into the following three categories: (a) poly(alkyl isocyanate) homopolymers having side chains $4 \leq n \leq 12$ long, n being the number of carbon atoms in the normal alkyl side chain; (b) poly(alkyl–aralkyl isocyanate) copolymers in which the aromatic residue is at least two $-CH_2-$ groups removed from the chain backbone; and (c) substituted homo- and copolymers, and certain poly(alkyl isocyanate) copolymers.

Because of the relative simplicity of their preparation, and especially because of the high solubility of many members of the poly(isocyanate) family in common solvents, these polymers lend themselves to studies of liquid crystal polymers in general and to tests of the theory expounded in ref 1 in particular.

In this paper we wish to report results of studies conducted on two polymers: poly(hexyl isocyanate) (PHIC), and poly(50% butyl + 50% *p*-anisole-3-propyl isocyanate) (PBAPIC). (The monomer composition of the copolymer was determined by nuclear magnetic resonance (NMR) spectroscopy and is given in mol %.)

Experimental Section

The polymers were prepared according to the general procedure of Shashoua[5,6] as described in detail in ref 3. Butyl and hexyl isocyanate were obtained from Aldrich Chemicals and Eastman Chemicals, respectively, and were used without further purification. The comonomer *p*-anisole-3-propyl isocyanate was prepared[3] from 4-(*p*-methoxyphenyl)butyric acid which was procured from Aldrich Chemical Co.

Dilute solution viscosities were determined in Cannon–Ubbelohde glass viscometers operating at low to medium shear rates in a constant temperature bath set at 25 °C. The solvents most often used were 1,1,2,2-tetrachloroethane (TCE), chloroform, bromoform, and toluene. Concentrated solution viscosity was determined with the aid of a Nametre Direct Readout Viscometer operating at a fixed shear rate of 4060 s^{-1}, at 25 °C. The polymer batches studied with the Nametre Viscometer were of such a low molecular weight (M_w of PHIC was 65 000 and of PBAPIC about 35 000) that they did not show a significant increase in the viscosity when measured in several rapid consecutive runs. The same behavior was observed in the dilute solution glass viscometers for the low-M batches. High-M batches showed substantial increases in viscosity in several rapid runs on the same solution. When the solution relaxes overnight, the measured viscosity was, within experimental error, the same as the initial viscosity.

Light-scattering measurements were performed at 5461 Å wavelength on solutions maintained at ambient temperature in a Brice–Phoenix spectrophotometer. Weight average molecular weights, M_w, were obtained from dilute $CHCl_3$ solutions of polymer fractions isolated from the anisotropic and isotropic solution phases by the Zimm plot[7,8] method. Number average molecular weight, M_n, was determined in a Mechrolab membrane osmometer using chloroform and chlorobenzene solvents. Polarized light microscopy was performed in a Leitz Ortholux polarized light microscope. Because it is an excellent solvent for most poly(isocyanates) and evaporates relatively slowly at room temperature, TCE was the solvent of choice for most of the optical microscopy work. It should be noted, however, that mesogenic polymers were mesomorphic in quite a few solvents, once the critical concentration for the formation of the anisotropic phase, v_2^*, was surpassed.

Compositional studies were performed by means of a Varian A-60 NMR instrument on solutions of the polymers in deuterated TCE. The density of the polymers was determined by pycnometry in aqueous solutions of $ZnCl_2$, or in mixtures thereof with small amounts of methanol.

Results

When concentrated solutions of PHIC in solvents such as TCE, chloroform, bromoform, and toluene or PBAPIC

0024-9297/79/2212-0271$01.00/0

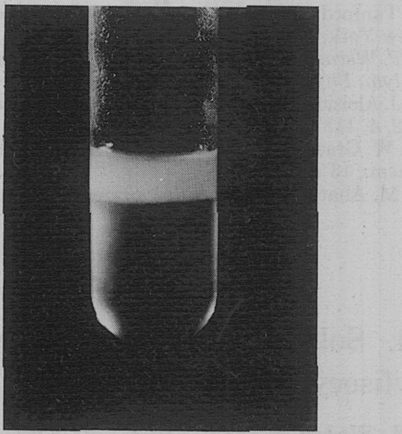

Figure 1. A two-phase solution of PHIC in TCE. The hazy, anisotropic phase is on top and the clear, isotropic phase is at the bottom.

in TCE are allowed to rest at room temperature, they tend to separate into a hazy, anisotropic phase and a clear, isotropic phase. Whether the anisotropic phase will float on top of the isotropic one or settle to the bottom of the vessel depends on the densities of the polymer and solvent in any given solution. We have measured the density of PHIC to be 1.000 ± 0.005 g/cm^3 and that of PBAPIC to be 1.119 ± 0.005 g/cm^3. It is natural, then, that for solvents of density higher than that of the polymer the polymer-rich phase will float on top of the polymer-poor phase. For solvents of lower density than that of the polymer, the reverse will happen. A typical two-phase solution of PHIC in TCE (the density of which is 1.586 g/cm^3) is shown in Figure 1, which was obtained about a week after the initial preparation of the solution. Because of the high viscosity of both phases in the polymer solutions, one could easily retrieve with the aid of a sharp spatula the top and the bottom phases. The intermediate layer containing the interface and a small quantity of both phases adjoining the interface were used for the dual purpose of insuring that the hazy and the clear phases do not mix and for gravimetrically estimating the polymer concentration at the interface.

The rate of phase separation did not appear to be directly and solely dependent on the viscosities of the dilute or concentrated polymer solutions. The PHIC polymer had an intrinsic viscosity, $[\eta]$, in $CHCl_3$ of 2.14 dL/g and a viscosity peak in concentrated solution of about 1500 cP. A PBAPIC batch had a $[\eta]$ of 1.5 dL/g and a viscosity peak of about 700 cP. Nevertheless, the PHIC solution separated within a few hours into two reasonably well defined phases, while the PBAPIC did not reach this level of phase definition after a whole week at ambient temperature. This, and the exceptionally well defined phase separation of PHIC in bromoform (density of 2.89 g/cm^3), may indicate that the larger difference between the density of solvent and solute serves to accelerate the phase separation in the PHIC solutions in the bromoform relative to TCE and in the PHIC TCE solution relative to the PBAPIC solution in the same solvent.

In all cases tested, the concentration of polymer in the hazy anisotropic phase was substantially higher than the concentration in the clear isotropic phase. The results of one such gravimetric determination of polymer concentration in the two phases and intermediate layer of PHIC and PBAPIC in TCE are presented in Table I. It should be noted that in both instances the anisotropic phase comprised only about one-third the volume of the polymer solutions. It should also be noted that the PBAPIC solution was not as well resolved into two phases as the PHIC solution, resulting in differences of concentration between the phases of the PBAPIC solution smaller than those measured in the PHIC solution. A concentrated solution of higher *M* PBAPIC, of $[\eta]$ = 3.30 dL/g, in TCE yielded similar results. The poorly resolved anisotropic phase contained 21.0 vol/vol % polymer and the isotropic phase contained 18.7 vol/vol % polymer. An extreme in the opposite direction was shown by the PHIC solution in bromoform. Here, the anisotropic phase, comprising about 35% of the total solution volume, contained 61.6 vol/vol % polymer and the isotropic phase contained only 10.4 vol/vol % polymer.

Table I
Polymer Concentration (vol/vol %) in Isotropic and Anisotropic Phases

		vol/vol % concentration of polymer in TCE		
polymer	intrinsic visc, dL/g	isotropic phase	intermediate layer	anisotropic phase
PHIC	2.14	27.1	32.0	44.4
PBAPIC	1.5	18.8	21.7	22.8

Table II
Characteristics of PHIC in Anisotropic and Isotropic Phases in TCE Solution

method	anisotropic phase	isotropic phase
light scattering	M_w = 96000 ± 2000 $A_2 = 1.8 \times 10^{-3}$	M_w = 56000 ± 2000 $A_2 = 1.8 \times 10^{-3}$
osmometry	M_n = 70000 ± 1000 $A_2 = 1.9 \times 10^{-3}$	M_n = 40000 ± 1000 $A_2 = 3.1 \times 10^{-3}$
viscosity	$[\eta]$ = 3.15 dL/g	$[\eta]$ = 1.25 dL/g

Table III
Characteristics of PBAPIC in Anisotropic and Isotropic Phases in TCE Solution

method	anisotropic phase	isotropic phase
light scattering	M_w = 38000 ± 2000 $A_2 = 2.5 \times 10^{-3}$	M_w = 33000 ± 1500 $A_2 = 1.4 \times 10^{-3}$
viscosity	$[\eta]$ = 1.62 dL/g	$[\eta]$ = 1.35 dL/g

After securing photomicrographs from samples taken from the anisotropic and isotropic phases, the solutions were carefully separated, analyzed gravimetrically to determine the polymer concentrations, dried, and then redissolved in the appropriate solvent for viscosity, light scattering, and osmometry studies. The results for the solutions described in Table I are presented in Table II (PHIC) and Table III (PBAPIC). It is clear that in the case of PHIC a substantial partition of the high-*M* fractions of the polymer into the anisotropic phase and the lower *M* fractions into the isotropic phase took place. In the case of PBAPIC the fractionation according to molecular weight was not as dramatic as in the case of PHIC. Nonetheless, three different determinations clearly establish that such a partition did indeed take place. On the PBAPIC sample of $[\eta]$ = 3.30 dL/g only membrane osmometry tests were conducted. It was found that the molecular weight of the polymer from the anisotropic phase was M_n = 65000 and for the polymer from the isotropic phase M_n = 53500. The fractions of PBAPIC described in Table III were analyzed by means of ^1H NMR and the composition of the copolymer in the two phases was found to be the same, within experimental error.

Three batches of PBAPIC were tested visually to find at which concentration the anisotropic hazy phase begins to be noticed. The results were compared with solution viscosity measurements, typified by Figure 2, and indicated, to our surprise, that the decrease in viscosity takes

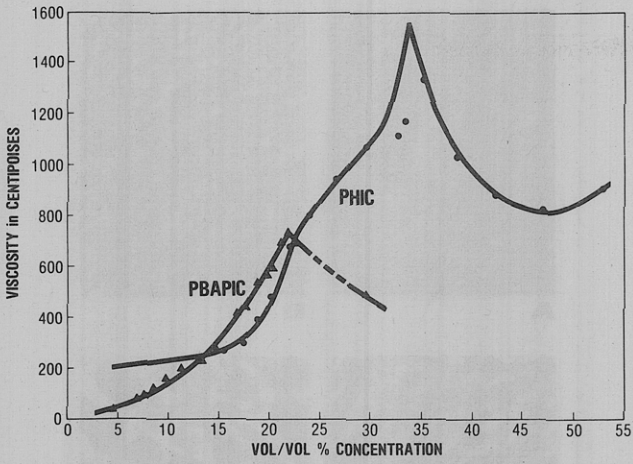

Figure 2. Concentrated solution viscosity of PHIC (●) and PBAPIC (▲) in TCE as a function of vol/vol % polymer concentration. In chloroform, the intrinsic viscosity of the PHIC batch was 2.14 dL/g and that of the PBAPIC was 1.5 dL/g.

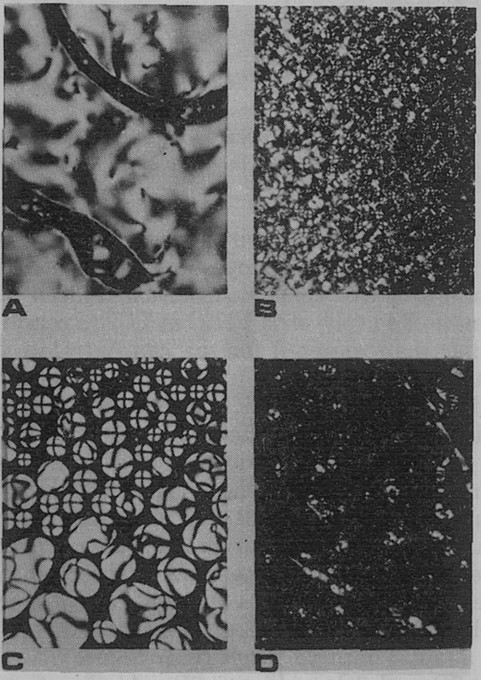

Figure 3. Typical areas of anisotropic solution of PBAPIC in TCE as seen in cross-polarized light. Further details in text.

place not at the concentration of the incipient phase separation, but at significantly higher concentration. At these concentrations, close to one-third the volume of the solutions appeared visually to be anisotropic.

The points at which the whole TCE solution volumes appeared visually to consist of the anisotropic phase only were at about 35.4 vol/vol % for PBAPIC of $[\eta] = 0.52$ dL/g and at about 51.4 vol/vol % for the PHIC sample at our disposal. As will be indicated later, the visual observations need not necessarily agree with other, microscopic determinations.

Figures 3A through 3D depict typical areas of the anisotropic solution of PBAPIC in TCE as observed through cross-polarized light under an original magnification of 200×. Figures 3A, 3B, and 3C were obtained at the same time from different areas of the hazy part of a solution whose total polymer concentration was about 35 vol/vol % and Figure 3D was obtained from the hazy part of a solution of 28.5 vol/vol %. Besides demonstrating the lyotropic mesomorphic nature of PBAPIC, the figures also indicate the textural richness observed in the poly(isocyanate) liquid crystals in general. It should be noted that rotation of the microscope stage brought into light many other birefringent spherulitic entities, most noticeably in the solutions from which Figure 3D was obtained. This indicates that the amount of birefringent material in Figure 3D or Figure 3C, for example, may be larger than it appears to be from the static photographs. Application of pressure or shear, by pressing or moving the microscope cover glass, caused the spherulitic entities to deform, break up, or coalesce into new ones, all attesting to the fluid nature of the observed birefringent structures. The Schlieren texture covering most of Figure 3A appears in all the anisotropic phases obtained in solutions of PBAPIC, PHIC, and other poly(isocyanates) described in ref 3. The inclusions observed in the Schlieren texture, of isotropic phase containing miniature anisotropic spherulites, are instructive since they reveal that the visually uniform hazy and anisotropic phase may contain inclusions of the isotropic phase. We believe that because of the very high viscosity of both phases the phase separation on a microscopic level was not completed before the photomicrographs were obtained. Isotropic inclusions in an anisotropic phase were observed under the microscope, in many instances two weeks after the visual phase separation took place.

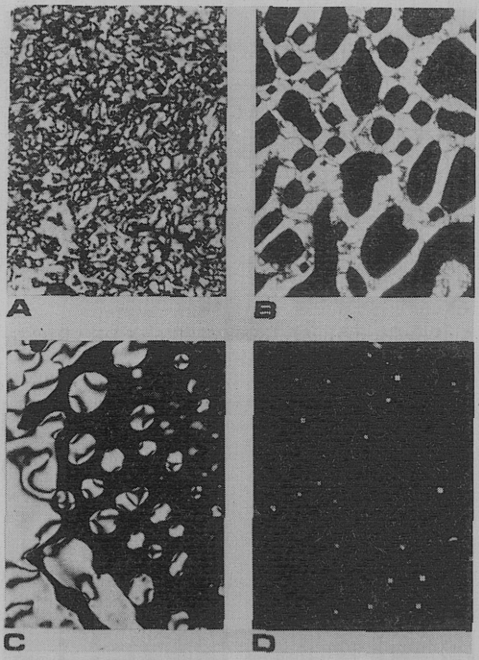

Figure 4. Typical areas of concentrated solution of PHIC in bromoform as seen in cross-polarized light. Further details in text.

Figure 4A is characteristic of the anisotropic hazy phase of PHIC in bromoform. In Figure 4B, obtained from an area close to anisotropic/isotropic interface, inclusions of isotropic phase in an anisotropic matrix appear. In Figure 4C, from as close as possible to the interface, inclusions of anisotropic phase in an isotropic matrix coexist with an adjacent continuous anisotropic phase. Figure 4D was obtained from the visually clear isotropic solution of PHIC in bromoform. Unlike most isotropic samples observed, this sample still contained a small number of birefringent fluid spherulites. It should be noticed that the original magnification of Figure 4D was 400× while that of Figures 4A, 4B, and 4C was only 200×.

When an anisotropic solution of PBAPIC is sheared on the microscope stage, by moving the cover glass, a characteristic texture of elongated domains, typified by Figures 5A and 5B, appears. Because of the slow relaxation of the

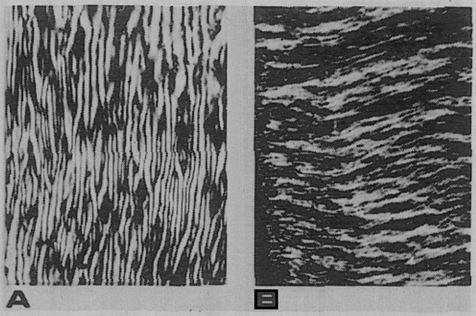

Figure 5. Sheared anisotropic solution of PBAPIC in TCE as seen in cross-polarized light.

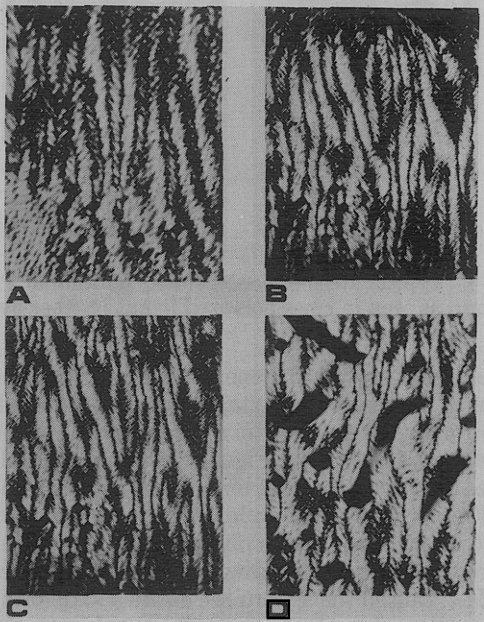

Figure 6. Sheared anisotropic solution of PHIC and TCE as observed with cross-polarized light. Some isotropic inclusions are visible.

PBAPIC solutions, such textures did not relax back to the unsheared texture, in Figure 3, even after 16 h (overnight) at room temperature. Sheared anisotropic solutions of PHIC, of substantially higher concentration, produce initially similar sheared textures but relax to the unsheared texture within minutes.

In several sheared anisotropic samples the elongated domains revealed internal light and dark striations usually at angles of about 45° to the shear direction. Figures 6A through 6D for PHIC in TCE are typical. The striations in adjacent domains appear to alternate in their direction such that about a 90° angle exists between the striations in adjacent domains. The overall effect is that of a herringbone texture. It should be noted that in other regions of the very same microscope preparation, sheared elongated domains, similar to Figure 5, were also observed. The herringbone texture is not characteristic to PHIC alone. Such a texture was observed also in the sheared anisotropic phase of a poly(50% butyl + 50% nonyl isocyanate) solution in TCE.

Even though the vol/vol concentration of PHIC in TCE in the sample described in Figure 6 was 44% and the bulk sample appeared hazy and visually uniform, isotropic inclusions tended to appear in the anisotropic phase. As can be clearly seen in Figure 6, the isotropic inclusions did not tend to form circular droplets, but maintained a substantial degree of angularity. The smaller of these isotropic inclusions were distinctly tetragonal in nature. Similar small isotropic tetragonal inclusions are distinctly visible in Figure 4B. No birefringence appeared in the inclusions when the microscope stage was rotated through 360°, indicating that these inclusions are indeed isotropic.

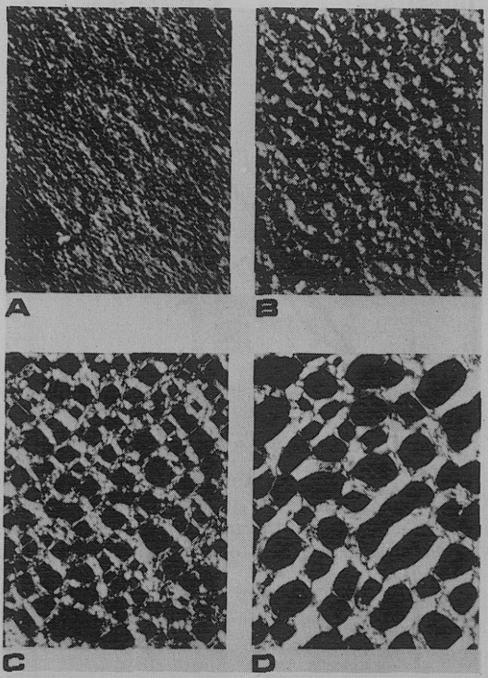

Figure 7. The process of phase separation in a concentrated PHIC solution in TCE as observed in the microscope with cross-polarized light. Original magnification 200×. Additional details in text.

A sample of 44 vol/vol % PHIC in TCE, a concentration far higher than required for the concentrated solution viscosity to start dropping (ca. 34%, see Figure 2), was allowed to relax on the microscope stage and produce isotropic inclusions. When the system reached equilibrium, i.e., no increase in the size and number of the isotropic inclusions and no change in their shape, it appeared similar to Figure 7D. At that point, the microscopically heterogeneous system was stirred to produce the microscopically homogeneous system in Figure 7A. Observed in cross-polarized light, it appears as a uniformly anisotropic phase. After about a minute or two, phase separation took place, taking about 1 min to reach from Figure 7A, through Figures 7B and 7C, to Figure 7D. At the structure of Figure 7D, the system stabilized and no further changes took place for at least the following 15 min.

The microscopically heterophase systems are visually hazy and often contain the nematic thread-like features. Once a certain equilibrium is reached (as in Figure 7D), the visually hazy and clear phases do not change substantially. The ability of the hazy anisotropic phase to carry in it small inclusions of the isotropic solution was demonstrated in ^1H and ^{13}C NMR studies to be published. Here, even after 16 h in the instrument's cavity, the hazy PHIC solution used to obtain Figure 6 showed peaks whose width may be explained by the existence of a minor amount of isotropic inclusions in an anisotropic major phase.

Discussion

From the results above, one concludes that solutions of PHIC and PBAPIC above a certain critical concentration are liquid crystalline in nature. This was previously described for many homopolymers and copolymers of the poly(isocyanate) family[3,4] and for several poly(isocyanide) homologues.[9,10] X-ray diffraction results to be published separately,[11] the molecular weight polydispersity preventing rigid molecules from forming uniform thickness layers, and the ability of the anisotropic phase of the poly(isocyanate) solutions to transmit torque all indicate that the polymeric liquid crystals described in this work are nematic in character. (An inability to transmit torque is one of the criteria employed by de Gennes[12] for smectic liquid crystals.)

The partition of a given polymer in a particular solvent into a more concentrated anisotropic phase and a more dilute isotropic phase, in agreement with the predictions of Onsager[13] and Flory,[1,2] was clearly demonstrated. It was calculated by Flory[2] that for monodisperse rodlike particles of large axial ratio, x, in an anisotropic phase in equilibrium with an isotropic phase, their concentration will be about:

$$v' \approx 1.5v \tag{1}$$

where v' is the volume fraction of the solute polymer in the anisotropic phase and v is its volume fraction in the isotropic solution. This is somewhat greater than the value of

$$v' \approx 1.34v \tag{2}$$

calculated by Onsager[13] for monodisperse rodlike particles of unspecified axial ratio. From our experiments, we find that besides the effects of polydisperisty and other thermodynamic consideratins, the difference in densities between the polymer and the solvent may also affect the results. In the case of PBAPIC in TCE, in Table I, the ratio of solvent density, d_s, to polymer density, d_p, is 1.417 and the v' to v ratio is about 1.21. For the corresponding case of PHIC, $d_s/d_p = 1.586$ and $v'/v = 1.64$. For the same molecular weight PHIC in bromoform, $d_s/d_p = 2.89$ and $v'/v = 5.92$. It may be that the latter high value is due in part to crystalline precipitation that took place in the anisotropic phase, but such a precipitation was not observed in the microscopic studies.

The treatment of v'/v ratios above must be viewed with caution; from the results, it is obvious that the visually anisotropic phases contained some isotropic inclusions. Furthermore, eq 1 and 2 were obtained for a monodisperse homopolymer and may not describe appropriately the behavior of polydisperse copolymers such as PBAPIC.

The partition of the higher M polymer out of an initially uniform solution into an anisotropic phase and the lower M polymer into an isotropic phase occurred in both PHIC and PBAPIC solutions. A comparison of the data in the anisotropic and isotropic phase columns in Tables II and III clearly demonstrates this fact. We believe that the partition according to molecular weight is an experimental verification of such a prediction recently published by Professor Flory.[1] The relatively small separation according to M in the case of PBAPIC in Table III seems to go hand in hand with the small differences in concentration between the phases, previously mentioned, and the very slow rate of visual phase separation. The higher viscosity PBAPIC sample that was studied by osmometry shows, however, a better molecular weight partition associated with about the same concentration differential and a rather poor visual phase separation.

It should be noted that partition according to concentration and molecular weight in the coexisting isotropic and anisotropic solutions of aromatic polyamides was recently observed by Morgan and co-workers.[14-16]

The magnitudes of the second virial coefficients, A_2, obtained from light scattering in chloroform and membrane osmometry in chlorobenzene, for PHIC and PBAPIC, appear to be of the same order of magnitude as obtained by Fetters and Yu[17] for PHIC, poly(butyl isocyanate), and poly(octyl isocyanate), in chloroform. These values are substantially larger than the values of A_2 obtained for the same polymers[18-20] in tetrahydrofuran (THF) or in toluene. The variation of A_2 of PHIC, especially the fraction originating from the isotropic phase, may indicate a measure of chain flexibility in said phase. The reason for A_2 of PBAPIC in the isotropic phase being smaller than in the anisotropic phase is not clear to us as of now.

From the intercepts and initial slopes of the zero concentration extrapolated lines of the Zimm plots obtained from the PHIC and PBAPIC in the anisotropic and isotropic phases characterized in Tables II and III, respectively, the z-average radius of gyration, R_G, of the polymer molecules in each phase was calculated:

$$\frac{\text{(initial slope)}}{\text{(intercept)}} = (16\pi^2/3\lambda^2)R_G{}^2 \tag{3}$$

with λ being the light wavelength. The calculated R_G's for PHIC were 315 and 180 Å for the anisotropic and isotropic phases, respectively. The R_G's for PBAPIC in the anisotropic and isotropic phases were 427 and 325 Å, respectively.

In general, as can be learned from the optical microscopy observations, the overall performance of the concentrated PHIC and PBAPIC solutions is rather similar to solutions of low molecular weight mesogenic substances, undergoing a phase separation or a transition to the mesomorphic state, except for the slowing effects caused by the very high viscosities of the polymer solutions.

The angular inclusions of isotropic in anisotropic phase of PHIC solutions, as observed in Figures 4B and 7D, appear to be in a state of equilibrium, because when disturbed on the microscope stage, they regain the original overall shape, size, and number of inclusions within a few minutes.

The tetragonal appearance and angularity of such inclusions is explained by Chandrasekhar[21] to be a consequence of orientational and translational order associated with the inclusions. We believe that as the isotropic inclusion emerges from the apparently uniform system (Figure 7A) and grows, the rigid polymer chains are being pushed in front of the expanding isotropic/anisotropic interface. The polymer chains in the anisotropic phase are thus being oriented parallel to the edge of the growing inclusion, giving rise to a measure of lateral, translational order. The birefringence of the anisotropic phase in between the inclusions (Figures 4B and 7D) indicates that the polymer chains in this phase are aligned parallel to the edges of the isotropic inclusions. The usually four, fine, dark lines emitting from each isotropic inclusion into the anisotropic phase indicate the areas at which the orientation of the polymer chains in the ordered phase changes to follow the contour of the isotropic inclusions.

The textures in Figure 6 are especially interesting because of their richness. The largely anisotropic phase appears to have been separated into domains of differing orientation. The direction of the rigid molecules in each domain appears to be perpendicular to the direction of the molecules in the adjacent domains. This is similar to the observation of Panar and Beste[22] on poly(1,4-benzamide) solutions. In our case, it is clear, however, that the molecular orientation is parallel to an edge of a tetragonal isotropic inclusion. The striations within the domains may have been induced by undulation of the polymer molecules within these domains. This undulation was apparently induced by the mechanical shearing of the anisotropic phase and was "frozen" in because of the very high viscosity of the solution. These undulations may be close to undulations in nematic liquid crystals brought about by the application of electrical voltage and manifested by the light and dark alternations known as Williams Domains.[12,23]

Acknowledgment. We would like to acknowledge the help of Mrs. E. L. Szollosi in obtaining the optical microscope photographs.

References and Notes

(1) P. J. Flory, *Ber. Bunsenges. Phys. Chem.*, **81**, 885 (1977).
(2) P. J. Flory, *Proc. R. Soc. London, Ser. A*, **234**, 73 (1956).
(3) S. M. Aharoni, *Macromolecules*, **12**, 94 (1979).
(4) S. M. Aharoni and J. P. Sibilia, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, in press; S. M. Aharoni and E. K. Walsh, *J. Polym. Sci., Polym. Lett. Ed.*, in press.
(5) V. E. Shashoua, *J. Am. Chem. Soc.*, **81**, 3156 (1959).
(6) V. E. Shashoua, W. Sweeny, and R. F. Tietz, *J. Am. Chem. Soc.*, **82**, 866 (1960).
(7) B. Zimm, *J. Chem. Phys.*, **16**, 1093 (1948).
(8) B. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).
(9) F. Millich, *Adv. Polym. Sci.*, **19**, 117 (1975).
(10) S. M. Aharoni, *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(11) S. M. Aharoni, to be published.
(12) P. G. DeGennes, "The Physics of Liquid Crystals", Clarendon Press, Oxford, 1975, pp 78, 79, 192, and 193.
(13) L. Onsager, *Ann. N.Y. Acad. Sci.*, **51**, 627 (1949).
(14) P. W. Morgan, *Macromolecules*, **10**, 1381 (1977).
(15) S. L. Kwolek, P. W. Morgan, J. R. Schaefgen, and L. W. Gulrich, *Macromolecules*, **10**, 1390 (1977).
(16) T. I. Bair, P. W. Morgan, and F. L. Killian, *Macromolecules*, **10**, 1396 (1977).
(17) L. J. Fetters and H. Yu, *Macromolecules*, **4**, 385 (1971).
(18) N. S. Schneider, S. Furusaki, and R. W. Lenz, *J. Polym. Sci., Part A*, **3**, 933 (1965).
(19) M. N. Berger and B. M. Tidswell, *J. Polym. Sci., Polym. Symp.*, **42**, 1063 (1973).
(20) M. R. Ambler, D. McIntyre, and L. J. Fetters, *Macromolecules*, **11**, 300 (1978).
(21) S. Chandrasekhar, *Mol. Cryst.*, **2**, 71 (1966).
(22) M. Panar and L. F. Beste, *Macromolecules*, **10**, 1401 (1977).
(23) R. Williams, *J. Chem. Phys.*, **39**, 384 (1963).

Molecular Weight and Temperature Dependence of Polymer Dimensions in Solution

A. Ziya Akcasu*

Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Michigan 48109

Charles C. Han

Center for Materials Science, National Measurement Laboratory, National Bureau of Standards, Washington, D.C. 20234. *Received November 6, 1978*

ABSTRACT: The molecular weight (M_w) and temperature (T) dependence of the radius of gyration (R_G) and hydrodynamic radius (R_H) of a polymer in a dilute solution are investigated. The theoretical predictions are compared with experimental results on polystyrene in various solvents as functions of M_w and T. It is found that the existing data fall in a region of values where R_H cannot be represented by a simple power law $R_H \sim N^{\nu'}$, whereas most of the data on R_G satisfy $R_G \sim N^{\nu}$. It is concluded that a power law fit to data would yield a $\nu' < \nu$ in this region, even though the theory predicts $\nu' = \nu$ in the asymptotic region. The quantitative aspects of the blob theory are also discussed and compared in some cases to the modified Flory theory.

This paper investigates the molecular weight and temperature dependence of polymer dimensions in solution under actual experimental conditions and presents a quantitative comparison of the existing data on polystyrene in various solvents, with the theoretical predictions.

In equilibrium, the mean size of a polymer molecule is characterized by its radius of gyration R_G, which is a static property of the polymer measured in static experiments, e.g., by observing the static structure factor $S(q)$ as a function of momentum transfer q.

In the interpretation of dynamic experiments the hydrodynamic radius R_H of the polymer is defined by

$$R_H = k_BT/6\pi\eta D_0 \tag{1}$$

where k_BT is the temperature of the solution, η is the viscosity of the solvent, and D_0 is the zero concentration translational diffusion coefficient. It is the latter which is actually measured in a dynamic experiment, e.g., by observing the relaxation in time, of the dynamic scattering function $S(q,t)$ for small momentum transfers $qR_G \ll 1$. The reason for introducing R_H through eq 1 in preference to D_0 is that it is less sensitive to the conditions of the solution, such as the temperature and viscosity, and facilitates comparison with R_G. One may interpret R_H as an equivalent radius, when the polymer is visualized as a rigid sphere with stick boundary conditions, obeying Stoke's law.

It is known that $R_G \sim N^{\nu}$ in a good solvent and for large N, where N is the equivalent number of links in the statistical chain. The scaling arguments by De Gennes[1] and our earlier calculations based on the linear response theory[2] also yield $R_H \sim N^{\nu}$ for large N. But recent light-scattering experiments by Adam and Delsanti[3] in dilute solutions of polystyrene in benzene at room temperature yielded an exponent $\nu' = 0.55 \mp 0.02$ in the molecular weight range 2.43×10^4 to 3.8×10^6, which differs from the most accurate value of $\nu = 0.588 \mp 0.001$.[4]

In a very recent paper, Des Cloizeaux[5] proved the inequality

$$R_H > KR_G \tag{2}$$

where K does not depend on N for large N but depends on the type of the chain. He concluded from eq 2 that $\nu' \geq \nu$ must hold even if one postulates[6] the existence of a new dynamical exponent ν' in $R_H \sim N^{\nu'}$.

Des Cloizeaux[7] suggested that this discrepancy may be due to the fact that R_H does not reach its asymptotic power law behavior, as predicted by the theory, within the range of experimental values of the molecular weight.

The aim of this paper is to study this question quantitatively by comparing the theoretical calculations of R_G[8] and R_H[2] as a function of the molecular weight and temperature in the nonasymptotic regions with the experi-