Rigid Backbone Polymers. 2. Polyisocyanates and Their Liquid-Crystal Behavior

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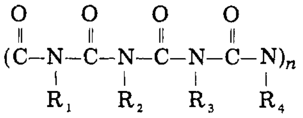
ABSTRACT: It is shown that certain isocyanate polymers are mesogenic in concentrated solutions at ambient temperatures and in bulk at elevated temperatures. These polymers may be categorized into two classes: (1) alkylisocyanate homopolymers in which the alkyl side chains are long enough to facilitate concentrated solutions, yet short enough to prevent predominant side-chain interactions; and (2) copolymers of aralkyl and alkyl isocyanate where the aromatic residue is at least two ($-CH_2-$) units removed from the backbone. Preliminary X-ray, IR, thermal analysis, dilute solution, and mechanical properties data are also presented.

The presently known liquid-crystal polymers, exhibiting mesogenic behavior in concentrated solution or in the pure form, may be divided into the following categories: (1) highly rigid, aromatic, and linear polymers with no side groups, behaving in the concentrated solution[1] or in the "melt"[2-4] as nematic liquid crystals; (2) helical macromolecules, rendered rigid by means of intramolecular or intrahelix hydrogen bonding, behaving in solution as nematic liquid crystals;[5] and (3) polymers having a relatively flexible backbone to which rigid, mesogenic, side groups are attached. These polymers may show, in solution or in bulk, smectic or nematic behavior, depending on the length of the mesogenic side groups.[6]

To these three well-known families of polymeric liquid crystals we wish to add another category: (4) polymers having relatively rigid backbone, which may be planar or helicoidal, to which relatively flexible side groups are attached. These side groups must not distort the backbone out of its rather extended form, must be of such a size and nature to facilitate high concentration solutions, but not be of such length that interactions between side chains will completely dominate the behavior of the whole ensemble.

A family of polymers fitting the above description is the polyisocyanate family



$$(\overset{O}{\overset{\|}{C}}-\underset{R_1}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{R_2}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{R_3}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{R_4}{\underset{|}{N}})_n$$

where the R's may be the same or different.

In the first paper of this series,[7] and in the literature,[8,9] it was shown that, at least, several members of the polyisocyanide family also manifest mesomorphic behavior. The polyisocyanides may be classified in category (4) above. Many of the polyorganophosphazenes exhibiting mesomorphic behavior[10-12] may also be classified in this group.

In this paper, it will be shown that many polyisocyanates do indeed behave as liquid crystals in the concentrated solution or in the pure form. In forthcoming papers of this series, dilute solutions[13] and X-ray[14] studies of several of the polyisocyanates will be described in greater detail.

Experimental Section

Monoisocyanates were prepared from the corresponding acids by first preparing acid chlorides and then making the azides and performing on them the Curtius transformation to produce the isocyanates. The procedure for the last two reactions is described, for instance, by Boehmer[15] and by Allen and Bell.[16] Both, however, are using benzene as the solvent of choice. In light of the recently discovered carcinogenicity of benzene, a different solvent was sought to run the reactions in. It was found that cyclohexane, by virtue of having a boiling temperature and water-azeotroping properties very close to those of benzene, was eminently suitable for this purpose. Surprisingly, reactions conducted in toluene gave much lower yields of the monoisocyanates than reactions performed in cyclohexane. A detailed typical procedure for the preparation of monomers will be given below.

The polymerization procedure used by us was essentially that of Shashoua et al.[17,18] It was found, however, that at the recommended polymerization temperature, many of the higher molecular weight monomers tended to crystallize out of the recommended dimethylformamide (DMF) solvent. Therefore, pure toluene or mixtures of 1:1 by volume of toluene and DMF were used as the solvent for most runs, eliminating monomer precipitation and solvent freezing during the polymerization procedure. A typical polymerization procedure will be given below.

Preparation of Isocyanate Monomers. The following procedure is for 1 mol of starting material. The acid was mixed in a round-bottom flask under dry atmosphere with at least 2 mol of thionyl chloride and stirred at $35\ °C < T \leq 40\ °C$ for 3 h. After the reaction, the mixture was often allowed to stand overnight at room temperature. Then the excess thionyl chloride was removed by the application of vacuum accompanied by gentle heating. The acid chloride was stored in sealed vessels until used in the next step.

In a three-neck flask were placed 1.5 mol of sodium azide (NaN_3), 300 mL of water, and 300 mL of cyclohexane. The contents were cooled in an ice bath and stirred to dissolve the NaN_3. To this solution, a solution of acid chloride in 300 mL of acetone was added dropwise at a rate such that the temperature in the flask never exceeded 15 °C. After the addition was completed, the flask was stirred between 10 and 15 °C for at least 1 additional h. The solution was then cooled to about 0 °C with the azide maintained in solution by small additions of cyclohexane. The cold contents were transferred to a separatory funnel and the aqueous layer was removed. The organic layer must be maintained below 15 °C. Traces of water, which tend to coalesce into droplets which adhere to the glassware at this temperature, are removed by repeated decantation from one vessel to another.

The cyclohexane solution of the azide was added to twice its volume of boiling cyclohexane at such a rate that the temperature was kept throughout above 65 °C and preferentially at about 70 °C. After the addition was complete, the solution was stirred between 60 and 70 °C for at least 1 additional h. Treatment with decolorizing carbon and filtration followed. Then the solution was cooled, the excess solvent removed in a rotary evaporator, and the residual isocyanate purified by vacuum distillation from which the forerun was removed. The purified isocyanate was stored and protected from air, humidity, light, and heat until used.

Preparation of Isocyanate Polymers. To insure the absence of all traces of water, the catalyst and the polyisocyanates were prepared in flamed glassware. In a typical procedure, about 1 g of NaCN is finely ground. The NaCN powder is suspended in 25 to 50 mL of DMF previously treated with molecular sieves. The suspension is stirred for at least 1 h prior to use.

A 150 mL three-necked flask is equipped with a dropping funnel, a mechanical stirrer, and nitrogen inlet and outlet both fitted with drying tubes. The dropping funnel is filled with 10 mL or more of the catalyst suspended in DMF. The composition of the solvent depends on the monomer. For very long aliphatic chain monomers, toluene is used. For intermediate length chains,

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Table I
Polyisocyanates Prepared, Their Composition, and Reduced Viscosity

	composition[a,b]	reduced viscosity at $C = 0.5\%$[c,d]
I	poly(methyl isocyanate)	0.16 in $CHCl_3$ and 0.06 in trifluoroethanol
II	poly(ethyl isocyanate)	0.11 in trifluoroacetic acid
III	poly(butyl isocyanate)	8.06, 3.2, 2.76, 2.05, and 1.92 in $CHCl_3$, 2.15 in THF
IV	poly(hexyl isocyanate)	3.28, 2.71, and 2.08 in $CHCl_3$, 4.22 in toluene, 4.15 in Θ solvent
V	poly(octyl isocyanate)	1.7 in $CHCl_3$
VI	poly(nonyl isocyanate)	0.66 and 0.62 in $CHCl_3$
VII	poly(1-decenyl isocyanate)	3.26 in $CHCl_3$
VIII	poly(undecyl isocyanate)	0.12, 0.26, and 1.00 in $CHCl_3$
IX	poly(tridecyl isocyanate)	0.14 in $CHCl_3$
X	poly(pentadecyl isocyanate)	0.18 in $CHCl_3$
XI	poly(octadecyl isocyanate)	1.00 and 0.70 in $CHCl_3$
XII	poly(phenyl isocyanate)	insoluble in $CHCl_3$
XIII	poly(phenyl-3-propyl isocyanate)	0.95 in $CHCl_3$
XIV	poly(*p*-tolyl isocyanate)	0.5 in $CHCl_3$
XV	poly(*p*-anisole isocyanate)	0.38 in $CHCl_3$
XVI	poly(*p*-anisolemethyl isocyanate)	0.8 in $CHCl_3$
XVII	poly(*p*-anisole-2-ethyl isocyanate)	1.1 in $CHCl_3$
XVIII	poly(*p*-anisole-3-propyl isocyanate)	1.34, 0.60, and 0.26 in $CHCl_3$
XX	poly(50% butyl + 50% nonyl isocyanate)	2.4 in $CHCl_3$
XXI	poly(52% butyl + 48% phenyl-3-propyl isocyanate)	0.61 in $CHCl_3$
XXII	poly(30% butyl + 70% *p*-anisolemethyl isocyanate)	0.42 and 0.32 in $CHCl_3$
XXIII	poly(32% butyl + 68% *p*-anisolemethyl isocyanate)	1.05 in $CHCl_3$
XXIV	poly(50% butyl + 50% *p*-anisole-2-ethyl isocyanate)	0.93 in $CHCl_3$
XXV	poly(33% butyl + 67% *p*-anisole-3-propyl isocyanate)	7.92 in $CHCl_3$
XXVI	poly(50% butyl + 50% *p*-anisole-3-propyl isocyanate)	12.08, 8.51, 8.1, 0.81, and 0.52 in $CHCl_3$
XXVII	poly(75% butyl + 25% *p*-anisole-3-propyl isocyanate)	4.1 in $CHCl_3$
XXVIII	poly(47% *p*-anisolemethyl + 53% *p*-anisole-3-propyl isocyanate)	2.8 in $CHCl_3$
XXIX	poly(52% *p*-anisolemethyl + 48% *p*-anisole-3-propyl isocyanate)	0.86 in $CHCl_3$
XXX	poly(81% butyl + 19% cyclohexyl isocyanate)	0.4 in $CHCl_3$
XXXI	poly(77% butyl + 23% methylcyclohexyl isocyanate)	0.6 in $CHCl_3$

[a] Except for the cyclohexyls, all alkyl side chains are linear. [b] Copolymer composition is in mol % and was determined by NMR analysis. [c] Variations in reduced viscosity merely reflect the fact that optimization of reaction conditions was not attempted. [d] The low reduced viscosities in acidic solvents such as trifluoroacetic acid and trifluoroethanol reflect the fact that the polyisocyanates hydrolyze in acidic media. A deterioration of the polymers was detected upon prolonged standing even in solvents such as TCE and $CHCl_3$.

a toluene/DMF mixture is used such that after the addition of the catalyst suspension in DMF, the volume ratio of toluene to DMF will be 1:1. For short chain monomers or for ones containing aromatic residues only DMF may be used as solvent. The three-necked flask is cooled to about −79 °C in a dry ice/acetone bath. Thirty milliliters of the desired solvent are placed in the three-necked flask and 10 mL of monomer is added upon cooling. After the mixture reaches the cold bath temperature, about 1 mL of the catalyst suspension is added. More catalyst is added dropwise over the course of the following 20 min. After a total of 30 min, the reaction is quenched by the addition of about 100 mL of cold methanol. The resulting mixture is stirred in order to break the gel particles. The solid polymers are filtered and rinsed several times with methanol before being finally dried under high vacuum at room temperature.

Characterization. Dilute solution viscosities were determined at 25 °C using Cannon-Ubbelohde glass viscometers. The solvents most often used were chloroform and toluene. Higher concentration viscosities were measured with the aid of a Nametre Rheodynamics direct readout viscometer at a shear rate of 4060 s^{-1}.

Proton and carbon-13 NMR spectra were obtained using Varian T-60A and Varian CFT-20 NMR spectrometers, respectively. The solvents most often employed were deuterated Me_2SO and chloroform and trifluoroethanol. All samples were internally calibrated with tetramethylsilane (Me_4Si).

Infrared spectra were obtained from pulverized samples in KBr pellets, from films cast from chloroform on KBr plates, and from concentrated and dilute solutions in tetrachloroethane. The solution spectra were obtained, after subtracting the solvent absorption, on a nicolet 7199 Fourier transform infrared (FTIR) spectrometer. Solid sample spectra used for comparison with the solution spectra were also obtained with the Nicolet instrument. All other solid sample spectra, from KBr pellet and films, were obtained using a Perkin-Elmer infrared spectrophotometer Model 2B.

Thermogravimetric analyses (TGA) using a Cahn electrobalance and a DuPont 951 thermogravimetric analyzer were performed at a heating rate of 10 °C/min. Differential thermal analyses (DTA) and differential scanning calorimetry (DSC) scans using a DuPont 990 thermal analyzer were performed at heating rates of 20 °C/min, with the polymers in an Argon atmosphere.

Optical microscopy studies on solutions were conducted using a Leitz Ortholux polarized light microscope. Hot-stage microscopy was performed on a Leitz hot-stage microscope.

X-ray diffraction patterns were obtained with a Norelco X-ray diffractometer in parafocus geometry using Cu Kα radiation. The samples were submitted to thermal cycling, mounted in a controlled temperature sample holder, under nitrogen atmosphere.

An oriented film was studied using Philips microcamera with a sample to film distance of 1.413 cm. The photographic film was then scanned with a microdensitometer in the meridional and equatorial directions. A solution sample was studied for wide- and small-angle X-ray scattering patterns with a small angle and a Debye–Scherrer camera. With the geometry employed, it was possible to scan an angular range corresponding to Bragg spacings of 140 to 6.3 Å on the small-angle camera, producing a considerable overlap with the range of 10 to 1.50 Å of the Debye–Scherrer camera.

Light-scattering experiments were performed on a Brice Phoenix light-scattering photometer and osmometry on a Mechrolab high-speed membrane osmometer. Filtration was done through 0.45 mμm Millipore filters.

Stress–strain curves were obtained in an Instron testing instrument from dogbone-shaped samples punched out of films cast from solution in a mixture of 1:2 toluene/chloroform, following the procedure of Haward et al.[19]

Results

The polymers tabulated in Table I were synthesized from the corresponding monomers. For convenience, the polymers would be referred to herein by their number.

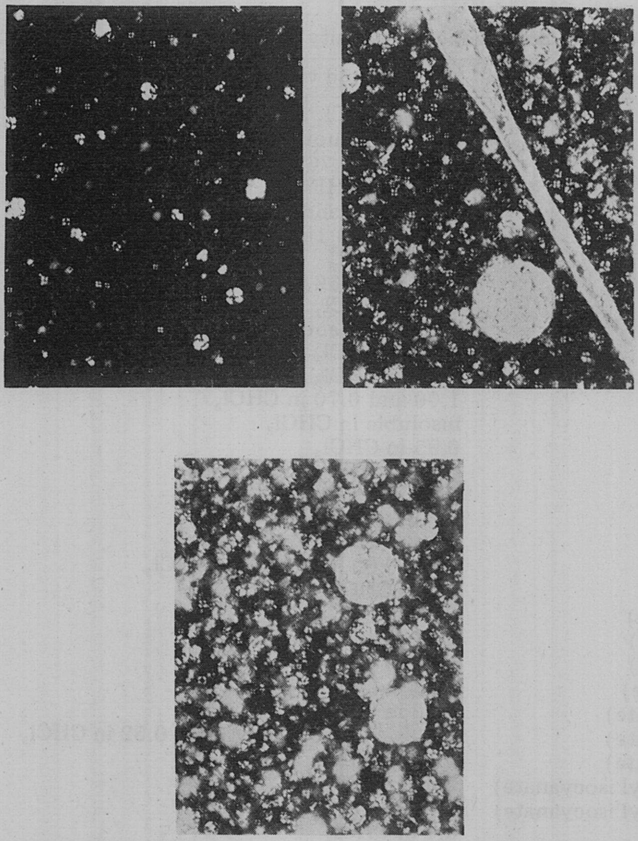

Figure 1. Mesomorphic structures in a 25% solution of poly(hexyl isocyanate) (IV) in TCE at room temperature. Original magnification 200×.

Polarized light microscopy studies at room temperature were conducted on solutions of the polyisocyanates in conventional solvents and were restricted only by the limited solubility of several of the polymers. By the use of high-boiling solvents having refractive index significantly different from that of the polymers evaporation of the solvent from under the microscope cover glass was better controlled, and the polymer was clearly visible in the solvent.

From the homopoly(alkyl isocyanates), polymers IV, V, VI, and VII clearly exhibited liquid-crystalline behavior in solutions above a certain critical concentration, v_2^*. Figures 1 through 5 are typical. Similarly, the copolymer XX showed the same mesomorphic behavior, Figure 6. From the aryl and aralkyl isocyanates, only the copolymers XXI (Figure 7), XXIV, XXV, and XXVI (Figure 8) were liquid crystalline above their critical concentrations, v_2^*. At concentrations below v_2^* the solutions are isotropic, at v_2^* the anisotropic phase appears, and above v_2^* the solution is anisotropic. Only at much higher concentrations, usually significantly above 50% polymer, separation of polymeric gel out of the anisotropic solution becomes evident. The aryl isocyanates XII, XIV, and XV are only sparingly soluble and produce microscopic particles floating in an isotropic, highly dilute solution of the polymer. The aralkyl homopolymer XIII is only sparingly soluble in the conventional solvents tested, yielding an isotropic dilute solution. The three aralkyl homopolyisocyanates XVI, XVII, and XVIII showed, in this order, increasing solubility in chlorinated solvents such as TCE or chloroform. They all produced isotropic solutions when completely dissolved, but it may be that their low solubility precludes them from surpassing v_2^* and forming mesomorphic structures. The polymers do show nonetheless, a tendency to become ordered in the same sequence: XVI < XVII < XVIII. When polymers XVII and XVIII are swollen in solvent during the process of dissolution, small

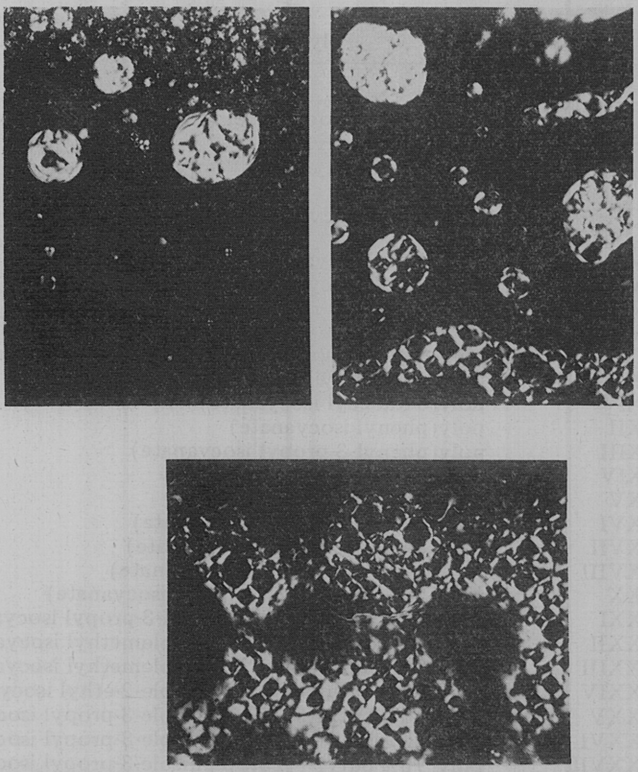

Figure 2. Mesomorphic structures in a 15% solution of IV in TCE at room temperature. Original magnification 200×.

Figure 3. Mesomorphic structures in ~25% IV in bromoform at room temperature. (a), (b), and (c) were obtained from a visually hazy layer, original magnification 200×. (d) was obtained from a visually clear layer, original magnification 400×.

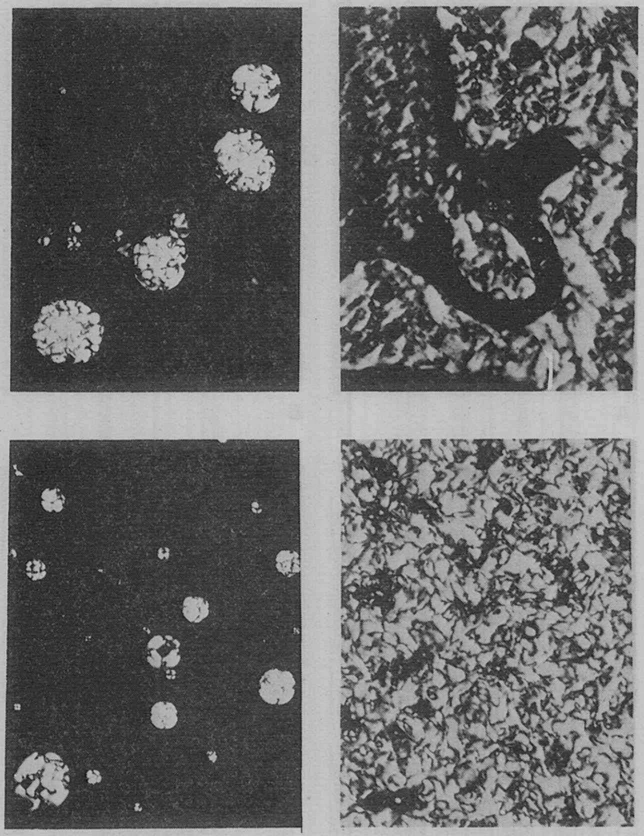

Figure 4. Mesomorphic structures in ~25% VI in TCE at room temperature. Original magnification 200×.

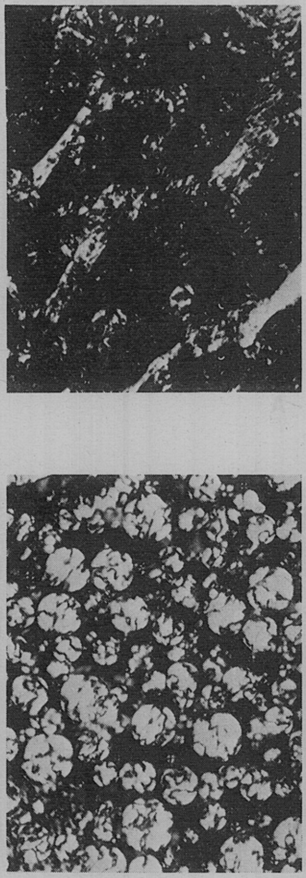

Figure 5. Mesomorphic structures in ~25% VII in TCE at room temperature. Original magnification 200×.

particles exhibiting Maltese crosses in cross-polarized light become clearly visible, as is shown in Figure 9. Similar Maltese crosses appear also in microparticles of the poly(alkyl isocyanate) VIII in the state of dissolution. When filtered through fine-pore fritted glass filters, dilute solutions of XVII and especially XVIII tended to deposit fine fibrillar matter that, when observed under the microscope, was found to be highly oriented polymers. The tendency to orient was so strong in the case of polymer XVIII that fast stirring of its concentrated solution was sufficient to produce fibrillar precipitation of the polymer. Poly(butylisocyanate), III, also tended to deposit fibrillar precipitate when filtered through fine pore fritted glass or Millipore filters, but this tendency was not as pronounced as, say, that of polymer XVIII.

From the linear alkyl homopolymers, I, II, III, VIII, IX, X, and XI yielded isotropic solutions at room temperature. Polymers I and II were only very sparingly soluble in the solvents employed so that one may invoke solutions too dilute to exhibit liquid crystallinity. This argument cannot hold for the highly soluble polymers III, VIII, IX, X, and XI. When solutions of these polymers at ever increasing concentrations are prepared at room temperature, a point is reached where the polymer precipitates out as a crystalline solid out of the supersaturated, yet isotropic, solution. When a hot and highly concentrated solution of III in TCE is placed on the microscope stage, liquid spherulites showing Maltese crosses are clearly visible. Upon cooling to room temperature, spherulites of the solid polymer appear floating in an isotropic solution. Later it will be shown that the polymers IX, X, and XI show side-chain crystallization, but such crystallization was not observed in III and VIII. From the above, one may conclude that alkyl isocyanate homopolymers (and copolymers such as XX) form liquid crystals when the alkyl chains are sufficiently long to facilitate high-concentration solutions, yet short enough in order for side-chain interactions not to dominate completely the behavior of the polymeric solution or its pure form. Polymers III and VIII, both showing a tendency toward chain alignment, but not liquid crystallinity in the sense of Figures 1 through 8, appear to be the limiting cases of transition from mesogenic to nonmesogenic polymers.

The two aralkyl copolymers XXVIII and XXIX, even though highly soluble in chlorinated solvents, failed to show liquid crystalline behavior. The cyclohexyl- and methylcyclohexyl-containing copolymers XXX and XXXI also showed no mesomorphic behavior. This behavior may be explained by noting that the molar fraction of butyl residues was very high in these polymers, 0.81 and 0.77, respectively.

Within the class of alkyl–aralkyl copolymers, when the three polymers XXV, XXVI, and XXVII are compared, one finds that XXV and XXVI do produce liquid crystals while XXVII does not. Here, again, a high molar fraction of butyl residues, namely 0.75, is responsible for the inability of XXVII to form liquid crystals at room temperature.

In the same class of alkyl–aralkyl copolymers, when one compares the number of $-CH_2-$ groups separating the aromatic residue from the backbone, one finds that for copolymers, such as XXII and XXIII, where only one $-CH_2-$ group is present, no liquid crystallinity is obtained, while in copolymers with two or three $-CH_2-$ groups between the aromatic residue and the backbone, mesomorphic behavior is very strongly evident (polymers XXI, XXIV, XXV, and XXVI). It is important to note that with the appropriate number of $-CH_2-$ groups, it is immaterial whether the aromatic residue is a polar anisole or a nonpolar phenyl. Polymers XXI and XXVI both

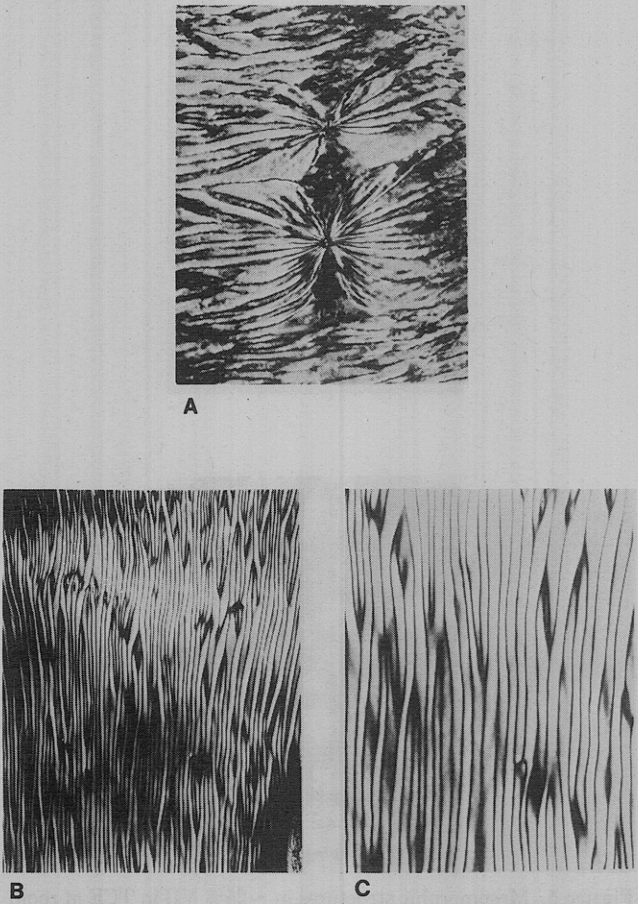

Figure 6. Mesomorphic structures in a sheared ~25% solution of XX in TCE at room temperature. Original magnification for (a) 850×, (b) 400×, and (c) 850×.

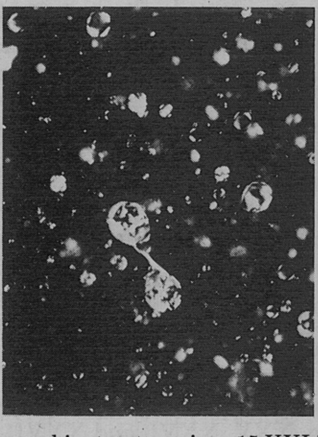

Figure 7. Mesomorphic structures in ~15 XXI in TCE at room temperature. Original magnification 200×.

contain about 50 mol % butyl, both have three $-CH_2-$ groups between their backbone and the aromatic residue, and both are liquid crystals. Yet, XXI has a phenyl while XXVI has an anisole residue.

One may conclude that the homopolymers of aralkyl studied here do not produce liquid crystals. If, however, the very same monomers are copolymerized with normal alkyl monomers, then the ability to form liquid crystals rests on the existence of two parameters: (a) the concentration of the aralkyl monomer cannot be too low (below ~0.33), and (b) the aralkyl must possess two or more $-CH_2-$ groups between the aromatic residue and the backbone chain.

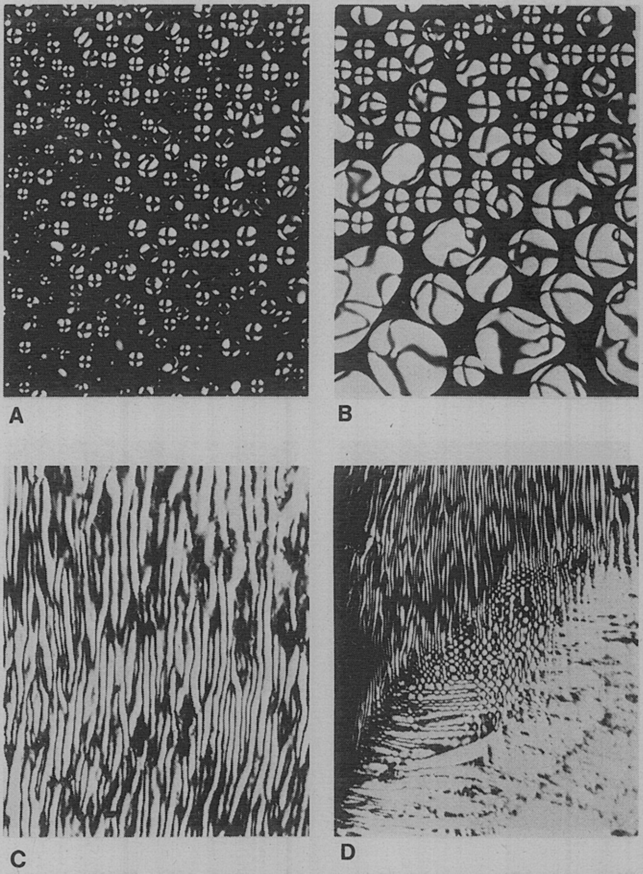

Figure 8. Mesomorphic structures in a 30% solution of XXVI in TCE at room temperature: (a and b) the solution as prepared, (c and d) a sheared solution.

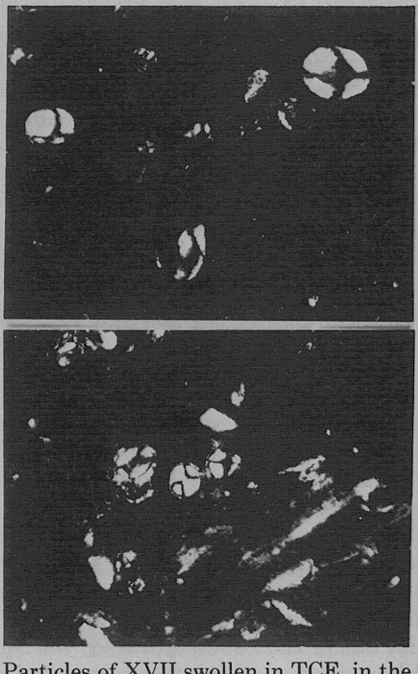

Figure 9. Particles of XVII swollen in TCE, in the process of dissolution, at room temperature. Original magnification 200×.

Several flexible-backbone polymers were studied in solution and in bulk with respect to their ability to form liquid crystals. Poly(hexyl methacrylate) was studied in the range of 23.8 to 100% polymer concentration, poly(octyl acrylate) was studied in the 21 to 100% concentration range, and poly(lauryl methacrylate) was studied in the 23 to 100% concentration range, all in toluene. None of the polymers showed liquid crystallinity or even a tendency toward chain alignment, under the conditions leading to order in the mesogenic polyisocyanates. It is apparent that extended rigid backbones are necessary for mesomorphic behavior of the polyisocyanates besides the structural requirements characterizing the side groups. The rigidity and extension of such chains will be discussed below.

The polymerization of aromatic and aralkyl isocyanates in homo- and copolymers was very facile. In all cases, the molar ratios in the copolymers were essentially the same as in the feed. Conversely, attempts to homopolymerize cyclohexyl and methylcyclohexyl isocyanates (which should be number XIX in Table I) failed completely. When copolymerized with butyl isocyanate, the amount of butyl residues in the copolymers is much higher (81% in XXX and 77% in XXXI) than the 50% butyl isocyanate that was in the feed. In agreement with Shashoua et al.,[18] one concludes that the bulkiness of the cyclohexyl and methylcyclohexyl prevents their homopolymerization. When copolymerized with small comonomers, such as butyl isocyanate, each bulky monomer requires more than one small residue to be inserted in the polymer chain, apparently as "spacers" between the bulky residues.

It is well documented in the literature that poly(aryl isocyanates) possess relatively flexible[20-25] chain and an average Gaussian segmental distribution. The poly(alkyl isocyanates), on the other hand, are known to be endowed with very rigid and highly extended backbone.[26-33] We thought it would be of interest to determine whether the backbone chains of poly(aralkyl isocyanates) are flexible or rigid and extended. Because of the poor solubility of polymers such as XIII, XVI, and XVII in chloroform, the properties of the polymer XVIII were studied. The differential refractive index of a 1% solution of XVIII in chloroform as measured at 22 °C using light wavelength of 546 mμm was determined to be $\Delta n/\Delta c = 0.170$. The weight average molecular weight of one sample of XVIII was determined in chloroform by the light-scattering Zimm plot procedure to be $M_w = 27\,000$ and the radius of gyration, R_G, to be 190 Å. From a dissymmetry number of ~1.19 a chain end-to-end distance, h, of 650 Å was calculated. The degree of polymerization, N, of this polymer is 140 and the projection of each repeat unit along the contour direction, b, was calculated by Bur and Fetters[30] to be ~2.0 Å. Following Benoit et al.[34] the theoretical radius of gyration R_{GT} of a rigid rod macromolecule whose thickness is negligible relative to its length is

$$R_{GT}^2 = (Nb^2 + h^2)/12 \tag{1}$$

introducing the above numerical values for N, b, and h into the equation yields a R_{GT} value of 188 Å. From this, one obtains through

$$C_\infty = R_{GT}^2/Nb^2 \tag{2}$$

a characteristic ratio C_∞ of 63 for the polymer XVIII. We have no additional information about other molecular weight samples of polymer XVIII, but a $C_\infty = 63$ is of the same order of magnitude as poly(butyl isocyanate)[28,30] and poly(hexyl isocyanate).[26,27]

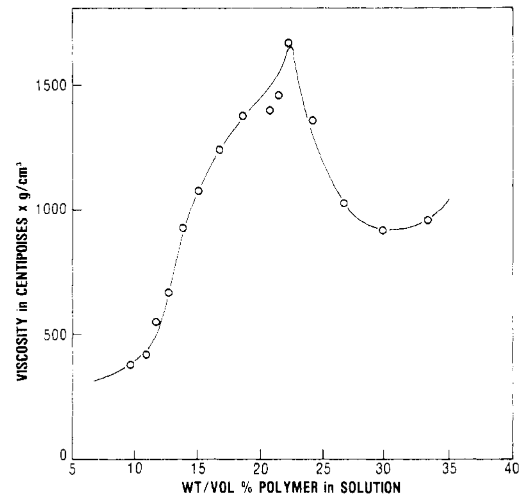

Figure 10. Viscosity of concentrated solutions of poly(hexyl isocyanate) (IV) in toluene at room temperature. The particular batch used here had a molecular weight of $M_w = 65\,000$. Measured with a Nametre viscometer.

Table II
Results of Thermal Studies on Polyisocyanates

	TGA, onset of dec, °C[a]	DTA-DSC obsd transitions, °C[a]
I	~50	sharp transition at −96
II	~70	T_m ~72
III	~150	T_g(?) −15; T_c 68; T_m ~185
IV	~180	T_c 65; T_m ~155
V	~180	T_g(?) −10; T_{c_1} 60; T_{c_2} 114; T_m 159
VI	ND	T_{c_1} 55; T_{c_2} 91
VII	~150, 2 distinct steps	T_c 68
VIII	~155, 2 steps	T_{c_1} 69; T_{c_2} 102; T_{m_1} 41
IX	~190	T_{c_s} 65; T_{c_2} 107; T_{m_1} 51
X	~180	T_{c_s} 38; T_{c_2} 105; T_{m_1} 62
XI	ND	T_c 104; T_{m_1} 54
XVIII	~195	T_g 2; T_c(W) 56
XXII	~170, 2 steps	T_g(?) −20; T_c 83
XXV	~125	T_g 24; T_{c_1} 58; T_{c_2} 71; T_m 125
XXVI	~185	T_g(?) −11; T_c 66; T_m 170
XXVIII	~195	T_g 4

[a] T_c(W) indicates a very weak transition. T_{c_s} indicates a shoulder. ND = not determined.

It has been demonstrated by Berger and Tidswell[26] that the intrinsic viscosity of poly(n-hexyl isocyanate) in various solvents, including Θ mixtures, is about constant, a strong indication of the inherent stiffness of the chains. We have repeated these measurements for one sample of polymer IV at 25 °C, obtaining $[\eta] = 2.6$ dL/g in toluene, $[\eta] = 2.2$ dL/g in chloroform, and $[\eta] = 2.38$ dL/g in a mixture of 19.5 vol/vol % methanol in toluene, a Θ mixture according to Berger and Tidswell.[26] Our results are in excellent agreement with theirs, indicating a $M_w = 65\,000$ for the studied sample. A study of the viscosity of this sample as a function of concentration, presented graphically in Figure 10, revealed a sharp drop in the viscosity of the toluene solution at concentrations higher than 23%. This change in the viscosity is in general agreement with the microscope observations of solutions of this sample. Here a 25% solution of IV in TCE at 25 °C was anisotropic essentially throughout its volume, while a solution of 15% concentration appeared as anisotropic islands floating in an isotropic liquid. Similar behavior was observed when the solvent was changed to bromoform.

The results of the thermal studies are presented in Table II. It should be noted that in many instances the onset of thermal decomposition corresponds to the upper melting point T_m. Also, many glass transition temperatures, T_g, were not observed, and some low-temperature transitions that were observed and are denoted by T_g(?) may not be true glass transition temperatures. Transitions above T_g and below T_m were denoted by T_c (or T_{c_1} and T_{c_2} when there were two of them). In Figure 11, three typical thermal scans are shown, of mesomorphic (VI), inter-

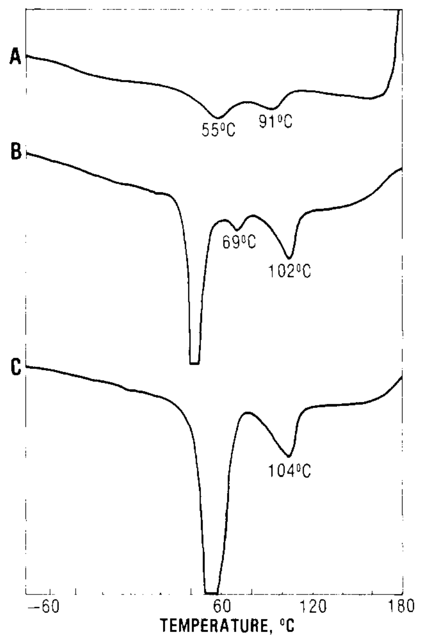

Figure 11. DTA scans of poly(alkyl isocyanates): (a) poly(nonylisocyanate), VI; (b) poly(undecyl isocyanate), VIII; and (c) poly(octadecyl isocyanate), XI. Polymer VI is mesogenic, VIII is at the borderline, and XI is nonmesogenic but with side-chain cocrystallization.

Table III
Carbonyl Stretching Band Position, (cm^{-1})

	solid state	conc soln	dil soln	liquid crystal formed
I	1675 + 2 weak	1680 + 2 weak	1685 + 1 weak	no
III	1700		1690–95	no
IV	1700		1700	yes
V	1695		1695	yes
VI	1695 + 2 weak	1695	1695	yes
VII	1695	1695	1695	yes
VIII	1685 + 1695	1690	1692	no
IX	1685 + 1695 + 1 weak	1690	1690	no
X	1687 + 1696	1686	1690	no
XI	1698		1685 (very dilute)	no
XII	1710 + 2 weak		1700	no
XIII	1700		1692 (very dilute)	no
XVI	1710	no solution data		no
XXI	1695	1695	1695	yes
XXII	1700		1718	no
XXVI	1700	1700	1700	yes
XXVIII	not obtained		1690	no
XXXI	1698 + 1 weak	1695	1695	no

mediate (VIII), and long side chain (XI) poly(alkyl isocyanates). The low decomposition temperatures in Table II are in a reasonable agreement with those recorded by Shashoua et al.[18] and by Bur and Fetters.[30] Several conformational transitions of poly(hexyl isocyanate) and poly(nonyl isocyanate) in dilute solutions were claimed.[35] As of now, we have insufficient data to correlate the transitions in the pure polymer with those in dilute solution.

The poor thermal stability of the polyisocyanates limited our hot-stage microscopy studies to only nine polymers. In perfect agreement with the results obtained from concentrated solutions, polymers IV, V, XXV, and XXVI behaved as liquid crystals over a narrow temperature interval below their melting point, T_m, while polymers III, XVI, XVIII, XXII, and XXIX melted at T_m without showing a mesomorphic phase below it. The quality of the photographs obtained with hot-stage experiments was far inferior to the quality of the photographs obtained from the solution microscopy. The observed morphological features were, nonetheless, about the same for the mesomorphic state of the pure polymer as in the highly concentrated solution.

Proton and carbon-13 NMR spectra were obtained from several polyisocyanate solutions. As is customary, concentrations of 10 wt/vol % or more were used. Polymers exhibiting no mesomorphic nature produced spectra completely normal with respect to the line width of either the protons in ^{1}H NMR or the carbons in ^{13}C NMR. Among such polymers one finds I, III, XVII, XVIII, and XXX. The spectra of the alkyl-aralkyl copolymers XXIV and XXVI were, however, different. In both instances, the two ^{1}H-NMR peaks of the two methylene groups adjacent to the backbone nitrogen, $>NCH_2CH_2-$, were remarkably broad, often showing a multiplicity of poorly resolved peaks. Integration of the areas under the peaks of the $BuCH_2CH_3$ and the aromatic protons gave the molar ratios given in Table I. The $>NCH_2CH_2-$ groups belonging to the very same aralkyl residue gave much smaller area under their integrated peaks. In the ^{13}C NMR each of these two $-CH_2-$ groups exhibits a very broad region with a multiplicity of unresolved peaks. The behavior of the two methylene groups adjacent to the nitrogen atom of XXIV and XXVI in both ^{1}H NMR and ^{13}C NMR seems to indicate that some sort of chain rigidity or molecular association is present in these polymers. This rigidity, or association, was manifested also in certain infrared characteristics to be described below.

Infrared spectra of polyisocyanates were obtained in a Fourier transform infrared instrument with a 1–2-cm^{-1} resolution. To obtain the desired signal-to-noise ratio, between 200 and 500 scans were obtained from each sample. Spectra were taken from solid samples (2% pulverized polymer in KBr matrix), concentrated solution in tetrachloroethane (20 wt/vol %), and dilute solution in TCE (2% polymer) when possible. Several samples were only slightly soluble, even at up to 75 °C, and the spectra were obtained from their saturated solutions.

The $C{=}O$ ($\sim$1700 cm^{-1}) stretching vibration was used in the analysis. This vibration is well separated from other bands in the infrared spectra of polyisocyanates. Because of the flat background obtainable, even in dilute TCE solutions, the subtraction capabilities of the FTIR spectrometer can provide quantitative analysis regarding band intensity, position, and shape. Even though the $C{=}O$ stretching vibration is a highly localized motion, it is coupled to the motions of the backbone, i.e., angle bending and C–N stretching, and can be sensitive to conformational changes in polyisocyanates. It has been shown, for example, that poly(*p*-tolyl isocyanate), XIV, exists as two rotational isomers, each having its own absorption band in the $C{=}O$ stretching region.[36] Our results on the $C{=}O$ stretching band position for polyisocyanates in the pure form and as a solution are presented in Table III. In Table

III the position of the intense C=O band (or bands) is recorded, while the existence of additional weak bands or shoulders is merely mentioned. The intense band in the neighborhood of 1700 cm^{-1} is similar to the C=O band in the corresponding cyclic timer (isocyanurates),[37] but the high solution viscosity of all the samples studied by infrared assures that the observed spectra belong to high molecular weight isocyanate polymers.

The most important observation in Table III is that the frequency of all the C=O stretching vibrations associated with polyisocyanates which exhibit mesomorphic behavior remained unchanged upon going from the solid through the concentrated solution to the dilute solution. On the other hand, all the samples known not to produce liquid crystals in solution showed a change in the frequency of the C=O stretching motion in going from solid to dilute solution. The magnitude of the shift for each polymer appears to be concentration dependent, but, as of now, we understand neither the fact that the frequency may increase or decrease upon dissolution nor the differences between one polymer and another in the size of the frequency change. The spectra of the solid VIII, IX, and X showed a strong doublet in the frequency range of interest, and only a singlet in solution. This may be due to interchain interaction or to the strong side-chain interaction, manifested by the lower melting point, T_{m_1}, of these polymers in Table II. In either case, the absence of such a doublet in poly(octadecyl isocyanate) (XI) is puzzling.

Even though much more work must be done in order to explain the whole spectra of the polyisocyanate family, in solid and solution, certain hypotheses may be put forth. Accordingly, alkyl and aralkyl polyisocyanates that show no mesomorphic behavior have a somewhat different conformational distribution in solution than in the solid state. The polyisocyanates exhibiting mesomorphic behavior maintain the same distribution in the solid and in solution. The reason for this may be that the backbone rigidity of these polymers is higher than that of the former group, or that these polymers, even in solution, are organized in "swarms" while in the former polymers the macromolecules are not associated in solution. Either of these tentative explanations results in the macromolecules of the mesogenic polyisocyanates being highly associated in the solid and the solution and as such maintaining their extension and stiffness.

The preliminary X-ray diffraction studies performed by us may be divided in two parts: studies on poly(alkyl isocyanates) and on poly(aryl or aralkyl isocyanates) and their copolymers with one another and with alkyl isocyanates. Polymers such as XII, XIV, and XV were found to be amorphous at room temperature and were not studied further. The poly(*p*-anisole-3-propyl isocyanate) (XVIII) and its copolymer with *p*-anisolemethyl isocyanate, polymer XXVIII, were amorphous for all practical purposes. The poly(*p*-anisolemethyl isocyanate) (XVI) showed, in addition to a broad, medium-intensity peak centered at about 4.69 Å, a strong and sharp peak at about 11.85 Å. The copolymer XXII showed essentially the same pattern. As is evidenced from the strong and sharp diffraction peak at low 2Θ angles, polymers XVI and XXII indicate a strong tendency toward some ordering, not necessarily mesogenic. The polymers showing liquid crystallinity, XXV and XXVI, showed a slightly higher tendency toward organization, as is evident from the appearance of two additional weak diffraction peaks in their X-ray patterns. As a rule, these additional peaks appear in the *d*-spacing interval between the broad medium peak in the neighborhood of 4.5 Å and the sharp intense peak which is always the largest *d* spacing for the polymer in question. Curve A in Figure 12, of poly(octyl isocyanate) to be discussed below, is typical. Polymer XXVI was successfully oriented while swollen with TCE. After fully drying, it still retained a substantial measure of orientation. Photographic films obtained by using a microcamera were scanned with a microdensitometer in the meridional and equatorial directions. The strong and sharp peak observed in polymer XXVI at $d \simeq 15.7$ Å ($2\Theta = 5.6°$) in an annealed and unoriented sample was observed in the equatorial scan of the oriented sample, but significantly weaker and broader. The medium peak at ~4.5 Å *d* spacing is of the (00*l*) type while the equatorial *d* spacing of ~15.7 Å spacing is associated with some lateral distance between chains. The sharpness and intensity of these peaks in the mesogenic and other tending to order polyisocyanates indicates that the interchain lateral distances are held very close to constancy, and that a large fraction of the polymer chains in the sample adhere to this lateral order. It is of interest to note that even though polymer XXVI forms liquid crystals and its X-ray pattern shows an intense and sharp peak at ~15.7 Å, for a sample of $\eta_{sp}/c = 8.1$ dL/g in 0.5% solution in TCE, the percent crystallinity (about 30%) did not increase at all after annealing for 18 h at 110 °C, significantly above the $T_c = 66$ °C determined by means of DTA.

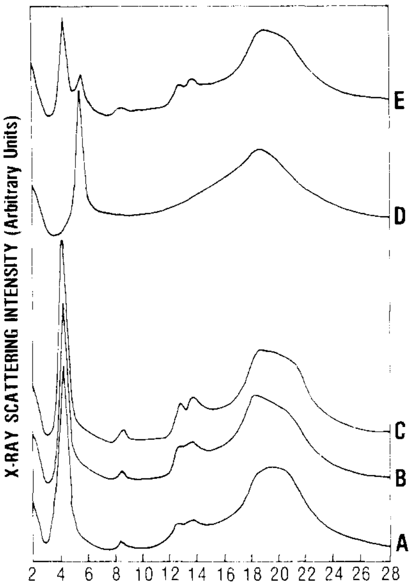

Figure 12. Diffraction patterns of a mesogenic poly(alkyl isocyanate), V: (a) at room temperature; (b) at 80 °C; (c) at 32 °C after cooling from 80 °C; (d) at 130 °C; and (e) at room temperature after cooling from 130 °C. After 48 h at room temperature, the structure was as in curve C.

A 30% solution of XXVI in TCE produced only a very broad X-ray diffraction peak centered at ~4.5 Å, again indicating that such a *d* spacing is, most likely, associated with some repeat along the chain direction. No additional *d* spacing was observed in the wide- or small-angle X-ray patterns.

The poly(alkyl isocyanates), a more detailed study of which will be published separately,[14] may be classified into two categories. One, of which Figure 12A of polymer V is typical, has an intense and sharp X-ray peak at low 2Θ, that is, at their largest *d* spacing. The other peaks are weak, broad, and superimposed on an amorphous background. Polymers belonging to this class are II, III, IV, V, VI, VIII, and IX. Polymer VII was not studied but, in light of its similar behavior to VI and VIII, this polymer also should fall in the same category. Polymer I exhibits

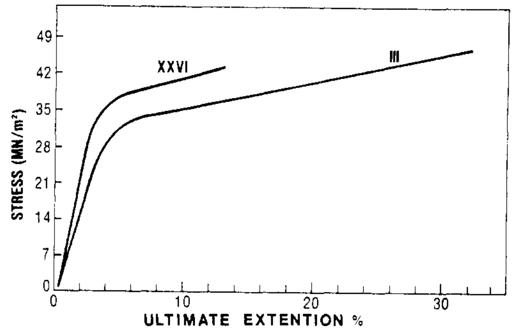

Figure 13. Stress–strain curves for mesogenic XXVI and nonmesogenic III polyisocyanates. Both polymers had a viscosity of η_{sp}/c = 8.1 dL/g at C = 0.5% in chloroform at room temperature.

a multitude (35) of sharp peaks in its X-ray pattern. We believe that because of its poor stability, the majority of these peaks may belong to the degradation product of the polymer, an isocyanate trimer. The second class of poly(alkyl isocyanates), including IX, X, and XI, are typified by an intense peak at about 4.2 Å, associated with a reduced intensity of the peak at the largest *d* spacing. Because these polymers also show a second, low-temperature, melting point, T_{m_1}, we believe that the intense peaks at ~4.2 Å reflect the fact that the long side chains in these polymers crystallize separately.

Preliminary results indicate that the largest *d* spacing of polymers belonging to the first category should correspond to twice the length of the side chain extended in a trans conformation. In the polymers belonging to the second category, this correlation fails and the largest *d* spacing is less than twice the extended side chain.

The polymers III, IV, V, XVI, XVIII, XXII, XXV, XXVI, and XXVIII were studied by X-rays at room temperature, at fixed elevated temperatures, and then again at room temperature. In all instances, the elevated temperature was intermediate between the highest transition temperature, T_c or T_{c_2}, and the polymer melting point, T_m. Except for polymer V, all polymers exhibited at the elevated temperature a slightly better definition of the X-ray pattern obtained initially at room temperature. Upon return to room temperature, the peaks that became better defined at elevated temperature remained so. Apparently, the effect of heat cycling on all these samples, mesogenic or not, was a mere minor increase in order.

Polymer V, poly(octyl isocyanate), of all the polyisocyanates studied, showed dramatic effects of heat cycling. In Table II, it is shown that polymer V has two transition temperatures, T_{c_1} at 60 °C and T_{c_2} at 114 °C, below a melting point of T_m = 159 °C. In Figure 12, curve A is the X-ray diffraction pattern of polymer V obtained at room temperature. Curve B was obtained at 80 °C, in between T_{c_1} and T_{c_2}. Curve C was obtained at 32 °C, after cooling from 80 °C. It is obvious that no significant changes take place in polymer V up to T_{c_2}. Curve D was obtained at 130 °C. Two major changes are evident, the largest *d* spacing decreased from 20.52 Å (2Θ = 4.3°) to 16.2 Å (2Θ = 5.45°) and all the peaks at larger 2Θ were replaced by an apparently amorphous very broad peak. Curve E in the figure was taken at 25 °C after cooling over a period of about 1 h from 130 °C. Here we find that the peak at 16.2 Å lost most of its intensity, and concomitantly, the intense peak at 20.52 Å reappeared. At the same time, all the peaks at higher 2Θ that were apparent at temperatures up to 80 °C reappeared. An additional scan of polymer V, taken 48 h after completion of the above temperature sequence, revealed that the peak at 16.2 Å disappeared completely and the sample regained its original structure, producing a scan exactly the same as scan C in Figure 12.

To the best of our knowledge, there are only two X-ray experimental studies on the structure of polyisocyanates in the solid state. One study, by Shmueli et al.,[38] deals with poly(butyl isocyanate) and another, by Clough,[39] deals with poly(*n*-hexyl isocyanate). Several theoretical papers,[40–43] nonetheless, differ about the chain conformation of the poly(alkyl isocyanate) family of polymers. We hope that our[14] forthcoming report on the X-ray studies of poly(alkyl isocyanates) will facilitate the resolution of these differences.

Only one study[19,44] devoted to the study of the mechanical properties of solid polyisocyanates is known to us. This study involved poly(butyl isocyanate), poly(ethyl isocyanate), several of their copolymers, and poly(hexyl isocyanate). The polymers appear to undergo uniform tensile deformation, and their stress–strain curves, all similar to each other, lack a yield point. Changes in percent crystallinity were not reflected in changes in the nature of the curves. It should be noted that the stress–strain curve for poly(ethyl isocyanate), which showed no mesogenic behavior or tendency toward alignment (conceivably because of poor solubility), was of the same shape as poly(hexyl isocyanate), a liquid crystal former.

Attempts were made, following the procedure of Haward et al.,[19,44] to cast films of several of our polyisocyantes and measure their stress–strain relationships. We have found that coherent films that could be handled without crumbling, and cut into dogbone-shaped samples, were obtained only from polymers whose η_{sp}/c was over 4.5 dL/g at C = 0.5% in TCE or $CHCl_3$. Films were prepared, through casting, from polymers III and XXVI whose η_{sp}/c in chloroform was 8.1 dL/g. Polymer III, poly(butyl isocyanate), was used to compare our results with those of Haward et al.[19,44] Polymer XXVI, a strongly mesogenic polymer, was chosen to compare the stress–strain curve obtained from a mesogenic polymer with that of a nonmesogenic or poorly mesogenic one. The results, obtained at room temperature, are shown in Figure 13. It is obvious that the nature of the stress–strain curve is about the same and is in perfect agreement with that of Haward et al.[19,44] Polymer XXVI is somewhat more rigid than III, as is evidenced from its higher modulus and smaller elongation at break. As these polymers have rather close T_g's and T_c's, straddling the test temperature, the reason for the difference between the polymers may be a difference in chain rigidity, molecular peaking, or entanglements, and not a particular dependence on the test temperature.

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Optically Active Polyelectrolytes with Variable Hydrophobicity. 3. Effects of pH-Induced Chromophore and Conformation Changes on Chiroptical Properties of Alternating Copolymers of Maleic Acid and Optically Active 1-Methylalkyl Vinyl Ethers

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ABSTRACT: Large modifications in ORD and CD spectra of three optically active maleic acid/alkyl vinyl ether alternating copolymers (MAc/R*VE with R* = (*S*)-1-methylpropyl, sample C4$_1$; R* = (*R*)-1-methylbutyl, sample C5$_1$; and R* = (*S*)-1-methylheptyl, sample C8$_1$) were found after adding an alkaline reagent to aqueous or methanolic solutions. When progressively ionized in water, these three polyelectrolytes show different conformational behaviors (respectively chain extension, compact coils-to-extended coils transition, and polysoap-like structure) depending on the length and, thus, on the hydrophobic character of etheral side-chain alkyl substituents. These differences of conformational behavior are not reflected in the observed pH-induced optical activity changes which primarily depend on chemical modifications of asymmetrically perturbed carboxyl chromophores and on consequent perturbations of the other chromophoric systems. The possibility for a folding of side chains on the polymeric backbone explaining the alkyl chain-length dependence of observed CD bands in water but not in methanol whatever the degree of neutralization is discussed.

In the field of optically active polymers, optical rotatory dispersion (ORD) and circular dichroism (CD) have been used mostly for structural studies.[1,2] They have provided us with a lot of relevant information on macromolecular conformations for helical biopolymers (poly(α-amino acids), polynucleotides, etc.)[3] and for some synthetic

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