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Communications to the Editor

Rigid-Backbone Polymers. 8. X-ray Studies of Poly(*n*-alkyl isocyanates)

The lyotropic[1-6] and thermotropic[1,7] liquid crystallinities of poly(*n*-alkyl isocyanates) and poly(*n*-alkyl + aralkyl isocyanates) are well-known at present. The ability to form anisotropic solutions and melts is related to the polymeric backbone rigidity[8,9] and extension.[1,10,11] There are, however, only two reports in the literature dealing with the determination of polyisocyanate crystal structures by means of X-ray diffraction procedures. In one report, Shmueli et al.[12] succeeded in elucidating the structure of poly(*n*-butyl isocyanate). A second report, by Clough,[13] gives only a few *d* spacings of poly(*n*-hexyl isocyanate). From our experience, we were led to believe that the scarcity of structural information may be due to poor single-crystal growing ability (including thermal degradation in hot solution) and to very poor drawability and orientability of cast fibers and films (specimens strain uniformly until failure and the fragments recoil back to the initial size and shape).

When the family of poly(*n*-alkyl isocyanates) is studied as a whole, then even X-ray powder patterns may yield valuable structural information. When viewed in light of information obtained by other techniques, the X-ray diffraction patterns may lead to understanding of the structure of poly(*n*-alkyl isocyanates) in the bulk. In this communication such data are presented for the first time and briefly discussed.

All polymers and necessary monomers were synthesized as described in detail in ref 1. X-ray diffraction patterns were obtained at 23 °C with a Norelco X-ray diffractometer in the rate mode and parafocus geometry (Cu Kα radiation). Each powdered sample was subjected to two scans, one with a 0.1-mm antiscatter slit, allowing the collection of data to start from an angle of $2\theta = 2°$, and the other with a 0.3-mm antiscatter slit, allowing the collection of data from $2\theta = 6°$. Except for minor changes in intensity at higher angles, the data collected in both modes were practically the same above $2\theta = 6°$. Therefore, only data collected with the 0.1-mm antiscatter slit are presented below. As will become obvious, a large volume of important information lies in the 2θ interval from 2 to 6°.

The X-ray diffraction patterns of 11 poly(*n*-alkyl isocyanates), starting at $2\theta = 2°$, are shown in Figure 1. Beyond $2\theta = 30°$ the patterns were devoid of any reflection of significant intensity or sharpness and were omitted from the figure. When the diffraction patterns are compared with each other, certain trends become apparent:

(a) The poly(*n*-alkyl isocyanates) are characterized by two major peaks. One peak, at about $2\theta = 20°$, is essentially fixed in position. The other major peak, at lower 2θ angles, changes its position with changes in *n*, the number of carbon atoms in the polymeric side chain.

(b) The area under the fixed major peak increases with *n*, probably reflecting the increased amount of scattering mass in the side chains. The fixed peak sharpens dramatically for poly(tridecyl, pentadecyl, and octadecyl isocyanates), indicating that side-chain crystallization had set in.

(c) Concomitantly with the sharpening of the fixed peak at $2\theta \cong 20°$, there appeared for the poly(tridecyl, pentadecyl, and (most probably) octadecyl isocyanates) a secondary peak in close proximity to the mobile peak at low 2θ angles. (The fact that only one low-angle peak was observed for poly(*n*-octadecyl isocyanate) is most likely because the other peak is too close to the incident X-ray beam to be detected by our equipment.)

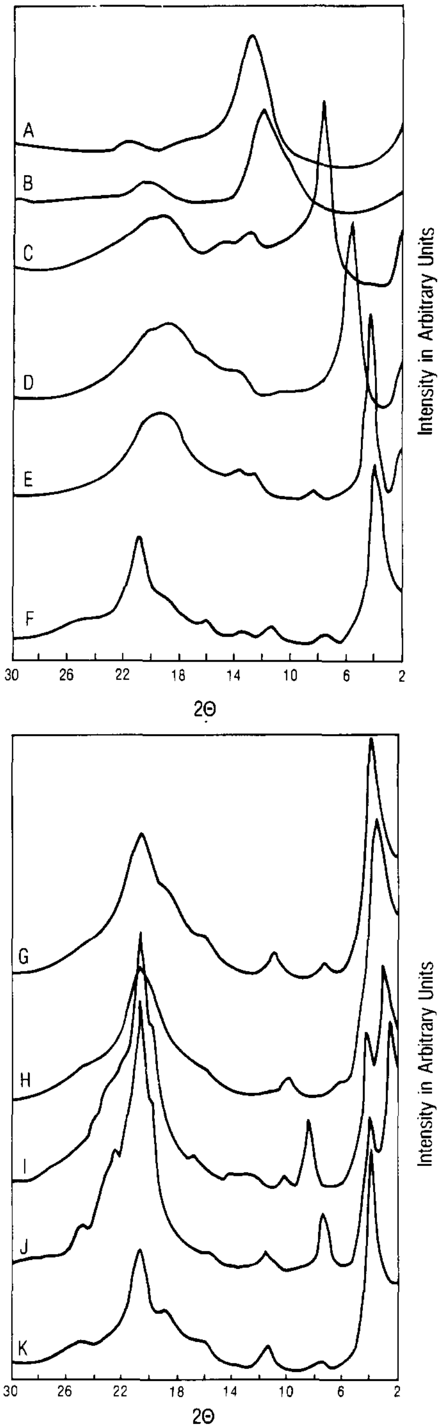

Figure 1. X-ray diffraction patterns of poly(*n*-alkyl isocyanates). *n*-Alkyl: (top) (A) ethyl, (B) *n*-propyl, (C) *n*-butyl, (D) *n*-hexyl, (E) *n*-octyl, (F) *n*-nonyl; (bottom) (G) 1-decenyl, (H) *n*-undecyl, (I) *n*-tridecyl, (J) *n*-pentadecyl, (K) *n*-octadecyl.

(d) There appear in the system several minor peaks in

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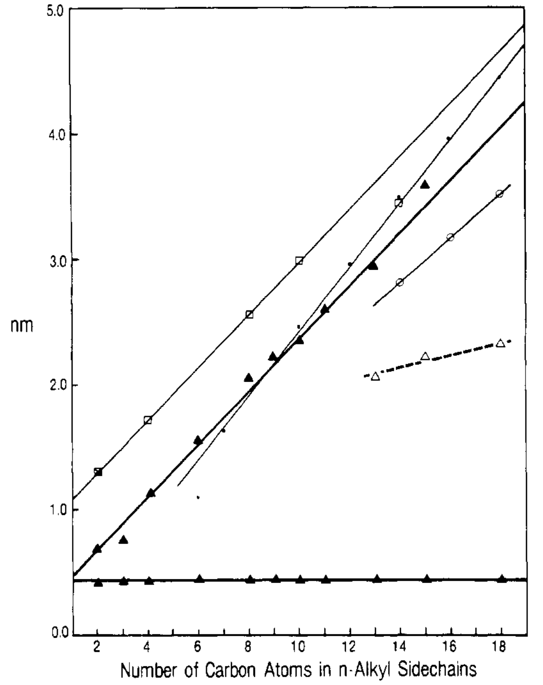

Figure 2. d spacings, in nm, plotted against the number of carbon atoms in n-alkyl side chains. Poly(n-alkyl isocyanates): (▲) main peaks; (△) secondary peaks. Isotactic polyolefins: (●) modification I crystals; (○) modification II crystals. N-Alkylmaleimides: (□) data from ref 15, (⊠) data from ref 16 (corrected).

the 2θ interval between the major peaks. The minor peaks are poorly resolved for polymers with side chains of $n < 13$. They become better resolved for $n \geq 13$, and one or two additional minor reflections appear at higher 2θ angles.

The positions of the two major peaks, and of the secondary peak for polyisocyanates with $n \geq 13$, are plotted in Figure 2 in terms of d spacings in nm. The major fixed peak is at about 0.44 ± 0.01 nm, and the major mobile peak changes its position linearly with n. The movement of the mobile peak indicates that it is somehow associated with the distances between parallel aligned polymeric backbone chains. This conclusion is in agreement with similar observations on other polymer families with long side chains. Among them one may mention isotactic polyolefins,[14] N-substituted polymaleimides,[15,16] poly(alkyl acrylates), poly(alkyl methacrylates), and poly(vinyl ethers).[17,18] In Figure 2, data of Turner Jones[14] on the crystalline modification I of isotactic polyolefins and of Balta-Calleja et al.[15] on polymaleimides are plotted for the purpose of illustration. The point of poly(ethylmaleimide) is a datum point of Cubbon[16] as corrected[15] by the Ehrenfest relation ($d = 1.25d_{\text{Bragg}}$). In the figure are shown three data points each for the secondary mobile peak of the polyisocyanates and a crystalline modification II of isotactic polyolefins.[14]

The distances associated with the major mobile peaks are far larger than the length of the fully extended side chains, the latter being 0.127 nm times n. This was repeatedly taken to indicate that the variable d spacings are somehow dependent on the length of two side chains.[14,17,18] Calculating on the basis of two side chains, the slope of the line describing the d spacings of the variable major peak yields increments of 0.1044 nm per carbon atom in the side chains of poly(n-alkyl isocyanates). This is very close to the increments of 0.1047 nm calculated by us for the polymaleimides. The increments for the amorphous form of isotactic polyolefins were calculated by Plate and Shibayev[18] to be 0.118 nm per carbon atom. For the crystalline modification I of the same polyolefins, the increments are 0.125 nm per carbon atom, and for the crystalline modification II, the increments are 0.090 nm. Because of the closeness of the increments of crystalline modification I to the 0.127 nm expected from the fully extended side chain, it was deduced[14] that in this modification the side chains are extended at right angles to the backbone chains and approach one another head-to-head. All other systems mentioned above have increments that do not lend themselves to such a side-chain arrangement. The small size of the increments led to the conclusion that the side chains are tilted at an angle other than 90° relative to the polymer backbone.[14] Since crystallinity is not apparent in polyisocyanates with $n < 13$, one may reach a tentative conclusion that the side chains in this polymeric family are also tilted relative to the backbone. Because in this study the variable d spacings of all the poly(n-alkyl isocyanates) fall on the same line, it appears that even in the cases of $n \geq 13$, where some side-chain crystallinity becomes apparent, the crystallizing side chains maintain the same angular tilt as the lower homologues.

The organization of the poly(n-alkyl isocyanates) side chains merits special consideration. As was repeatedly shown in the literature[14,17-21] for polymer families having long side chains, it is the fixed major peak at about $2\theta \cong 20°$ which is associated with the packing, and crystalline structure, of the side chains. For poly(n-alkyl isocyanates) with side chains of $n < 13$, it is important to notice that this peak (d = 0.44 ± 0.01 nm) is not accompanied by additional peaks at higher 2θ sufficiently intense to be observed. The absence of a peak corresponding to a d spacing of about 0.375 nm precludes the possibility of the side chains packing in the orthorhombic form of polyethylene and long-chain hydrocarbons.[14,19-22] This is because the reflection at 0.375 nm is one of the two strongest reflections in the diffraction pattern of orthorhombic polyethylene and paraffins.[14,19-21] The absence of reflections of significance at 2θ angles higher than that of the major fixed peak may indicate that the side chains are not frozen in position and possess a significant level of rotational freedom.[18] In fact, our NMR data[8] clearly show a remarkable degree of side-chain mobility in the bulk polyisocyanates starting from the CH_2 group second from the backbone. The ability of the poly(n-alkyl isocyanates) with side chains of $4 \leq n \leq 12$ to form liquid crystals in solution[1-6] and in the bulk[1,7] and the small thermal transitions associated with the side chains[1] both indicate a low level of side-chain order. Another possible explanation of the side-chain disorder at $n < 13$ hinges on the fact that the polyisocyanate backbone for the n-butyl[12] and n-hexyl[13] homologues is helical in nature. This helicity is expected to hold true for homologues of $n > 6$. Close to the main chain, the side chains must necessarily deviate from the planar zigzag configuration commonly adopted by long-chain n-alkanes[14] and bend round to approach the helical backbone. Thus, side chains of $n < 13$ are too close to the backbone and too short to organize themselves in crystalline order.

Poly(n-alkyl isocyanates) with side chains of $n \geq 13$ show a dramatic sharpening of the peak at d = 0.44 ± 0.01 nm, indicating that side-chain crystallization set in. This crystallization need not necessarily encompass the whole length of the side chains. The side-chain crystallization resulted in the loss of mesomorphicity for these polymers[1,7] and caused a dramatic increase in the magnitude of the thermal transition associated with the side chains.[1] In this case, it is obvious that this transition is the melting of the crystallized side-chain crystallites. For side chains of $n \geq 13$, the absence of a substantial peak in the X-ray patterns corresponding to $d = 0.375$ nm indicates that they did not pack in an orthorhombic polyethylene fashion[14,19–22] but may resemble more closely the packing of the triclinic form[14,23] of polyethylene or the monoclinic form[20,21] of paraffins. At present we have insufficient information to make a decision on the possible resemblance to the triclinic or monoclinic forms of polyethylene and paraffins, the powder patterns of these forms being so similar to one another. The absence of measurable sharp reflections beyond the 0.4-nm region suggests[14] that the side chains are only packed regularly locally, and the regularity extends over limited lengths of the backbone, even though the backbones are well aligned to produce the sharp large-spacing, mobile peaks. This is, of course, in agreement with the suggestion that only parts (most likely, the remotest from the backbone) of the side chains are involved in side-chain crystallinity.

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Halato-Telechelic Polymers. 1. Gel Formation and Its Dependence on the Ionic Content

In the early 1960s, the du Pont de Nemours Co. commercialized the first ionomer material under the trade name Surlyn.[1] From that time, scientists have shown increasing interest in the behavior of this type on ion-containing polymer which consists of a lipophilic polymeric backbone carrying randomly distributed pendant ionic groups.[2–4] Ionomers are mainly characterized in bulk.[5–14] However, Joanny has theoretically studied the expected phase diagram of ionomers dissolved in a nonpolar solvent. Two phase transitions are expected: gelation and demixing.[15] In nonpolar solvents indeed, the ionic groups (usually carboxylate or sulfonate) are not dissociated but form electric dipoles, the attractive interaction of which can lead to their aggregation, i.e., gelation, and ultimately to the demixing of the system. The gelation was expected to vary inversely with the fraction of ionic groups along the chain.[15] Experimental data were therefore needed to give further insight into the behavior of ion-containing polymers in nonpolar solvents.

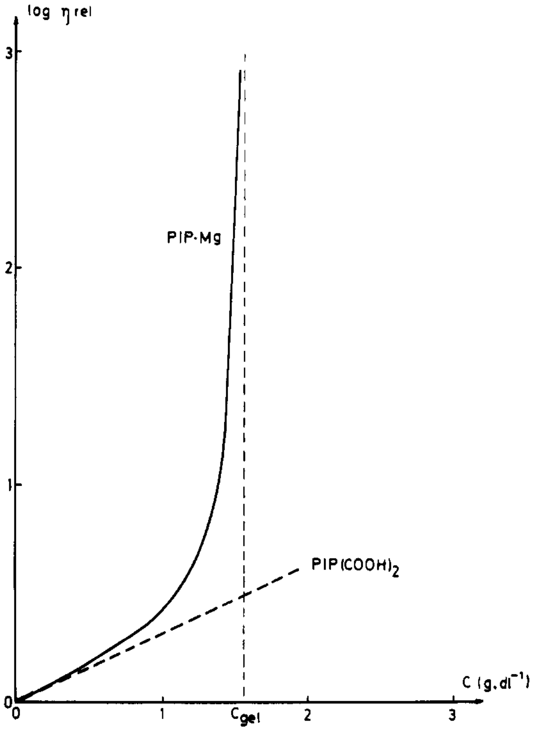
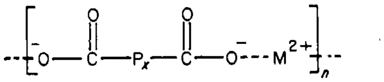


Figure 1. Relative viscosity (log scale) vs. concentration for carboxy-telechelic-PIP ($\bar{M}_n = 7 \times 10^4$) (- - -) and the same stoichiometrically neutralized with Mg^{2+} (—).

For this purpose, we have explored the synthesis of model-ionic polymers and, more especially, of halato-telechelic polymers (HTP). They are obtained from the complete neutralization of carboxy-telechelic polymers by alkaline-earth cations[16] and have the general formula



$$\cdots\left[\overset{-}{O}-\overset{\overset{\displaystyle O}{\|}}{C}-P_x-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{O}\cdots M^{2+}\right]_n\cdots$$

The distribution of the ionic groups within the chain can largely be controlled by the length and the polydispersity of the prepolymer P_x. Previously, Otocka et al.[17] and Pineri et al.[18] were interested in similar materials, and aliphatic and aromatic dicarboxylic acid salts with a number of divalent cations have also been investigated.[19]

In the present work, carboxy-telechelic-polyisoprenes (PIP) with a good functionality (>1.95) and a low polydispersity ($\bar{M}_w/\bar{M}_n < 1.15$) were prepared anionically. The carboxylic acid end groups were neutralized in dry toluene by addition of a stoichiometric amount of magnesium methoxide. The methanol formed was completely displaced by azeotropic distillation of toluene under reduced pressure to ensure quantitative neutralization.

At high dilution in toluene, the magnesium α,ω-dicarboxylato-PIPs (denoted PIP-Mg) form homogeneous

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