# Rigid backbone polymers: 6. Ternary phase relationships of polyisocyanates

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*(Received*

The ternary systems poly(n-hexyl isocyanate) (PHIC)/poly-(n-octyl isocyanate) (POIC)/tetrachloroethane (TCE), POIC/polystyrene (PS)/TCE, poly(50% n-butyl + 50% *p*-anisole-2-ethyl) isocyanate (PBAEIC)/PS/TCE, and POIC/PBAEIC/TCE, were studied by means of cross-polarized light microscopy and proton nuclear magnetic resonance (n.m.r.) observations. The system PHIC/POIC/TCE had a polymer concentration range in which a single anisotropic phase was observed over all polymer/polymer ratios. The system POIC/PBAEIC/TCE suggested a similar behaviour. Lower polymer concentrations exhibited an anisotropic/isotropic biphasic concentration interval, and even lower concentrations produced a single isotropic solution. In the systems POIC/PS/TCE and PBAEIC/PS/TCE a single anisotropic phase existed in the high concentration region only where the amount of PS was negligible. In the presence of substantial amounts of PS the systems were either biphasic or isotropic, depending on the polymer/polymer ratio and the concentration of polymer in TCE. The above is in agreement with Flory's recent theory[1–7] concerning the behaviour of mixtures of rod-like particles and mixtures of rods with flexible coils.

## INTRODUCTION

High molecular weight, flexible polymers are incompatible with one another, with very few exceptions. When two such polymers are dissolved in a common solvent at a high or moderate concentration, the resulting solution separates into two coexisting isotropic solutions, each containing a high concentration of one polymer and a low concentration of the other.

The behaviour of rigid backbone polymer molecules is dramatically different. In a theory recently put forward by Flory[1–7], it is stated that if a stable concentrated solution of two kinds of rod-like molecules in a single solvent can be prepared, then a single anisotropic phase (a lyotropic, nematic liquid crystal) may be obtained. Upon dilution of such a single phase solution, an isotropic phase will appear and will be in thermodynamic equilibrium with the anisotropic phase. The concentration range in which the two phases coexist is much wider than in the case where the solution is of only one rod-like polymer in a single solvent[1]. In the latter case, when the solvent is a good solvent for the polymer, the biphasic concentration interval is usually rather narrow[8]. Upon further dilution, the anisotropic phase vanishes and a single isotropic phase remains. The concentration of the polymer in, and the molecular weight distribution between, the two coexisting phases were recently demonstrated by Kwolek *et al.*[9] and by Aharoni and Walsh[10,11] to be in general agreement with the theory[1,8].

The theory further maintains[6] that when one of the rod-like polymers is replaced by a flexible chain polymer, then the anisotropic phase that forms at sufficiently high concentration would contain practically none of the flexible polymer. On the other hand, the coexisting isotropic phase, containing practically all the coiled molecules, may tolerate a minor, but not necessarily negligible, amount of the rigid backbone polymer.

In this work, several triangular phase diagrams will be presented. Each describes a system containing one solvent and two polymers. Two of the diagrams describe rigid backbone/flexible coil polymers, while the other diagrams describe rigid backbone/rigid backbone systems. Parts of the rigid/flexible/solvent diagrams and a partial diagram of rigid polymer/rigid polymer/solvent were recently published in a preliminary report[12]. It is our belief that the phase diagrams to be presented in this paper lend strong support to the theory expounded in refs 1–7.

The existence of an anisotropic phase in solutions of rigid backbone polymers, and the exclusion of other components from it, may be studied on three scale levels. Under no, or very low, magnification an anisotropic solution appears to be opaque or translucent. When sheared, the solution becomes brilliant, exhibiting 'shear opalescence'[13]. In general, isotropic solutions are clear and do not show 'shear opalescence'. When observed in cross-polarized light under high magnification, anisotropic solutions are highly birefringent and usually exhibit textures characteristic of the nematic liquid crystal phase of the particular solution in question. Because of the randomness of their molecular orientation, isotropic solutions of the same polymers become invisible when observed in cross-polarized light. Thus, when anisotropic and isotropic solutions are observed together in a cross-polarized light microscope, the invisible isotropic solution appears as a black background to the visible and often coloured and textured anisotropic phase.

On the molecular level, optical microscopy is not helpful. However, nuclear magnetic resonance (n.m.r.) spectroscopy may afford an indication of whether an investigated solution is anisotropic, isotropic or a mixture thereof. The n.m.r. studies of such systems were usually involved with the aromatic residues within the rigid stems or backbones of mesogenic substances (polymers and non-polymers) or with the solvent that is present in the mesomorphic phase[14–18]. Due to the anisotropy of the mesomorphic system, the protons of the aromatic residues of the rigid stems exist in

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relatively fixed spatial and angular positions experiencing different local fields. This produces a multitude of n.m.r. signals of the aromatic protons, instead of the very few signals obtained from them in an isotropic solution due to the positional and angular randomness, high mobility and the resulting averaged field effects. Since the total intensity of the signal from the isotropic and anisotropic phases is about the same, the existence of many peaks enveloped in the spectrum of the anisotropic phase decreases the size of each and depresses the signal envelope into the background noise. As a result, the signal from a mesomorphic substance may be either completely depressed into the background noise or appear as a very broad, shallow and noisy peak spread over a large portion of the spectrum. Conversely, because of 'motional narrowing', the signals of the same aromatic protons in an isotropic solution are very narrow and intense. Some linewidth broadening due to the high viscosity of isotropic polymer solutions is often encountered, but the substantial differences between spectra obtained from isotropic and anisotropic phases makes it easy for the experienced observer to differentiate between them. When the isotropic and anisotropic phases coexist in the same scanned sample, the signals of the isotropic phase usually dominate the spectrum. One may determine the fraction of the mesogenic substance in the mesomorphic phase by comparing the obtained and expected signal intensities, studying the effects of dilution, etc.

When the n.m.r. signals come from pendant groups having varying levels of mobility, the relationship between the n.m.r. signal and the phase of the sample, isotropic or anisotropic, may not be as straightforward as described above. That is, an anisotropic solution may still produce easily assignable signals belonging to the parts of the pendant groups enjoying sufficient mobility even in the mesomorphic state. As will be shown in this work, mesogenic polyisocyanates often produce such anisotropic solutions.

## EXPERIMENTAL

The polyisocyanates for this study were prepared by a procedure, essentially of Shashoua *et al.*[19], which is described in detail in a previous paper in this series[20]. Dilute solution viscosities were determined at 25°C using Cannon–Ubbelohde glass viscometers. The solvent most often used for the viscosity determinations was chloroform. The molecular weights of the polyisocyanates were determined from the relationship obtained by Bur and Fetters[21] for relatively narrow molecular weight distribution:

$$[\eta] = (7.58 \times 10^{-4}/M_0^{3.0})M_w^{2.0}$$

where $[\eta]$ is the intrinsic viscosity in dl $g^{-1}$, $M_0$ is the monomeric molecular weight, and $M_w$ is the weight-average molecular weight, $M$.

The samples studied in this work were individually weighed and placed in n.m.r. tubes or in small test tubes. Samples containing two polymers were carefully mixed together prior to being placed in the tubes. After thoroughly mixing the polymer with the solvent, the tubes were sealed with hermetic caps. For extended-time studies, the glass tubes were sealed by melting down their tops.

Ternary phase diagrams were constructed, each containing one of the following polymer pairs:

(a) poly(n-hexyl isocyanate) (PHIC) of $M_w$ = 34 500 and poly(n-octyl-isocyanate) (POIC) of $M_w$ = 38 000;

(b) POIC of $M_w$ = 108 000 and polystyrene (PS) of $M$ = 4000 (lot No. 11b of Pressure Chemical Co., $M_w/M_n \leqslant 1.10$), and PS polymerized *in situ*;

(c) poly(50% n-butyl + 50% *p*-anisole-2-ethyl) isocyanate (PBAEIC) of $M_w$ = 161 000 and the same PS as in (b) above;

(d) POIC and PBAEIC with $M_w$ as in (b) and (c) above, respectively.

The phase diagrams were constructed from microscope observations under magnifications of X100 to X800, using cross-polarized light. The X100 magnification microscopy was performed with the aid of a Reichert polarized light microscope equipped with a controlled temperature hot-stage. The observations under magnifications higher than X100, and the microphotography, were performed in a Leitz Ortholux polarized light microscope. Because of its low volatility and high solvent power for all polymers involved, the only solvent used for the phase diagrams work was 1,1,2,2-tetrachloroethane (TCE).

The observations were performed on mixtures that reached an apparent equilibrium, and did not change visually or under a magnification of X100 over a period of 24 h. This apparent equilibrium was usually attained between two and seven days from the time of mixing of the sample, a time interval strongly dependent on the viscosity of the resulting system. In the case of the PHIC/POIC/TCE system, the phase relationship determination was repeated 15 and 23 days after the first determination (almost a month from preparation). In the later determinations, the interface between the anisotropic and isotropic phases became well defined and the phase relationship in several samples appeared to be closer to what one would expect from a state of true equilibrium. The phase diagrams were all performed at ambient temperature. The measurements for the PHIC/POIC/TCE phase diagrams were also repeated at 48 ± 2°C on the hot-stage microscope.

For the determination of phase relationships in the two systems POIC/PS and PBAEIC/PS along the side of the triangle where there is no TCE, use was made of the fact that both polyisocyanates are highly soluble in monomeric styrene. Accordingly, solutions of the respective polyisocyanate in the desired concentrations were prepared in distilled styrene. To these solutions minute amounts of benzoyl peroxide were added and the sealed systems polymerized for 16 to 24 h at ~70°C. After several hours, phase separation became evident from the increasing turbidity of the systems. This did not happen to blank samples devoid of peroxide. PS blanks, polymerized concurrently with the mixture, but without the polyisocyanates, were clear. From their intrinsic viscosity in toluene, a viscosity-average $M$ of about 60 000 was determined. To eliminate residual monomer, all PS samples were degassed under high vacuum before being further studied.

In quite a few instances there were sufficient data points in proximity to each other to determine the position of phase boundaries in the phase diagrams with reasonable accuracy. In other cases, the location of such a boundary was estimated from the relative abundance of the various phases in individual points on both sides of the boundary.

Proton n.m.r. spectra were obtained using a Varian T-60A spectrometer operating at ambient temperature. The solvent most commonly used was TCE, and the plotted spectra were externally referenced to tetramethylsilane, $Si(CH_3)_4$ (TMS).

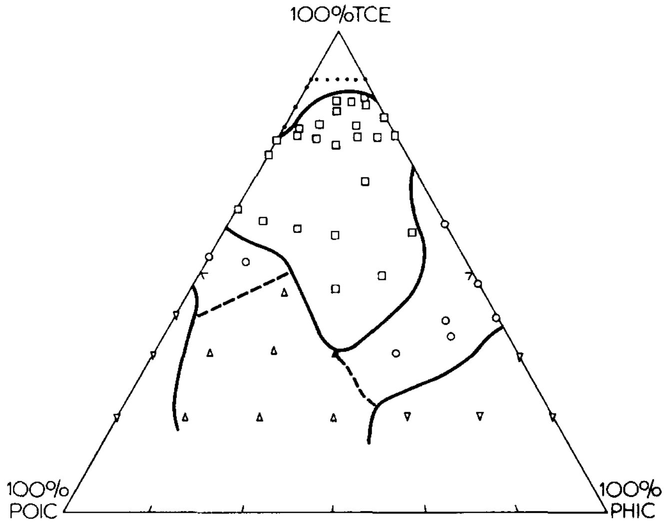

*Figure 1* Ternary phase diagram of the system PHIC/POIC/TCE at room temperature. ●, Isotropic; ⊙, liquid crystal; ⊡, liquid crystal + isotropic; △, liquid crystal + semicrystalline solids; ▽, swollen semicrystalline solids; ▲, liquid crystal + isotropic + semicrystalline solids

## RESULTS AND DISCUSSION

Because of the high viscosity of the systems under investigation, the rates at which they approach equilibrium are extremely slow. Often there were no changes noticeably by microscopy or n.m.r. techniques, over a period of 1–2 days. Yet, when the same samples were allowed to remain at room temperature for a period of several weeks, two coexisting phases exhibited an interface far sharper and better defined than that observed initially. Even so, it was found in at least one sample of PHIC/POIC/TCE containing coexisting and well-defined anisotropic and isotropic solutions, that the water-clear isotropic solution contained anisotropic entities that became visible when the clear solution was sheared on the stage of the high magnification microscope. Similarly, it was found that the anisotropic phase of the systems POIC/PS/TCE and PBAEIC/PS/TCE contained minute inclusions of an isotropic phase. These inclusions appeared to be in equilibrium with the anisotropic matrix, since they regained their size and shape and apparent number, within about 15 min from the moment the system was sheared on the microscope stage. The occluded isotropic entities maintained their size and shape for up to a month (the duration of our experiments), indicating that an apparent state of equilibrium was reached between the tendency to phase separate and the resistance of the highly viscous, anisotropic matrix to this separation.

In the régime of high polymer concentration, the phase diagrams became more complicated than anticipated by theory. The theory$^{1-7}$ assumes that the system will remain a true solution throughout the polymer concentration range, $c$, of $0 < c < 1.00$. In our case this assumption does not hold true. The polyisocyanates are semicrystalline polymers. Their percentage crystallinity, as determined by standard X-ray diffraction methods, is around 40%. At extremely high polymer concentrations, say, 80% polymer, the system was sometimes found to consist of a swollen pasty solid in which the solvent was apparently contained within the amorphous portion of the polymer. This system, which maintained its crystallinity and was highly birefringent in cross-polarized light, did not flow under shear and even though deformable, its particles recoiled back after the removal of stress and regained their initial shape. On other occasions the extremely concentrated system contained two distinct phases: the swollen solids described above, and a well-defined highly mobile and flowing liquid crystalline solution. As will be shown below, an increase in temperature may increase the amount of anisotropic solution at the expense of the swollen solids in such a system. As it turned out in the PHIC/POIC/TCE system, the concentration interval of around 2/3 polymer produced within a month from the moment of preparation well-defined phases that lent themselves to a convenient study by means of visual inspection and low magnification microscopy, and n.m.r.

From the numerous observations under the cross-polarized light microscope and n.m.r. scans of the many samples (over 150), each studied over a time span of a month, we were led to conclude that even though the samples in the higher concentration régime may not be at true equilibrium, their apparent equilibrium presents us with a reasonably close approximation of the state of true equilibrium.

The ternary phase diagrams are now described. *Figure 1* describes the system PHIC/POIC/TCE at room temperature (23°C). The data points were obtained 2 to 5 days after mixing the 57 individual samples in this phase diagram. After equilibrating for not less than 2 h at 45°–50°C, the phase relationships in the same samples were studied at 48° ± 2°C. The results are shown in *Figure 2*. A comparison of *Figures 1* and *2* shows that at the higher temperature the line between the single isotropic phase and the biphasic region is shifted to higher polymer concentration. Similarly, samples containing swollen solids show, with increased temperatures, a reduction in the amount of such solids accompanied by a corresponding increase in the amount of the liquid crystal phase. The substantial shift of the boundary line between the anisotropic phase and the biphasic range as a function of temperature served to indicate that a true state of equilibrium was not achieved up to 5 days from sample preparation. Nevertheless, when the samples were allowed to cool to room temperature and remain there for a day, the phase relationships described in *Figure 1* could essentially be reproduced.

15 days after the first study, the same samples of PHIC/POIC/TCE were studied again under the microscope

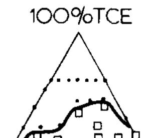

*Figure 2* Ternary phase diagram of the system PHIC/POIC/TCE. Data points are of the same composition as in *Figure 1*, but the temperature is 48° ± 2°C

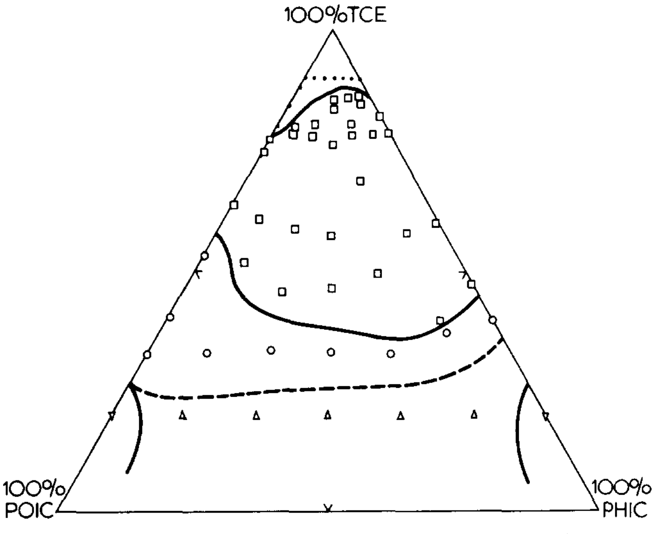

*Figure 3* Ternary phase diagram of the system PHIC/POIC/TCE at room temperature. Same samples as in *Figure 1,* but data obtained 23 days later

and by means of n.m.r. 8 days later the observations were repeated. The results of these two sets of observations were remarkably similar. We shall report here only the results obtained 23 days after the initial study, with the understanding that they also represent the results obtained 8 days earlier.

*Figure 3* describes the phase relationships of the system PHIC/POIC/TCE at room temperature 23 days after they were determined as in *Figure 1. Figure 4* describes the same relationships at 48° ± 2°C, and corresponds to *Figure 2.* It is clear that in the dilute solution part of the diagrams, no change took place within the 23 days interval. This indicates that the system, due to its relatively low viscosity, has reached a state of equilibrium before the initial observations (*Figures 1* and *2*). This does not hold true for the higher concentration region of the diagram. In general, these regions became less complex than previously. This simplification came as a result of the straightening of boundaries between the biphasic and the anisotropic regions, and the increase in the amount of anisotropic phase at the expense of swollen semicrystalline material in many samples of high polymer concentration. Photomicrographs of samples in the 50 to 70 vol/vol % polymer were obtained at room temperature with cross-polarized light. The photographs in *Figure 5a–5d* are typical of the anisotropic phase in *Figures 3* and *4.* Within this range of polymer concentration, the texture of the anisotropic phase appears to be remarkably similar throughout the whole range of PHIC/POIC ratios. In all samples containing both PHIC and POIC when an anisotropic phase was observed, it was always a single anisotropic phase, containing both polymers. At higher dilution, in the range of 30–40% polymer where isotropic and anisotropic solutions coexist, one may notice significant textural differences between the anisotropic phase of PHIC/solvent and that of POIC/solvent systems. As is shown in *Figure 6a* and *6b,* the anisotropic phase of PHIC reveals a fine 'grainy' texture which is completely absent from the anisotropic phase of POIC in close concentration in TCE. The anisotropic phase of mixtures of these two polymers, typified by *Figure 6c,* reveals a textural appearance intermediate between PHIC and POIC. Based on this and on the observations of solely anisotropic samples, we believe that in the PHIC/POIC/TCE system the two polymers are mixed in the anisotropic phase. When an isotropic phase exists in apparent or true equilibrium with the anisotropic phase, then the two polymers are mixed in the isotropic phase as well.

From the above, it is concluded that in the systems PHIC/TCE, POIC/TCE and PHIC/POIC/TCE, we move from a single isotropic solution at relatively dilute solutions to a single anisotropic solution at high concentration, traversing an isotropic/anisotropic biphasic region in between. This is in exact agreement with theory[1–3,8]. The theory predicts[1,3] that a mixture of two rod-like polymers in a solvent will produce a biphasic region spanning a wider concentration interval than that of the biphasic region of either polymer alone. Such behaviour is clearly observed in our *Figures 1–4.* The boundary between the anisotropic and biphasic regions is relatively flat in *Figures 3* and *4.* This may be explained by the fact that the two polymers are of very close $M$ and chain length. Allowing $1.94 \times 10^{-10}$ m per repeat unit[22], we obtain from the corresponding molecular weights in the Experimental section an average length of $475 \times 10^{-10}$m for the POIC and $527 \times 10^{-10}$m for the PHIC. The slight skewness of the biphasic region toward the PHIC is in agreement with the theoretical prediction[1,3] that the biphasic region will be skewed toward the longer rod-like polymer.

Proton n.m.r. spectra characteristic of intermediate and high concentration solutions of the PHIC/POIC/TCE system are shown in *Figure 7.* They are of a fixed PHIC/POIC ratio but with varying polymer in solvent concentrations. The TCE peak appears as a singlet at 5.92 downfield from TMS. The $-CH_3$ peak appears at about 0.8 ppm and the broader peak of all but one of the $-CH_2-$ groups reaches its maximum at about 1.2 ppm from TMS. When detectable, the signal of the $N-\underline{C}H_2-$ group appears usually as a very broad and weak peak centred at about 3.75 ppm from TMS. From the structure of PHIC and POIC, the areas under the $N-\underline{C}H_2-$ peaks were expected to be 15.4% and 11.8% of the total alkyl peaks areas of the corresponding polymers. In reality, the measured $N-\underline{C}H_2-$ peak areas were less than half the expected areas. This discrepancy was carried through after a considerable dilution, well into the single isotropic phase. The discrepancy appeared in systems containing either polymer or mixtures. From this, and from $^{13}C$ n.m.r. data reported elsewhere[23], it is our conclusion

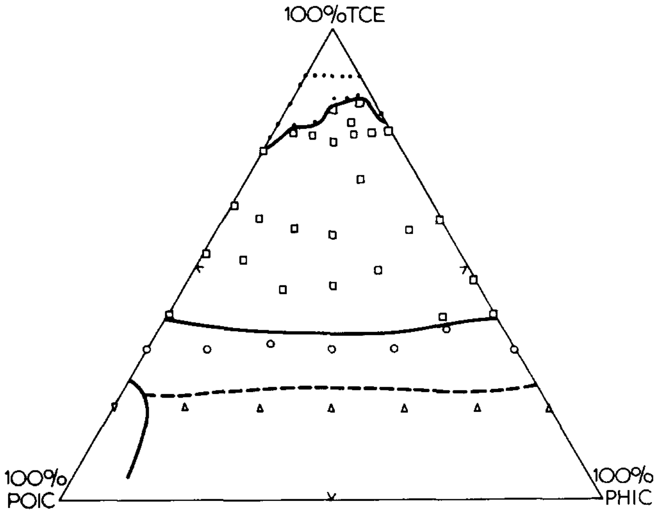

*Figure 4* Ternary phase diagram of the system PHIC/POIC/TCE at 48° ± 2°C. Same samples as in *Figure 2,* but data obtained 23 days later. Key as in *Figure 1*

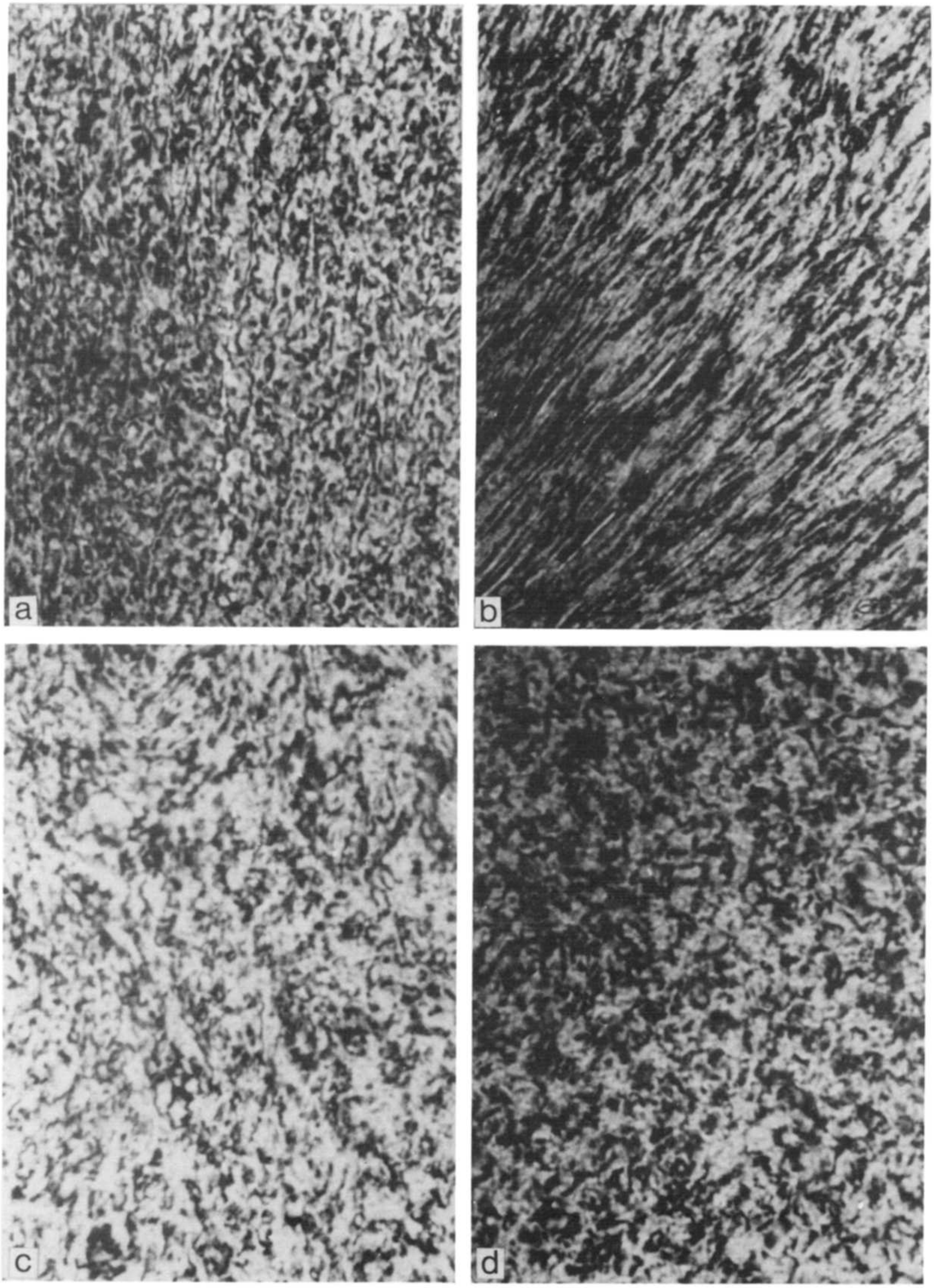

*Figure 5* A single anisotropic solution from the following samples: (a) 52.1 vol/vol % PHIC in TCE; (b) 31.6 vol/vol % of 33.3% POIC and 66.7% PHIC in TCE; (c) 54.5 vol/vol % of 66.7% POIC and 33.3% PHIC in TCE; (d) 67.7 vol/vol % POIC in TCE. Samples with other polymer/polymer ratios produced similar textures in their anisotropic phase (X 200)

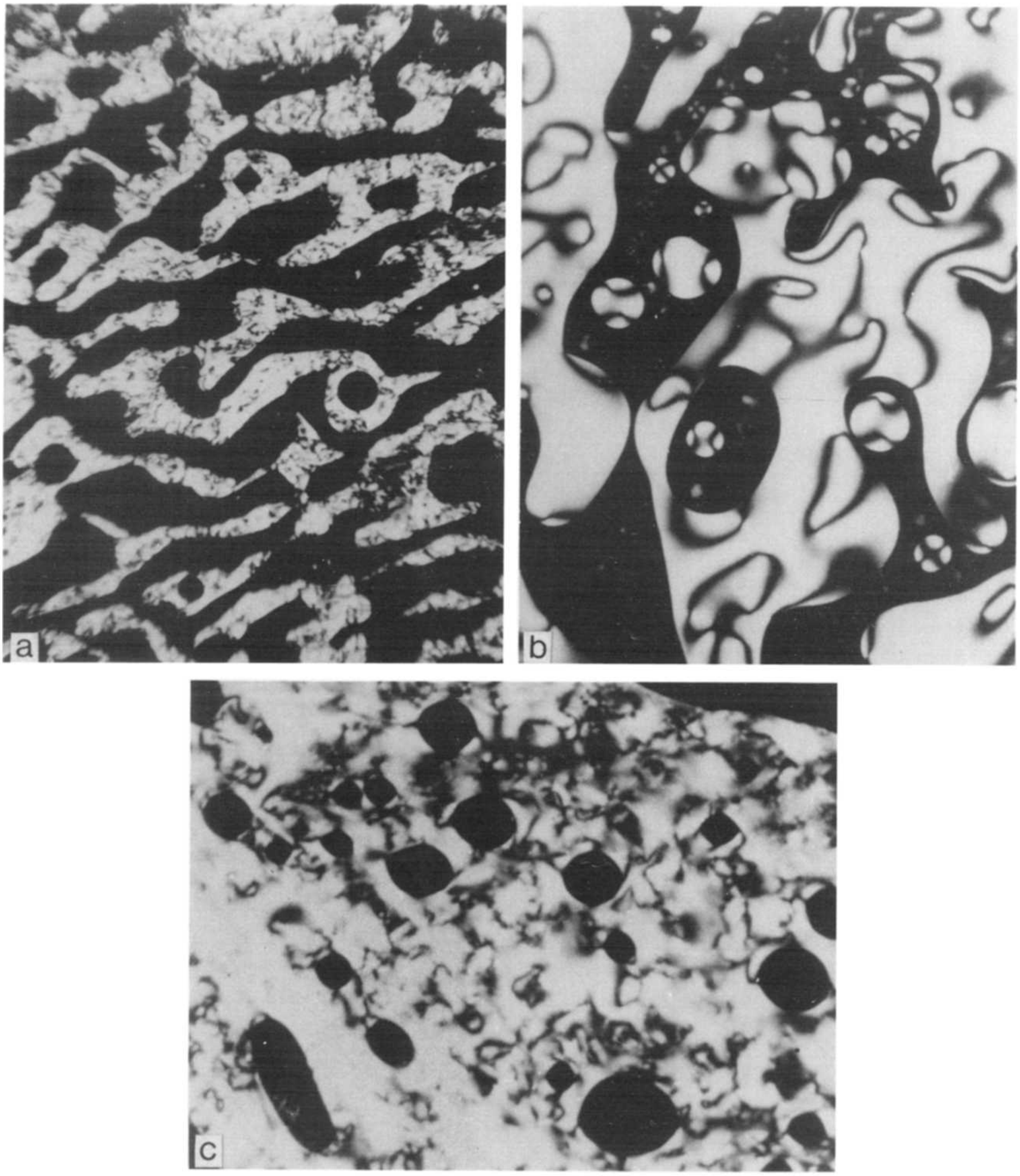

*Figure 6* Biphasic systems of: (a) about 30% PHIC in TCE; (b) 36.2% POIC in TCE; (c) 39.3% of 16.5% PHIC + 83.5% POIC in TCE. Samples with other polymer/polymer ratios produced textures intermediate between (a) and (b); similar to (c). Original magnification, X 200

that the methylene group directly attached to the backbone nitrogen is severely hindered in its mobility, leading to its broad and weak n.m.r. peak.

In *Figure 7a* a spectrum characteristic of the biphasic region, containing isotropic and anisotropic solutions in about equal volumes, is shown. The TCE peak has a linewidth at half-height, $W_{1/2}$, typically of 2 Hz or less. The polymer peaks are broad and poorly resolved. The $N-\underline{CH_2}-$ peak is barely detectable. In more dilute isotropic solutions, especially in the range of 1–2% polymer concentration, the polymer peaks are much sharper and better resolved. At these concentrations, the solvent peak and spinning sidebands are far too intense to be scanned at the same machine setting used for observing the polymer.

When the concentration of the polymer in the system is increased, and a single anisotropic phase is scanned, the spectrum obtained in *Figure 7b* is typical. In this case, the alkyl peak at about 1.2 ppm (and the adjacent $-CH_3$ peak) is broader than when originated from the biphasic system. Often a broad additional peak or two appear downfield from the alkyl peak. The TCE peak at 5.92 ppm becomes very broad with $W_{1/2}$ = 15 to 20 Hz, and is attended by an addi-

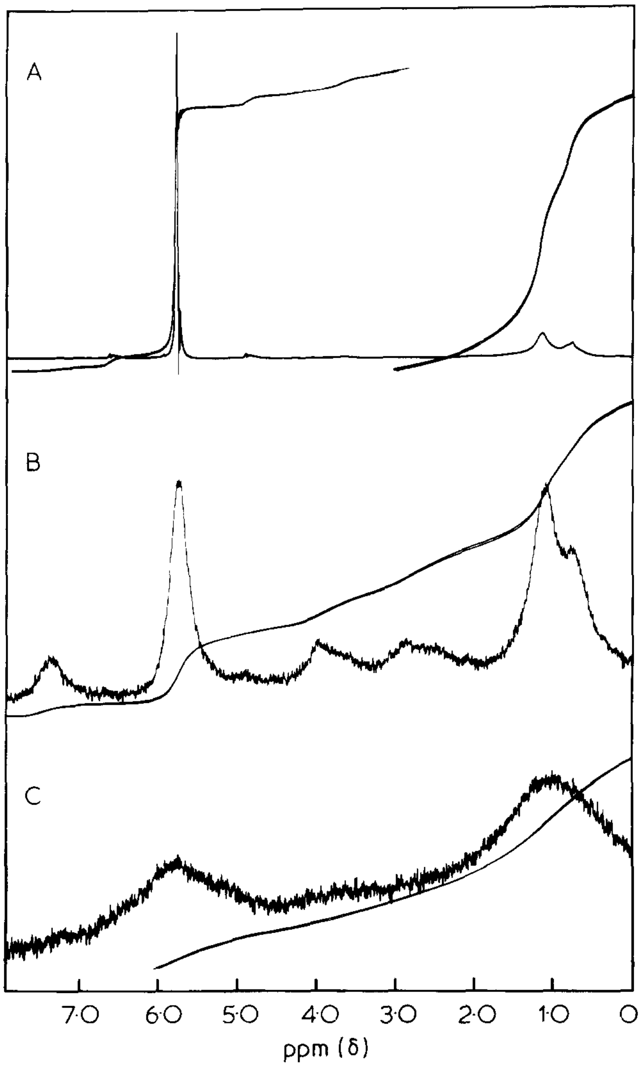

*Figure 7* Proton n.m.r. spectra from samples containing 33.3% POIC and 66.7% PHIC: (a) a biphasic system, 31.6 vol/vol % polymer in TCE; (b) anisotropic system, 67.6 vol/vol % polymer in TCE; (c) anisotropic solution containing swollen semicrystalline polymer, 80 vol/vol % polymer in TCE. All spectra were obtained with spinning at room temperature

tional doublet. The peaks of this doublet are spaced about equidistantly up and downfield from the major TCE peak and the distance between them ranges from 130 to 210 Hz, depending on the sample. The spinning sidebands can still be seen in their expected positions between the major TCE peak and the doublet. The integrated area of the doublet varies, depending on the particular sample, from about a half to two-thirds the area of the 5.92 ppm singlet.

On further increasing the polymer concentration to regions where many microscopic swollen semicrystalline polymeric solids are visible in the liquid crystalline phase, the n.m.r. spectrum loses its resolution and appears as in *Figure 7c*. When the sample contains only a swollen semicrystalline polymer, for example, 80% PHIC at room temperature, then the spectrum loses even the two very broad peaks in *Figure 7c* and a flat, featureless and noisy scan is obtained.

The spectra in *Figure 7* were obtained with the samples spinning in the probe at the conventional spinning rate of about 50 rev $s^{-1}$. When the samples were allowed several min in the probe without spinning, and then scanned unspun, all linewidths became substantially broader, as is expected under such conditions. The samples from the biphasic range showed linewidths as if they were completely anisotropic (but without the TCE doublet), and the anisotropic samples lost the resolution they had and produced broad peaks as in *Figure 7c*.

When the mol % polymer in the systems, determined from the integrated n.m.r. peaks, were compared with the mol % polymer actually introduced into the various samples it was found that the results obtained from n.m.r. were biased in favour of POIC and against PHIC, at least in the range of 30 to 70 vol/vol % polymer. In other words, in this concentration interval, more POIC and less PHIC than introduced are observed by means of n.m.r. As may be gathered from *Table 1*, this trend is noticeable in the tricomponent system of PHIC/POIC/TCE, as well as in the systems PHIC/TCE and POIC/TCE.

It was recently demonstrated that, similar to poly(n-butyl isocyanate) (PBIC)[22], poly(n-hexyl isocyanate) and poly(n-octyl isocyanate) in the solid state are best described as rigid helices[24]. Poly(n-alkyl isocyanates) have the same extended rigid conformation in the solid state as well as in dilute solution[25,26] when $M$ is not exceedingly high. Based on these facts, we may propose a hypothetical structure for the anisotropic poly(n-alkyl isocyanate)/TCE solution that may possibly explain the n.m.r. observations. Accordingly, each polymer macromolecule has an overall shape of a long worm-like cylinder, the diameter of which may, but not necessarily, be approximated by the size of the helical backbone and the appended alkyl groups. This cylinder contains solvent molecules and is immersed in additional solvent, the amount of both being dependent on the concentration of the solution. Packing considerations indicate that most of the solvent molecules within the inscribed cylinder should be in its peripheral zone and only very few solvent molecules close to the cylinder axis. The farther away from the backbone a methylene group of the pendant is, the more solvated it finds itself. In other words, while the $N\text{–}\underline{C}H_2\text{–}$ and probably $N\text{–}CH_2\text{–}\underline{C}H_2\text{–}$ groups hardly have any solvent molecules in their near proximity, the tips of the pendant groups are immersed in solvent. The solvent molecules mixed with the pendant groups are, more or less, free to exchange positions randomly and to be in or out of the inscribed cylinder. The nature of the solvents in which the polyisocyanates were dissolved, and the nature of the side groups of these polymers appear to preclude the formation of thermodynamically meaningful polymer–solvent complexes. Solvent molecules

*Table 1* Actual and n.m.r.-measured mol % polymer in TCE

| Sample code | Polymer composition | Actual % polymer (vol/vol%) | (mol %) | N.m.r. measured % polymer (mol %) |
|---|---|---|---|---|
| I | POIC | 59.5 | 40.7 | 72 |
| II | PHIC | 52.1 | 43.5 | 33 |
| III | 16.5% PHIC + 83.5% POIC | 48.1 | 33.9 | 64 |
| IV | 33.3% PHIC + 66.7% POIC | 54.5 | 39.6 | 59 |
| V | 50.0% PHIC + 50.0% POIC | 53.6 | 40.3 | 58 |
| VI | 66.7% PHIC + 33.3% POIC | 31.6 | 24.6 | 47 |
| VII | 83.5% PHIC + 16.5% POIC | 60.0 | 48.3 | 25 |
| VIII | POIC | 67.7 | 46.3 | 66 |
| IX | PHIC | 67.7 | 56.3 | 27 |
| X | 83.5% PHIC + 16.5% POIC | 62.5 | 50.3 | 52 |
| XI | 66.7% PHIC + 33.3% POIC | 67.6 | 52.5 | 51 |
| XII | 50.0% PHIC + 50.0% POIC | 67.3 | 50.6 | 65 |
| XIII | 33.3% PHIC + 66.7% POIC | 66.7 | 48.5 | 56 |
| XIV | 16.5% PHIC + 83.5% POIC | 67.7 | 47.7 | 62 |

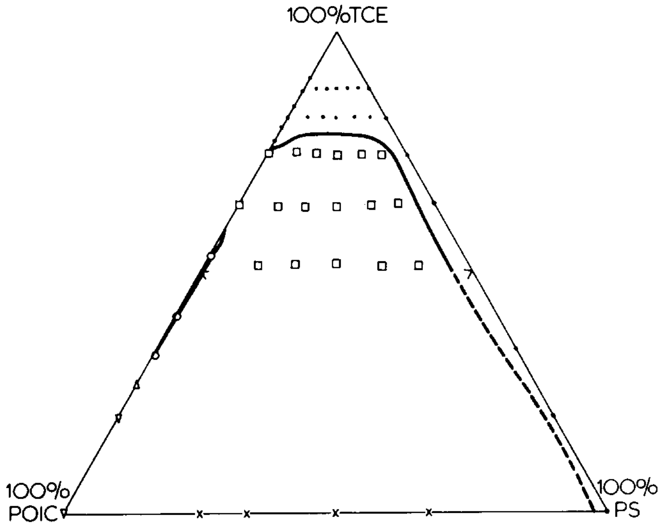

*Figure 8* Ternary phase diagram of the system POIC/PS/TCE at room temperature. ●, Isotropic; ⊙, liquid crystal; ⊡, liquid crystal + isotropic; △, liquid crystal + semicrystalline solids; ▽, semicrystalline solids; x, semicrystalline solid + isotropic solid

which are restricted in their mobility, for being close to the macromolecular backbone or for any other reason, may be oriented with respect to the applied field in the manner described by Sobajima[27] for methylene chloride solutions of poly($\gamma$-benzyl L-glutamate)(PBLG). These solvent molecules may produce the doublet in the n.m.r. scan. Solvent molecules less restricted in their mobility may produce the broad singlet at 5.92 ppm.

In concentrated solutions, the peripheral parts of the pendant groups may not be free to move as in dilute solution but they are endowed with sufficient mobility to produce n.m.r. peaks such as shown in *Figure 7b*. A preliminary $^{13}C$ n.m.r. study on bulk PHIC and POIC[23] indicates that the former shows no side chain mobility up to the melting point, $T_m$, while the latter possesses substantial pendant mobility much below $T_m$. The absence of motion is typical of short side chain polyisocyanates, while the long side chain polymers all exhibit such a mobility substantially below $T_m$. It may be that the bias of the n.m.r. in favour of POIC and against PHIC is a reflection of a difference in side chain mobility carried from the bulk to concentrated solutions.

When additional solvent is added to the anisotropic solution and the system becomes biphasic or isotropic, the process of exchange and randomization of solvent molecules becomes more facile and rapid, with the resulting n.m.r. solvent peak narrowing as in *Figure 7a*. Under conditions of high polymer concentration, there is insufficient solvent to allow pendant mobility and the polymer signal is first broadened and, at high concentrations, may be depressed into the background and lost. In such a system, the few solvent molecules are also impeded in their motion, leading to similar signal broadening and eventual disappearance into the background.

In the anisotropic PBLG/methylene chloride, the solvent was shown to exhibit a doublet with a peak-to-peak separation of 70[28] to 100 Hz[27]. It is tempting to cite this overall similarity as supporting evidence for the anisotropic solution structure proposed above, but the available data are now insufficient to exclude all other models.

Comparisons of the above n.m.r. observations with other n.m.r. observations in the anisotropic phase are unadvised. For the solvent, these results are usually characterized by a dipolar splitting of the signals which may cover several hundred Hz in the system poly(1,4-benzamide)/dimethylacetamide[14] or merely the splitting of each solvent peak into a relatively narrow multiplet in the case of PBLG/dimethylformamide[16,28]. Each particular polymer–solvent pair may exhibit, therefore, a unique splitting pattern in its n.m.r. spectrum.

It should be noted that solid crystalline polymers were previously observed to coexist in equilibrium with anisotropic solutions[29,30]. The systems in question were poly(1,4-benzamide)/dimethylacetamide–LiCl, and poly(*p*-phenylene terephthalamide)/sulphuric acid. It was suggested by Papkov[29] that the coexistence of crystalline and mesomorphic phases in these systems may reflect 'an unusual superimposition of two types of equilibrium in a lyotropic system', i.e., crystal–solution and anisotropic–isotropic equilibrium. It is possible that the presence of swollen semicrystalline polymer in conjunction with liquid crystals in our systems may represent a similar coexistence of two processes far from equilibrium (*Figures 1* and *2*) or in a state of apparent equilibrium (*Figures 3* and *4*). The available experimental data are too meager to reach a conclusion about this point.

When the polymer in the anisotropic phase is aromatic, then the high-resolution resonance of the polymer is not seen because of the intramolecular nuclear dipolar interactions of the highly-oriented molecules. The spectrum can be detected but is extremely broad[14]. In the case of the poly(n-alkyl isocyanates) the tips of the pendant groups enjoy substantial freedom of motion, randomizing somewhat their local environment and, as a consequence, making the signal sufficiently narrow to be clearly identifiable (*Figure 7b*).

The systems to be described below contained aromatic residues in the polymers. These suffered from interference by the TCE major n.m.r. peak and its spinning sidebands, especially in dilute or semi-dilute solutions. Therefore, proton n.m.r. spectra were usually obtained only from the aliphatic parts of the polymers. The conclusions from the spectra which were obtained were generally in agreement with the conclusions discussed above for the PHIC/POIC/TCE system. Therefore, no reference to specific n.m.r. spectra will be made in the following discussion.

The systems POIC/PS/TCE and PBAEIC/PS/TCE are described in *Figures 8* and *9*, respectively. In both systems, the addition of only minute amounts of polystyrene to the solutions of polyisocyanate in TCE was sufficient to produce two phases: anisotropic and isotropic. However, a somewhat larger amount of polyisocyanate could be added to solutions of PS in TCE before an anisotropic phase separated out. This was especially noticeable in the system PBAEIC/PS/TCE. The greater tolerance of random coil solutions for rigid molecules, so clearly observed in both systems above, is exactly what theory predicts[6].

A characteristic biphasic structure, containing about 63.5% TCE and the rest POIC and PS, is shown in *Figure 10a*. In the absence of solvent, along the PS–POIC facet of the phase diagram in *Figure 8*, the POIC tends to separate as solid spherulitic and lamellar material, as shown in *Figure 10b* for a 1:1 POIC/PS ratio. The appearance of the phases in the PBAEIC/PS/TCE system is similar to the comparable samples of POIC/PS/TCE such as in *Figure 10a* and *10b*.

The polyisocyanates used with PS were of substantially higher molecular weight than those in the system PHIC/POIC/TCE. Therefore, the solution viscosity of the former was much higher than that of the latter, making the work

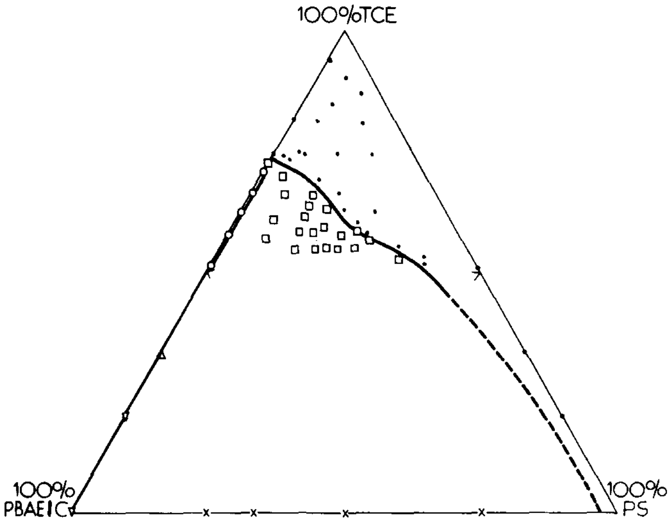

*Figure 9* Ternary phase diagram of the system PBAEIC/PS/TCE at room temperature. Key as in *Figure 8*

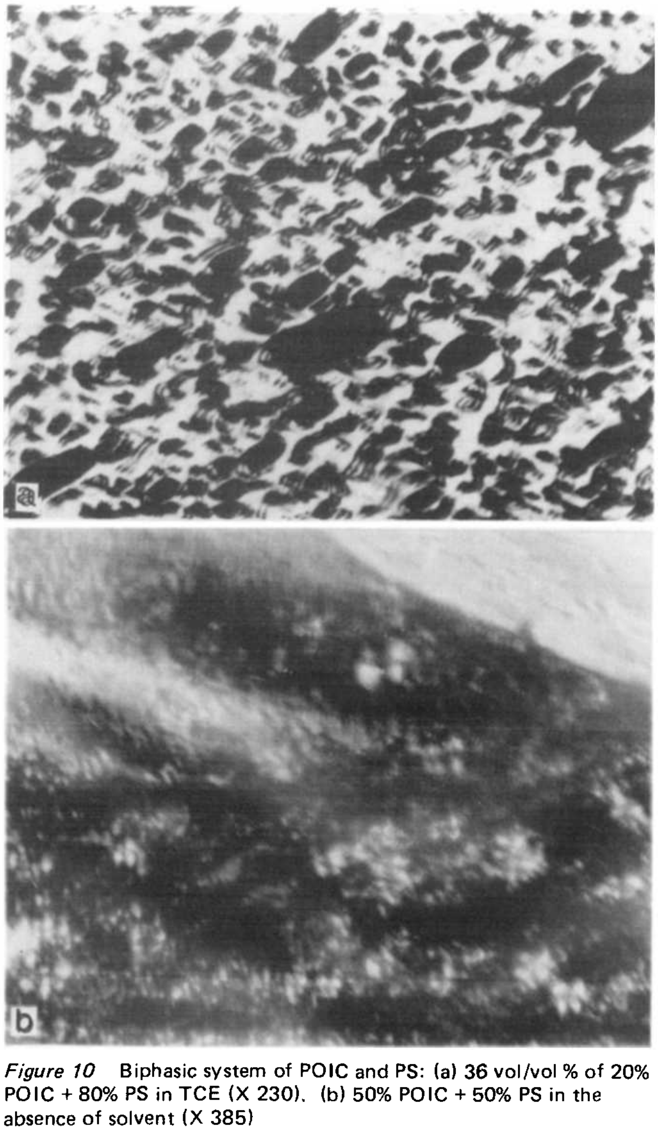

*Figure 10* Biphasic system of POIC and PS: (a) 36 vol/vol % of 20% POIC + 80% PS in TCE (X 230). (b) 50% POIC + 50% PS in the absence of solvent (X 385)

with polymer concentrations in the range of 50% to <100% impractical. From the results at <50% polymer and at 100% polymer, we may safely conclude that for any significant presence of at least one flexible polymer, the concentration range of 50 to 100% will be biphasic in nature.

The above observations appear to confirm Flory's theoretical conclusions about the incompatibility of rod-like and flexible polymers in solution[6].

Recently, fragmentary data on ternary systems similar to ours, namely, PHIC/PS/toluene and PBLG/PS/solvent appeared in the literature[31]. These systems were dilute in rod-like polymers, yet showed phase separation similar to our systems PBAEIC/PS/TCE and POIC/PS/TCE.

Because of the high molecular weight of both polymeric components and the resulting high solution viscosity, the system POIC/PBAEIC/TCE was studied at concentrations less than 50% polymer. The results are presented in *Figure 11*. The significance of this phase diagram rests on the fact that in its high concentration part there exists a single anisotropic phase containing a substantial amount of both polymers. This phase is separated from the more dilute isotropic phase by a concentration interval containing the two phases. Such behaviour is expected from theory[1,3]. It is not known as of now whether the two polymers, POIC and PBAEIC, are sufficiently compatible to form a single anisotropic phase covering all polymer ratios at higher concentrations. We recall that in the case of PHIC/POIC/TCE (*Figures 3* and *4*) the polymers were apparently sufficiently compatible so that packing considerations controlled their behaviour in the region of high polymer concentration, resulting in a single anisotropic phase traversing all polymer/polymer ratios.

The wide biphasic interval containing large amounts of both POIC and PBAEIC is as expected from theory[1,3]. However, it may reflect a possible incompatibility of the two polymers causing a separation into two phases not directly related to the theoretical considerations[1–7] invoked above.

## CONCLUSIONS

The ternary system PHIC/POIC/TCE has a polymer concentration range in which a single anisotropic phase over all polymer/polymer ratios is exhibited. The concentrations at which the anisotropic phase exists are separated from the region of a single dilute and isotropic solution by a biphasic interval which becomes wider in locations containing substantial amounts of both polymers. A partial phase diagram of POIC/PBAEIC/TCE suggests similar behaviour.

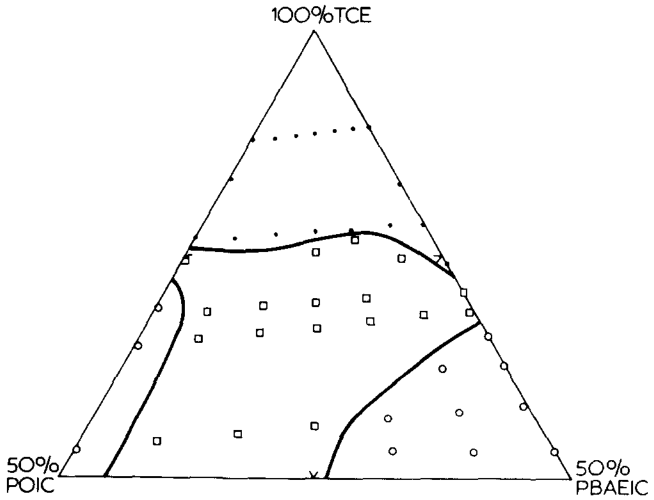

*Figure 11* Ternary phase diagram of the system POIC/PBAEIC/TCE up to about 50 vol/vol % polymer, at room temperature. ●, Isotropic ○, liquid crystal; □, liquid crystal + isotropic

In systems containing polyisocyanates, polystyrene and TCE, a single anisotropic phase exists only in instances of high polymer concentration where the amount of PS is negligible. In all other cases the ternary system is either an isotropic solution or an anisotropic solution coexisting with an isotropic one.

Both systems above, rod-like polymer/rod-like polymer/solvent and rod-like polymer/random coil polymer/solvent behave in excellent agreement with Flory's recent theory$^{1-7}$.

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