The Chain Structure, Polymerization, and Conformation of Polyisocyanates

A. J. BUR[†] and L. J. FETTERS*

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, and the Institute of Polymer Science, The University of Akron, Akron, Ohio 44325

Received May 28, 1975 (Revised Manuscript Received September 29, 1975)

Contents

- I. Introduction 727
- II. Chain Structure of Polyisocyanates Prepared from Monoisocyanates 727
- III. Polymerization of Monoisocyanates 729
- IV. Polymerization of Diisocyanates 731
- V. Copolymerization of Monoisocyanates 732
- VI. Physical Properties of Poly(*n*-alkyl isocyanates) 735
  - A. Qualitative Information from Unfractionated Samples 735
  - B. Quantitative Data from Dielectric and Intrinsic Viscosity Measurements on Fractionated Samples 735
    - 1. Dielectric Measurements 735
    - 2. Intrinsic Viscosity Measurements 738
  - C. Light-Scattering Measurements 739
  - D. Solvent Effects 740
  - E. Electric Dichroism in PBIC Solutions 741
  - F. Molecular Configuration and Conformational Energy Calculations 742
  - G. Solid-State Properties 743
- VII. Appendix 744
- VIII. Addendum 745
- IX. References 745

I. Introduction

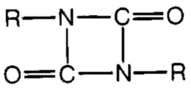
Since the original preparation of high molecular weight polyisocyanates in 1959, attention has been paid to their preparation, copolymerization behavior, and chemical structure. However, the stiff-chain molecular posture of the poly(*n*-alkyl isocyanates) in dilute solution has been the topic which has elicited the most attention in recent years. It is this feature which has been the object of measurement in many experiments. These measurements have examined both the dilute solution equilibrium and hydrodynamic properties of these polymers. All of these measurements, i.e., osmometry, light scattering, dielectric, electric dichroism, electric birefringence, rotatory diffusion, and intrinsic viscosity, have clearly demonstrated the rigid-rod conformation possessed by the poly(*n*-alkyl isocyanates).

However, the quantitative conclusions of these experiments, particularly the persistence length (q) and the projected intermonomer distance (L_0), are not in agreement. Experimental values of q range from 370 to 1000 Å, while values of L_0 range from 0.3 to 2.7 Å with the majority of these values found between 1.1 and 2.4 Å.

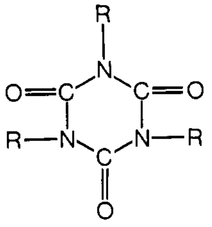
It is our intention in this review to discuss in a critical fashion the reasons behind the disparate values for these two parameters. In addition to the topic of the conformational behavior of the poly(*n*-alkyl isocyanates) in solution, we will also discuss the work dealing with the methods of polymerization and the chemical and crystalline structure of these polyisocyanates

II. Chain Structure of Polyisocyanates Prepared from Monoisocyanates

The polymerization of the monoisocyanates (RNCO) to high molecular weight polymer via an anionic addition mechanism was first reported by Shashoua, Sweeny, and Tietz.[1,2] Using dimethylformamide as the solvent and sodium cyanide as the initiator, a variety of monoisocyanates having either aliphatic or aromatic side groups were converted to high molecular weight "1-nylons". These polymerizations were carried out between −40 and −100 °C because of the known[3-9] ambient-temperature base catalyzed formation of the 1,3-disubstituted uretidinediones (**1**) and the 1,3,5-trisubstituted isocyanurates (**2**). It was also noted[2] that free radical and cationic initiators failed to generate high polymer. Also, the trialkylphosphines and -amines which promote dimer and trimer formation at ambient temperature do not initiate the formation of high polymer at low temperatures.

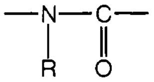


1



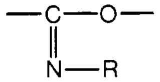
2

The potential exists in the anionic polymerization of the monoisocyanates for propagation to occur through the nitrogen–carbon or carbon–oxygen double bonds to yield either an amide structure (**3**) or an acetal structure (**4**). Enchainment of both structures would, of course, yield a "copolymer" containing both the amide and acetal units.



$-\underset{R}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-$

3



$-\underset{N-R}{\underset{\|}{C}}-O-$

4

The reported[1,2,10-12] infrared data show a strong absorption band at about 1700 cm^{-1} corresponding to the carbonyl group and a band from 1280 to 1390 cm^{-1} corresponding to the disubstituted amide structure. These data include observations made on polyisocyanates prepared from different anionic initiators in polar or nonpolar solvents. A representative infrared spectrum is given in Figure 1.

The infrared band at about 1700 cm^{-1} is strong evidence for the amidic structure but does not exclude its coexistence with structure **4**, particularly with the latter in minor proportions. The C═N group, such as in the ketimines, $R_2C{=}NH$, or in the gua-

---

[†] National Bureau of Standards.

* Author to whom correspondence should be addressed at the University of Akron.

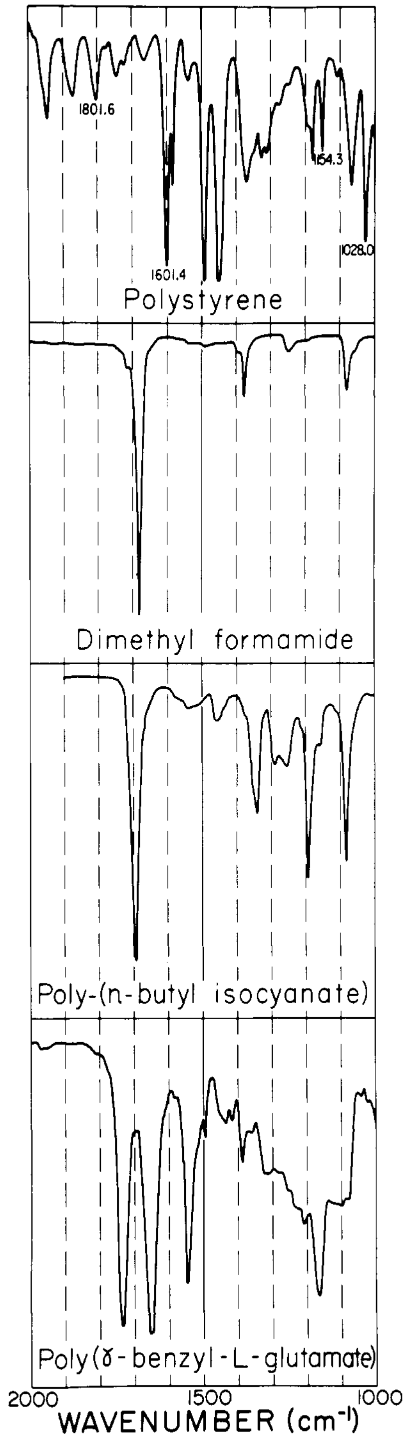
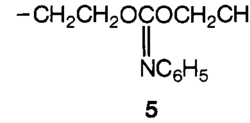


Figure 1. The infrared spectra of dimethylformamide, poly(*n*-butyl isocyanate and poly(γ-benzyl-L-glutamate) with the spectrum of polystyrene as the reference between 1000 and 2000 wave numbers.[12]

nidine derivatives, $(RHN)_2C{=}NH$, absorbs[13-15] in the region of 1680 to 1600 cm^{-1}, which is quite close to the carbonyl band. This has been demonstrated by the work of Furukawa and coworkers[16-18] who prepared alternating copolymers (via cationic initiation) of aromatic isocyanates and ethylene oxide. Chemical degradation demonstrated the presence of acetalic structures such as

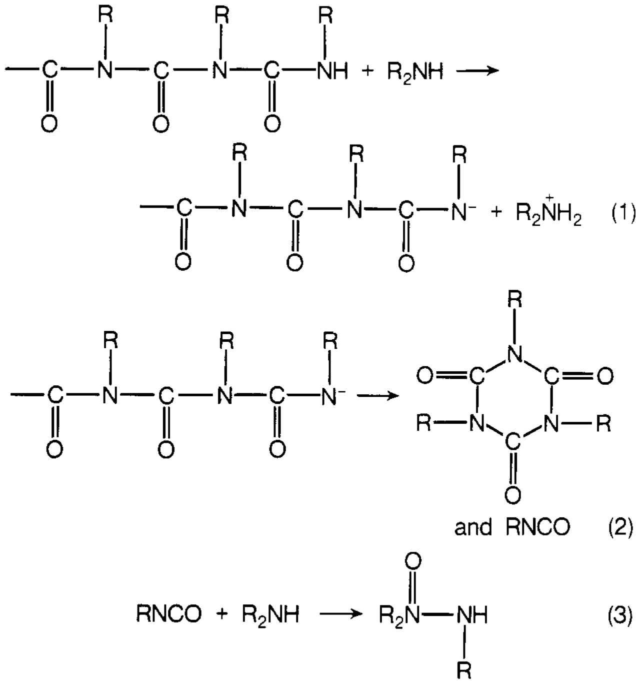


$$-CH_2CH_2O\underset{\underset{NC_6H_5}{\|}}{C}OCH_2CH_2O-$$

5

which is analogous to the acetal structure **4** for the homopolymer. The infrared spectrum of structure **5** showed strong absorption bands at 1760 and 1710 cm^{-1}. Hence, it is not possible to exclude entirely, on the basis of infrared spectra alone, the presence of some acetalic structure in the polyisocyanates synthesized from monoisocyanate monomers.

Evidence of a chemical nature for the chain structure of the polyisocyanates has been obtained from degradation studies. Iwakura, Uno, and Kobayashi[11] degraded various polyisocyanates in dimethylformamide with a catalytic amount of di-*n*-butylamine. Viscosity measurements demonstrated that the degradation step involved an unzipping of the polymer chain rather than random-chain cleavage; i.e., the viscosity values did not change with the degree of degradation. The products of these reactions, for two aliphatic and four aromatic polyisocyanates, were found to be monomer and the symmetric trimer (isocyanurate). There were no asymmetric trimers nor any symmetric trimers formed possessing the imino acetal structure. The following speculative reaction scheme was proposed[11] to account for these observations.



As can be seen the degradation reaction is initiated by proton abstraction at the chain end (eq 1). The formation of the cyclic trimer is visualized as occurring via intramolecular anionic attack on the third carbonyl group down the chain. Monomer formation is thought to be a competitive step and apparently takes place by an unzipping reaction. The reaction between the amine and monomer results in the formation of a urea. The cyclic trimer was also formed[2] when poly(*n*-hexyl isocyanate) was allowed to stand at room temperature in the presence of sodium cyanide. The formation of the trimer demonstrates that the trimer is thermodynamically more stable than the monomer.

It was observed that aromatic polyisocyanates tend to depolymerize more readily under the influence of bases than do the poly(alkyl isocyanates), again yielding products with intact carbonyl groups. Generally, it would be anticipated that this degradation reaction would be aided by electron-withdrawing substituents in the ring and retarded by electron-releasing groups. This general trend has been observed.[11]

With the combination of spectroscopic and chemical evidence, it can be concluded that anionic polymerization initiators produce, independent of counterion identity and solvent type, polyisocyanates with the disubstituted amidic chain structure **3**. This, however, does not rule out the possibility of the presence of a trace amount of the acetalic structure **4** in these polyisocyanates.

III. Polymerization of Monoisocyanates

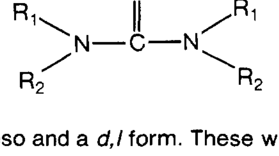
Natta, DiPietro, and Cambini[10] were the first to successfully polymerize *n*-butyl and phenyl isocyanate by ethyllithium initiation in a nonpolar solvent, viz., toluene. Parallel to Shashoua's[1,2] results, the infrared spectrum of their polymer had an intense band at 1700 cm^{-1} which was attributed to the carbonyl group of the disubstituted amide. Through cationic initiation, e.g., $AlBr_3$ amorphous, and apparently low molecular weight, poly(phenyl isocyanate) was prepared. However, *n*-butyl isocyanate failed to respond to this initiator.

X-ray measurements[10] revealed that the poly(*n*-butyl isocyanate) prepared in toluene had a far higher crystalline content than did a similar polymer prepared in dimethylformamide. This apparent difference in crystallinity was taken to suggest that configurational differences were present such as that between the cis and trans arrangements or that an increased amount of the acetalic structure was present in the poly(*n*-butyl isocyanate) prepared in dimethylformamide. Later work, however, convincingly demonstrated[19] that Natta's[10] results were the product of differences in the post-polymerization treatment (reprecipitation, annealing, and aging) of the poly(*n*-butyl isocyanate). These results demonstrate that the identity of the counterion and solvent do not affect the structure and crystallinity of the polyisocyanates.

Vinyl isocyanate[20] was polymerized at about −55 °C by using sodium cyanide as an initiator in dimethylformamide and dimethylacetamide. Vinylmagnesium chloride in tetrahydrofuran has also been used[21,22] to polymerize vinyl isocyanate at low temperature. Infrared analysis[20] of the poly(vinyl isocyanate) revealed a strong absorption corresponding to the carbonyl group. At room temperature, vinyl isocyanate was found[20,23] to spontaneously polymerize through the vinyl group to generate insoluble polymer. Infrared measurements indicated that the isocyanate groups did not participate to any detectable extent in this polymerization.

Transition metal compounds have been used[24] with limited success to initiate the polymerization of the monoisocyanates in toluene. Phenyl, ethyl, and *n*-butyl isocyanates were polymerized, and to a larger extent trimerized, by diethyldipyridylnickel, bis(dipyridyl)nickel, and tetrakis(triphenylphosphine) nickel. The reactions were initiated at −45 °C but were allowed to warm to room temperature where the reaction was allowed to progress for 8 h. Hence, it is not surprising that trimer was the favored product.

The γ-radiation-induced polymerization of methyl, *n*-butyl, and phenyl isocyanate has been reported[25] to occur at 20, −78, and −196 °C. The polymerizations were carried out in bulk and in dimethylformamide. The infrared spectrum of poly(*n*-butyl isocyanate) prepared in bulk (temperature not given) was identical with that found by others.[1,2,10-12] However, the spectrum of the poly(*n*-butyl isocyanate) prepared in solution (temperature not given), while still showing the carbonyl absorption band, was markedly different in the region of 1520 to 695 cm^{-1}. The authors[25] did not interpret the differences in the spectrum, which they attributed to differences in stereoregularity. The term stereoregularity would only be meaningful if it could be shown that compounds of the type



can exist in a meso and a *d,l* form. These workers most likely were observing the spectrum of the dimer and trimer of *n*-butyl isocyanate along with the polymer. The possibility also exists that their spectrum was, in part, influenced by residual dimethylformamide. It is known[26] that dimethylformamide will form a strong 1:1 complex with triaryl isocyanurates.

A reassessment of the paper by Sobue and coworkers[25] has recently appeared.[27] In this work it was found that the polymerization of *n*-butyl isocyanate does not occur to any significant extent (maximum yield 0.4 wt %) at −78, −131, −158, and −196 °C under irradiation. However, polymerization was found to take place during warming of the supercooled monomer to room temperature. The nature of the active species in this "post irradiation" polymerization was not identified.

Crystalline poly(phenyl isocyanate) was claimed[28,29] to have been obtained by electrochemical initiation in the presence of tetrabutylammonium iodide at −58 °C in dimethylformamide and a 1:3 dioxane–dimethylformamide mixture. The polymerization of the phenyl isocyanate is reported to take place by initiation and orientation at the cathode surface. Polymer was found to form in the zone of the cathode only. The yield of polymer increased with monomer concentration, a decrease in temperature, and a decrease in current density. However, no detailed mechanism was proposed for this polymerization system. Polymer was obtained which exhibited an infrared spectrum in accord with that seen by others;[1,2,10-12] i.e., the polymerization proceeds through the nitrogen–carbon double bond. This electrochemical polymerization system was also reported to lead to the formation of linear polymers from 2,4-toluene diisocyanate and 1,6-hexamethylene diisocyanate.

The first optically active polyisocyanate was synthesized by Goodman and Chen.[30] Using the polymerization procedures of Shashoua, Sweeny, and Teitz,[2] they successfully synthesized optically active poly(*d*-β-phenylpropyl isocyanate). The poly(*d*-β-phenylpropyl isocyanate) polymerization initiated by sodium cyanide showed $[\alpha]^{25}\mathrm{D}$ −468.8°, $[\mathrm{M}]^{25}\mathrm{D}$ −754.8° (*c* 0.333, $CHCl_3$); the polymer synthesized from the *dl* monomer initiated by sodium *l*-borneolate showed $[\alpha]^{25}\mathrm{D}$ +18°, $[\mathrm{M}]^{25}\mathrm{D}$ +29° (*c* 1, $CHCl_3$), while polymer prepared from *dl* monomer initiated by potassium *l*-mentholate showed $[\alpha]^{25}\mathrm{D}$ +60°, $[\mathrm{M}]^{25}\mathrm{D}$ +96.6° (*c* 1, $CHCl_3$). The optically active polymer was insoluble in most organic solvents although chloroform was an exception. The ability of chloroform to dissolve this polyisocyanate was ascribed to a specific interaction between this solvent and the urea-like nature of the polymer backbone, i.e., where chloroform interacts with a unit of two carbonyls and the nitrogen, which, of course, is the electron-rich center.

The polymer was found to have a negative optical rotation, opposite in sign and of greater magnitude than that of the monomer and the model compound, *d*-*N*,*N*-diacetyl-β-phenylpropylamine. The nuclear magnetic resonance spectrum of the racemic polymer showed broad absorption bands while the spectrum of the optically active polymer had sharp peaks. These results, taken in concert with the enhanced optical activity, were interpreted as indicating that the optically active polymer possesses a preferred conformation.

Circular dichroism spectra of the optically active polymer in chloroform and sulfuric acid led to the conclusion that this polyisocyanate exists in the acid in an extended form similar to a polyelectrolyte. It should be pointed out that it was shown some time ago[2] that strong acids will *rapidly* degrade poly(alkyl isocyanates). Hence, Goodman and Chen[30] were in reality viewing the molar ellipticity of degraded material. Furthermore, it has been shown[31-33] that weak acids, while not promoting poly(alkyl isocyanate) degradation, cause a change in chain conformation from the rodlike to coillike conformation.

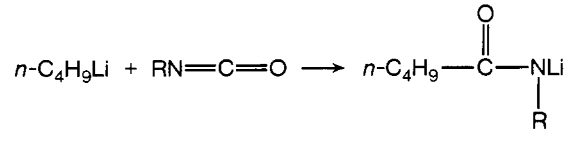
Optically active poly[(*S*)-(+)-2-methylbutyl isocyanate] was synthesized[32] via sodium cyanide initiation. This polymer exhibited $[\alpha]^{25}\mathrm{D}$ +160°, $[\mathrm{M}]^{25}\mathrm{D}$ +180.8° (*c* 0.005, $CHCl_3$). Unfortunately, Goodman and Chen[30] in their characterization of this poly(alkyl isocyanate) again relied on nuclear magnetic resonance spectra and circular dichroism spectra obtained, in part, from sulfuric acid solutions of both the racemic and optically active polymer. In view of the previously mentioned and long-recognized propensity of polyisocyanates to degrade in the presence of strong acids, doubts regarding the interpretation of some of their results must be expressed.

Minami and coworkers[35] have used the sodium derivatives of diethyl ethylmalonate, ethyl ethylacetoacetonate, and ethyl acetylacetone as initiators of phenyl and *n*-butyl isocyanate in toluene and dimethylformamide at −50 and −75 °C. It was claimed that initiation efficiency increased as the degree of enolization decreased. However, the polymers synthesized were not characterized (no molecular weight data), and studies of the actual mechanism and rates of initiation were absent. Hence, it would seem premature to attempt to classify the above-mentioned initiators in order of their "efficiency".

The monoisocyanate monomer structure has a pronounced influence on whether or not polymerization can occur. The most general statement that can be made is that substitution at the carbon atom in the α position, relative to the isocyanate group, will inhibit polymerization. Thus, *n*-butyl isocyanate[2] will readily polymerize while *sec*-butyl isocyanate will not.[36] Furthermore, vinyl isocyanate[20-22] will polymerize while isopropyl[2] and isopropenyl[37] isocyanate fail to do so. In the aromatic series, *o*-methoxyphenyl and α-naphthyl isocyanate fail to polymerize[2] while β-phenylvinyl isocyanate does.[38] Hence, for the aromatic series, substitution ortho to the isocyanate group inhibits polymerization. This conclusion is further substantiated by the fact that one can prepare via the anionic mechanism gel-free and virtually linear polymers through the selective polymerization of the unhindered isocyanate group in 2,4-toluene diisocyanate,[2] 3-(α-isocyanatoethyl)phenyl isocyanate,[2] and 1-methyl-2,4-diisocyanatocyclohexane.[38] It appears that for both the aliphatic and aromatic isocyanates these effects are steric and not electronic in nature.

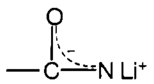
Through the use of (ethyl mercaptan)lithium[36] or *n*-butyllithium initiators[12,39] with a dilute monomer solution (ca. 5% w/v) in toluene at polymerization temperatures of −40 to −20 °C, poly(*n*-butyl isocyanate) has been synthesized possessing molecular weight distributions which are moderately narrow: $\langle M_w \rangle / \langle M_n \rangle \simeq 1.1$. Fractionation of these samples has demonstrated[36,39] that these poly(*n*-butyl isocyanates) do possess near-monodisperse molecular weight distributions. Hence, the implication of these results is that the use of the lithium counterion for the polymerization of the *n*-alkyl isocyanates yields a termination-free system. Thus, it would appear that control over the molecular weight distribution and molecular weight of a poly(*n*-alkyl isocyanate) is feasible via the use of the aforementioned polymerization system.

The direct attack of a monofunctional organometallic species, such as an organolithium, on the nitrogen–carbon double bond, i.e.,



$$n\text{-}C_4H_9Li + RN{=}C{=}O \longrightarrow n\text{-}C_4H_9{-}C({=}O){-}N(R)Li \quad (4)$$

probably represents the initiation reaction in the polymerization of these isocyanates. This is in accord with Sashoua's[2] observation that the polymerization reaction would be expected to proceed with attack by the nucleophile yielding the nitrogen anion since this is analogous to the reaction of nucleophilic reagents such as alcohol or water with the isocyanates. Thus, the propagation step would be expected to involve the nitrogen anion with, perhaps, the participation of the "hybrid ion"



This latter species has been invoked in the cyclopolymerization of the diisocyanates.[40,41]

It has been reported by Overberger and Moore[42] that Yu et al.[43] claimed that the carbonyl anion was the preferred anion in the propagation step. A perusal of the paper in question[43] reveals though that no such claim was made concerning which anion was the preferred one at the tip of the growing chain.

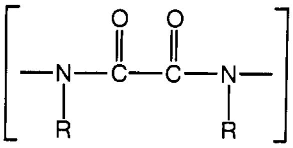
Initiation via the use of an electron transfer initiator, e.g., sodium naphthalene, can take place via two possible routes, to wit:

(a) The formation of an isocyanate ion-radical followed by coupling to yield a difunctional chain. In this case the naphthalene is regenerated. This mechanism is the one found for the electron transfer initiation of styrene.[44]

(b) The reaction of sodium naphthalene directly with an isocyanate monomer unit to yield first a monofunctional species. This reaction is then repeated with the subsequent creation of a difunctional carbanionic chain. This reaction where the naphthalene moiety is incorporated into the polymer chain is identical with the mechanism observed when ethylene oxide[45] or the cyclic siloxanes[46] are initiated via sodium naphthalene.

To date, the question as to which of the above initiation reactions exists in the electron transfer initiation of the monoisocyanate monomers remains unresolved.

The use of an electron transfer initiator for the synthesis of polyisocyanates is not recommended for samples used in conformational studies. This is a result of the possibility that the initiation step will "build in" a flexible or semiflexible bond, e.g., the carbon–carbon bond in the

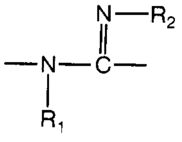


$$\left[{-}N(R){-}C({=}O){-}C({=}O){-}N(R){-} \right]$$

unit. In addition to interrupting the rigidity of the polyisocyanate chain, such a site could also serve as a point where helix reversal could occur. Hence, elucidation of the mechanism of isocyanate initiation via electron transfer initiators in conjunction with a study of the conformational behavior of the polyisocyanates so synthesized is needed. Only then will it be known whether or not electron transfer initiation can yield a polyisocyanate chain with an inherent rigidity equal to that thus far found in chains synthesized via monofunctional initiators, e.g., butyllithium.

The degradation temperature of the poly(*n*-alkyl isocyanates) where the alkyl group was *n*-hexyl or *n*-butyl was estimated[2] to be 138 °C. Thermal gravimetric measurements made under vacuum on poly(*n*-butyl isocyanate) and poly(*n*-hexyl isocyanate) have shown[47] that these polymers undergo rapid degradation commencing at a temperature of 140 °C. These results clearly indicate that the poly(*n*-alkyl isocyanates) possess low thermal stability. Additional data connected with the thermal stability of the poly(*n*-alkyl isocyanates) will be presented later.

The polymerization of the carbon–nitrogen double bond has not been limited to the isocyanate monomers. Carbodiimides such as the diethyl, di-*n*-butyl, di-*n*-hexyl, diphenyl, diallyl, and methylisopropyl forms have been polymerized[48] at 25 °C in toluene or dimethylformamide with *n*-butyllithium. The infrared spectrum of the polymers showed a carbon–nitrogen double bond stretch at 1640 cm^{-1} and a doublet due to the nitrogen in the polymer backbone near 1360 and 1250 cm^{-1}. Hence, the polymer structure was presumed to be



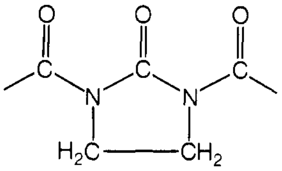
$${-}N(R_1){-}C({=}N{-}R_2){-}$$

6

It was also noted that when nitrogen is attached to a primary aliphatic group polymerization occurs readily while attachment to a secondary carbon prevents polymerization. This behavior is identical with that observed in the polymerizations of the isocyanates.

IV. Polymerization of Diisocyanates

In addition to the monoisocyanates, a variety of α,ω-polymethylene diisocyanates and *cis*-1,3-diisocyanatocyclohexane have been successfully polymerized by sodium cyanide in dimethylformamide to yield soluble material. King[49] was the first to demonstrate that ethylene diisocyanate, 1,2-propylene diisocyanate, 1,2-cyclohexylene diisocyanate, and glyceryl triisocyanate underwent a cyclopolymerization to yield linear (or near-linear) polymer having recurring units consisting of fused five-atom-ring heterocycles (**7**). These cyclopolymers showed carbonyl absorptions of equal intensity at 1785 and 1695 cm^{-1}, consistent with the foregoing *N*-ketoethyleneurea structure. No evidence was found for the "poly-dimer" structure which potentially would result from an intermolecular dimerization reaction of the diisocyanates. The absence of this alternative structure was confirmed by infrared measurements.



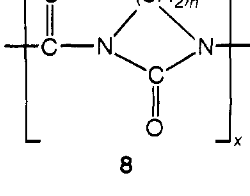
7

These cyclopolyisocyanates possessed solubility in a limited number of solvents, e.g., nitromethane, dimethyl sulfoxide, and pyridine. Solubility was also claimed in sulfuric and formic acids with no apparent attempt to ascertain whether chain degradation took place. It is known[2,32,33] that strong acids will readily degrade the poly(*n*-alkyl isocyanates).

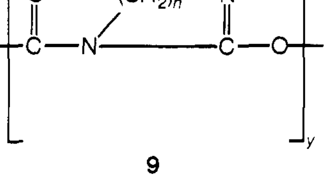
The absence of a crosslinking step was explained on the basis that these polymerizations proceed through an alternating intra-intermolecular anionic chain-growth mechanism similar to that postulated[50] for the 1,6-dienes. The polymerization of trimethylene diisocyanate led to insoluble material as did the polymerization of oxydimethylene diisocyanate. This led King[49] to propose that the cyclopolymerization of diisocyanates will proceed with the absence of crosslinking only when five-atom rings are formed.

However, Iwakura et al.[51] demonstrated that the sodium cyanide initiated polymerization of tetramethylene, trimethylene, ethylene, and methylene diisocyanates resulted in the formation of soluble polymer. Similar results were also obtained by others[52] for trimethylene isocyanate. The solvents included dimethyl sulfoxide, *N*-methylpyrrolidone, *m*-cresol, and ethylene carbonate. The γ-ray irradiation (-195 °C) of ethylene diisocyanate also led to the formation of soluble polymer. In addition, *cis*-1,3-diisocyanatocyclohexane has been polymerized[41,42,53] by sodium cyanide initiation to yield soluble polymer.

The structure of the α,ω-polymethylene diisocyanates was examined by means of an infrared study and by an analysis of the products formed by the di-*n*-butylamine induced degradation of the cyclopolymers. Tentative average structures, based in the main on the aminolysis data, for these cyclopolymers were proposed as **8** and **9**. Table I contains the estimated content of the two structures for the various α,ω-polymethylene diisocyanates. No evidence was foud which indicated the presence of the "polydimer" structure or pendant isocyanate groups.



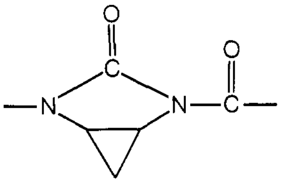
8



9

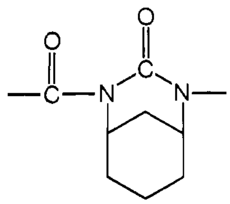
As was previously mentioned, whereas King[49] found only insoluble product from the polymerization of trimethylene diisocyanate, Iwakura[51] isolated soluble material. The reason for this discrepancy remains unsolved.

The polymerization of *cis*-1,2-cyclopropane diisocyanate to linear, soluble polymer was seemingly accomplished[54] in dimethylformamide and *N*-methyl-2-pyrrolidone at ca. -40 °C with sodium cyanide as the initiator. The infrared spectrum of the polymer showed two absorption bands, one at 1700 cm^{-1} and the other at 1780 cm^{-1}. These absorptions were taken to suggest the presence of two types of carbonyl groups, viz., inter-ring and intra-ring. Thus, this polymer is believed to have the following structure:



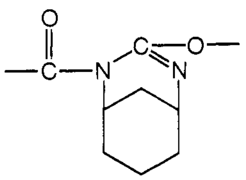
10

Similar results were observed for the polymer of *cis*-1,3-diisocyanatocyclohexane via sodium cyanide in dimethylformamide at -45 °C.[40,41,53] Under similar conditions the trans isomer failed to yield high polymer. The polymer obtained from the cis isomer was soluble in, for example, benzene and *m*-cresol and, based on infrared spectra, contained little or no residual isocyanato groups. Thus, via a cyclopolymerization mechanism, the two possible structures for this polymer are **11** and **12**. Using the aminolysis reaction, it was estimated these structures were present in the polymer in the ratio of 65:35, results which are similar to those found[51] for the methylene and trimethylene diisocyanates.



11

and



12

Corfield and Crawshaw[41,53] noted that the aminolysis reaction was initially quite rapid and then underwent a marked decrease in rate. It was shown that this fast reaction evidently involved a polymer degradation reaction (involving structures containing the ether linkage) leading to the formation of 2-(*N,N*-di-*n*-butylcarbamoyl)-2,4-diazabicyclo[3.3.1]nonan-3-one (**13**) and the bis(di-*n*-butylurea) **14**. This reaction scheme is shown in Scheme I. The slower of the two reactions was described as follows:

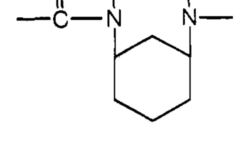
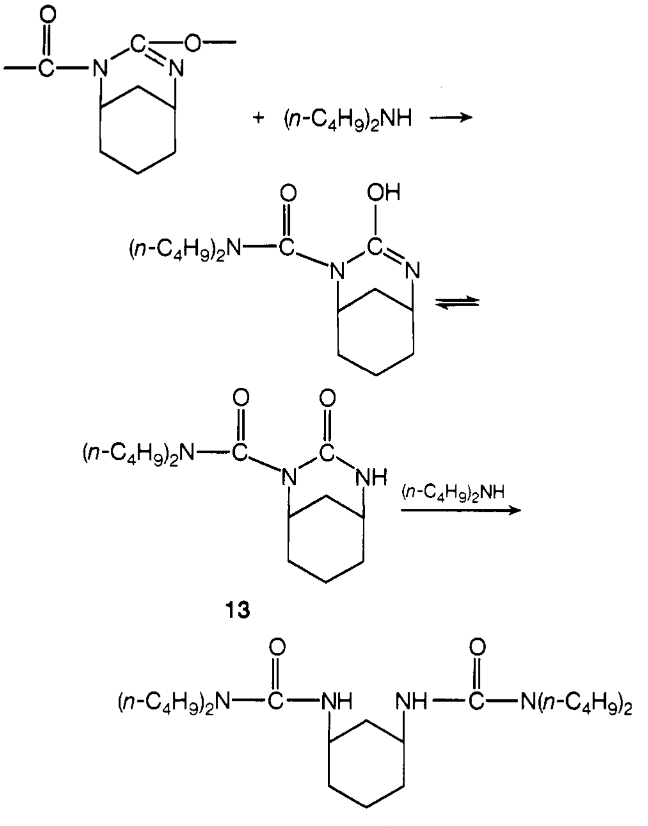


TABLE I. Composition of α,ω-Poly(methylene diisocyanates)[50]

n	% **8**	% **9**
1	66	34
2	0	100
3	76	24
4	40	60

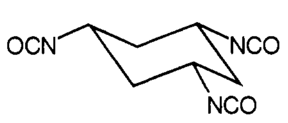
SCHEME I



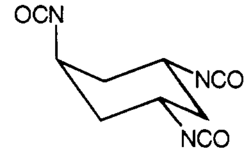
13

14

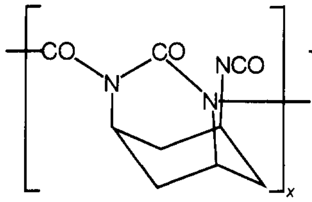
The cis and trans isomers of 1,3,5-triisocyanatocyclohexane, **15** and **16**, respectively, have been polymerized (in dimethylformamide via sodium cyanide) to yield polymer containing predominantly bicyclic structures, **17** and **18**. The primary structure of the polymer obtained from the cis isomer was shown to be



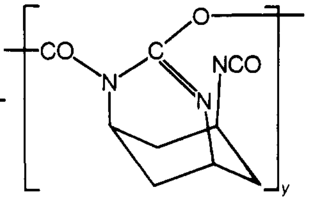
15



16



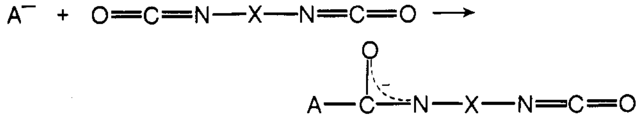
17



18

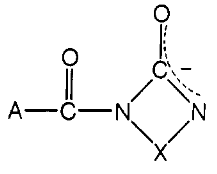
An analogous structure was also found for the polymer obtained from the trans isomer.

A polymerization mechanism has been put forward to explain the ability of these di- and triisocyanates to polymerize to essentially linear polymer. The initiation step occurs by attack of the anion leading the formation of a hybrid ion:



$A^- + O{=}C{=}N{-}X{-}N{=}C{=}O \longrightarrow$

where X denotes the aliphatic unit. The intramolecular step could then lead to the bicyclic anion **19**. If the intramolecular step occurs through the negative nitrogen in this hybrid ion, then structures **11** and **17** would be formed while reaction through the negative oxygen would lead to the unit shown in structures **12** and **18**.



19

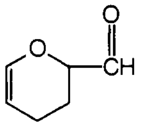
V. Copolymerization of Monisocyanates

Copolymerization studies involving the monoisocyanates have led to the preparation of random, alternating and block copolymers. As might be anticipated, the comonomers used in forming the first two types of copolymers have been polar in nature and have, for the most part, been aldehydes. In the main, anionic initiators have been used, although some success has been achieved with certain cationic systems. As was the case for the homopolymerizations of the monoisocyanates, free radical initiators have not been found to cause polymerization.

The first reported copolymerization involving a monoisocyanate was the work of Staudinger, Felix, and Geiger[56] in 1925. Indeed this work seems to be the first formal recognition that the isocyanate group was capable of participating in polymerization. Staudinger's group copolymerized diphenylketene with either phenyl, *p*-nitrophenyl, or α-naphthyl isocyanate in diethyl ether at −80 °C via the use of trimethylamine. Number-average molecular weights in the range of 3000 to 6000 g mol^{-1} were obtained.

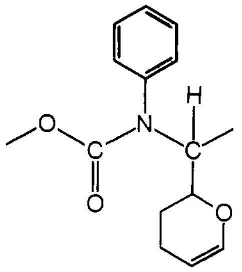
The copolymerization of aromatic isocyanates with ethylene oxide by Furukawa and his coworkers[16-18,57] represents the first use of a cationic initiator in connection with the copolymerization of an isocyanate monomer. Copolymerization in this case was initiated via triethylaluminum or by a water-triethylaluminum complex. This work revealed that the aromatic isocyanates, e.g., phenyl isocyanate, and ethylene oxide form an alternating copolymer containing iminoacetal units in the polymer chain. Their infrared and nuclear magnetic resonance analysis of the copolymer chain indicated that the mode of phenyl isocyanate incorporation apparently proceeds *exclusively* through the carbonyl group. The number-average molecular weight of the copolymers, using a substituted (chloral or nitro group) aromatic isocyanate, ranged from 1.1 to 1.9 × 10^3 g mol^{-1}. The three primary characteristics of these polymerization systems were (a) the inability of the aromatic isocyanate to homopolymerize, (b) the preparation (8 wt % or less) of polyethylene oxide, and (c) the inability of the aliphatic isocyanates to participate in copolymerization. This latter effect was tentatively ascribed to the electron-donating characteristics of the aliphatic group as compared to the electron-withdrawing characteristics of the aromatic groups. Thus, since the aluminum compound would be expected to coordinate with the atom with the highest electron density, the suggestion was made that the aluminum would, in the case of the aliphatic isocyanates, coordinate with the nitrogen. This coordinated species was assumed to be of sufficiently low activity so as to preclude the addition of ethylene oxide. It should be stressed that this explanation is a *speculative* one and awaits experimental verification. Furthermore, there remains lacking a quantitative explanation as to why the triethylaluminum initiator apparently leads to the formation of an alternating copolymer.

An additional alternating copolymer was obtained[58] from the copolymerization of phenyl isocyanate with 3,4-dihydro-2*H*-carboxyaldehyde **20**—the acrolein dimer—via the use of *n*-butyllithium at 15 °C in toluene. Changes in the comonomer ratio exerted no detectable effect on copolymer composition. Similar results were obtained when the initiator was changed to diethylaluminum chloride.



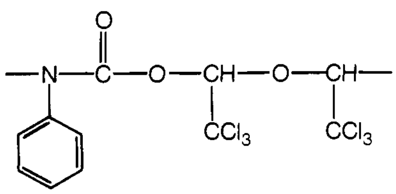
20

The infrared spectra of these copolymers showed a strong absorption band at 1740 cm^{-1} with bands at 1600, 1498, and 690 cm^{-1} due to monosubstituted benzene. Two bands found at 1242 and 1078 cm^{-1} were ascribed to the presence of the cyclic unsaturated ether group. These data, taken in concert with a nuclear magnetic resonance analysis, resulted in the proposed structure **21** for this copolymer. Unlike the results of Furukawa's[16-18,57] work, it was concluded in this copolymerization (initiated by either anionic or cationic species) that the isocyanate enters into the chain via the nitrogen-carbon double bond. Copolymers were also obtained when zinc diethyl or aluminum diethyl chloride was the initiator.



21

Aldehydes and isocyanates have been found to anionically copolymerize to yield a polymeric carbanilate[59-67] structure. Various authors[61-67] have studied the copolymerization of phenyl isocyanate with chloral. With lithium or sodium counterions in tetrahydrofuran or dimethylformamide at polymerization temperatures between −58 to −95 °C, it was found[62-64] that the resulting copolymer composition was only slightly dependent on comonomer concentrations. The data on the composition of the copolymers and their infrared spectra suggested that the basic structural unit of the chain was



22

This selective alteration was ascribed to steric effects from the penultimate isocyanate unit. This rationalization must, though, be viewed with some doubt since the aromatic isocyanates studied will themselves homopolymerize to high molecular weight polymer. It should also be noted that there was no attempt to elucidate the nature of this "penultimate" steric hinderance by the aromatic isocyanate unit.

Raes and co-workers[65] studied the copolymerization of chloral and phenyl isocyanate with tertiary amines as initiators in benzene at 25 °C or toluene at −75 °C. With the phenyl isocyanate present in the initial mixture in a concentration range of 50 to 70 mol %, the concentrations of chloral in the copolymers were found to be 52 and 77% for the low-temperature runs and 62 and 66% for the 25 °C copolymerizations. In the main, these compositions are similar to those found by Getmanchuk and co-workers.[62-64] It is interesting to note that Raes and co-workers[65] were able to obtain copolymers with number-average molecular weights as high as 2 × 10^4 g mol^{-1} with the use of the tertiary amine initiators.

TABLE II. Monomer Reactivity Ratios in Aldehyde (M_1)-Isocyanate (M_2) Copolymerizations[67]

Solvent	r_1	r_2
	n-Butyraldehyde	*n*-Butyl isocyanate
n-Hexane	∞	0
Tetrahydrofuran	70[a]	10[a]
Diethyl ether	500[a]	10[a]
	Chloral	Phenyl isocyanate
n-Hexane	∞	0
Diethyl ether	~0.5	~0
	Chloral	*n*-Butyl isocyanate
n-Hexane	∞	0
Diethyl ether	2–50	0

[a] With r_1r_2 much greater than 1, block copolymerization rather than random copolymerization undoubtedly took place.

TABLE III. Monomer Reactivity Ratios in β-Cyanopropionaldehyde (M_1) and Isocyanate (M_2) Copolymerizations[68,69]

M_2	r_1	r_2	r_1r_2	$1/r_1$
Methyl isocyanate	8.3 (±0.3)	0.01 (±0.01)	0.083	0.12
Phenyl isocyanate	0.18 (±0.05)	0.08 (±0.1)	0.0144	5.56

Odian and Hiraoka[66,67] have expanded upon the work of Getmanchuk[62-64] and Raes[65] to include formaldehyde, *n*-butyraldehyde, and *n*-butyl isocyanate. Their results with chloral and phenyl isocyanate are basically in agreement with the data reported by others.[62-65] Their results did indicate though that the use of lithium counterion in toluene at −75 °C seemed to cause a slight increase in the chloral content when compared to the copolymers obtained via the use of the potassium counterion in dimethylformamide at −68 °C. For this latter system, the copolymer obtained had a composition which seemed to reflect the comonomer mixture of the polymerization solution.

The order of reactivity for several aldehyde monomers in these copolymerizations was found to be chloral = formaldehyde > *n*-butyraldehyde, while the reactivity for isocyanates was phenyl isocyanate > *n*-butyl isocyanate. This reactivity seemed to be independent of the alkali metal counterion and solvent. However, the solvent did seem to influence the reactivity ratios for several aldehyde-isocyanate monomer pairs. These values are shown in Table II for the case where lithium was the counterion and the reaction temperature −75 °C.

The increase in reactivity of the aldehyde as solvent polarity decreased was explained, in a speculative fashion, as due to an increased solvation of the growing chain-end by the aldehyde. This would be expected to increase the aldehyde concentration in the vicinity of the active chain-end at the expense of the isocyanate. Hence, this rationalization can serve as an alternative to Getmanchuk's[64] explanation as to why chloral is the favored monomer in these copolymerizations.

Copolymers of β-cyanopropionaldehyde and methyl or phenyl isocyanate have been synthesized[68,69] in tetrahydrofuran at −78 °C. The initiator used was the benzophenone-dilithium species. The copolymers prepared were low molecular weight ($\langle M_n \rangle \simeq 3 \times 10^3$ g mol^{-1}) materials. The reactivity ratios for these copolymerization systems are contained in Table III. The results are in basic agreement with the general trend observed by others in regard to the copolymerization behavior of aldehydes and

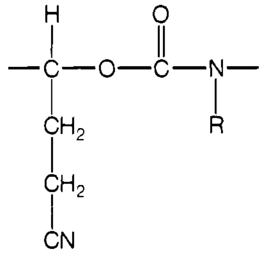
TABLE IV. Monomer Reactivity Ratios in Copolymerizations of Ketenes (M_1) with Phenyl Isocyanate (M_2)[74]

Ketene	r_1	r_2	r_1r_2
Diphenyl	0.10	0.29	0.029 (±0.006)[a]
Phenylethyl	1.6	0.10	0.16 (±0.02)[a]
Phenylmethyl	4.8	0.02	0.096 (±0.02)[a]

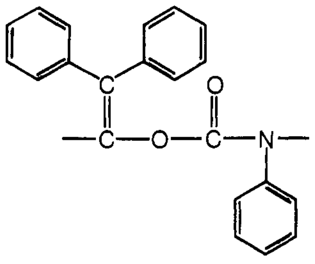
[a] Standard deviation.

isocyanates. The tendency of the two isocyanates to yield an alternating copolymer with β-cyanopropionaldehyde can be seen to be (from the r_1r_2 values) methyl isocyanate > phenyl isocyanate. From the $1/r_1$ values the rate of addition of M_2 to the alcoholate anion of the aldehyde is in the order of phenyl isocyanate > methyl isocyanate.

The chain structure of these copolymers was examined by both infrared and nuclear magnetic spectroscopy.[68,69] As a consequence of their analysis Hashimoto and Sumitomo[68,69] concluded that both isocyanates entered into the copolymer chain via the opening of the nitrogen-carbon double bond. Hence, structure **23** can be taken as a reasonably accurate representation of these copolymer species. Thus, the copolymerization of isocyanates with aldehydes seems to yield polymeric methylidene carbanilates (substituted polyurethanes). It appears that insofar as anionic initiators are concerned, isocyanates participate in these copolymerizations virtually exclusively through the nitrogen-carbon double bond.



23



24

The copolymerization of a ketene with isocyanates was first studied, as was mentioned previously, by Staudinger and his group.[56] The copolymerization of ketenes with isocyanates, though, has received only infrequent attention[70-74] since Staudinger's initial study. Nunomoto and Yamashita[70,71] copolymerized phenyl isocyanate with diphenylketene using sodium cyanide in dimethylformamide at −45 °C and obtained low molecular weight polymers. The structure of these copolymers was determined by acidic hydrolysis, hydrogenation, and bromination. These results indicated the presence of the carbanilate group (**24**). In addition to sodium cyanide, these authors[70,71] found that other effective initiators were sodium naphthalene, sodium ethoxide, lithium *tert*-butoxide, and *n*-butyllithium.

Recently Dyer and Sincich[74] examined in a quantitative fashion the anionic copolymerization of diphenyl-, phenylethyl-, and phenylmethylketene with phenyl isocyanate in dimethylformamide at −45 °C using sodium naphthalene as the initiator. These reactivity ratios are presented in Table IV. From the combination of infrared and nuclear magnetic resonance spectroscopy Dyer and Sincich[74] concluded that the structure of their copolymers was identical with that proposed by Nunomoto and Yamashita.[70,71] The hydrolysis products of poly(phenyl isocyanate-*co*-phenylethylketene) were consistent with structure **24**.

The data shown in Table IV reveal a tendency for alteration (r_1r_2 approaches zero) as one goes from phenylmethylketene and phenylethylketene. These data also show that the preference of the ketene anion for its own monomer is in the order of phenylmethylketene > phenylethylketene > diphenylketene. In every case the phenyl isocyanate prefers a crossover propagation step while only in the case of diphenylketene does the ketene anion prefer the crossover propagation reaction.

The reaction conditions used to obtain the data in Table IV were used for the copolymerization of phenylethylketene with *m*-chloro-, *p*-chloro-, *p*-methoxy-, and *m*-methoxyphenyl isocyanate as well as with phenyl isocyanate. The effect of these substituents on the order of isocyanate incorporation into the copolymer was in the order of the *m*-chloro = *p*-chloro > *m*-methoxy > H > *p*-methoxy groups. This order of reactivity is the expected one on the basis of the relative electron-withdrawing capacities of these various substituent groups.

Soluble, and apparently linear, copolymers of vinyl isocyanate were obtained[75] when the comonomer/vinyl isocyanate ratio in the copolymer was greater than 9:1. The comonomers were either styrene or methyl methacrylate with benzyl peroxide used as the initiator. The vinyl isocyanate was incorporated into the copolymer chain through the vinyl group exclusively. Relatively low molecular weight products were obtained since the intrinsic viscosity results were 0.22 and 0.44 dl g^{-1} for the methyl methacrylate and styrene copolymers, respectively.

Similar results were obtained[76] for β-allyloxyethyl isocyanate and 9-decenyl isocyanate when they were copolymerized with styrene, methyl methacrylate, or methyl acrylate. Soluble products of low molecular weight were obtained when the comonomer/isocyanate ratio was more than 7:1.

As might be anticipated, these copolymers containing vinyl, β-allyloxyethyl, or 9-decenyl isocyanate readily crosslinked through the pendant isocyanate groups upon the addition of water. The reaction of the vinyl isocyanate containing copolymers with *n*-butylamine, ethanol, or ethylenediamine yielded modified copolymers which exhibited higher melting points than the parent copolymers.

Two-segment block copolymers from vinyl monomers and isocyanates have been prepared[38] via anionic polymerization using *n*-butyllithium as the initiator. The vinyl monomers used were styrene, isoprene, and methyl methacrylate while the isocyanates used were *n*-butyl isocyanate, 2,4-toluene diisocyanate, and 1-methyl-2,4-diisocyanocyclohexane. The vinyl monomer–isocyanate monomer pairs represent a "unilateral" block copolymer synthesis system; i.e., the chain-end of the vinyl monomer will initiate the isocyanate monomer while the reverse reaction does not occur. Hence, the vinyl monomer was polymerized first. As might be anticipated,[2] infrared measurements revealed that the polyisocyanate segments prepared from the diisocyanate monomers contained unreacted isocyanate groups. Estimates of the weight-average molecular weights (from gel permeation chromatography) of these block polymers ranged from ca. 9×10^3 to 5×10^5 g mol^{-1}. These molecular weight values were undoubtedly in error since the authors[38] were apparently unaware that the poly(*n*-alkyl isocyanates) are relatively stiff chains.[12,32,33,39] This renders the application of *Q* values[77] and the standard gel permeation chromatography calibration methods inappropriate.

As was mentioned earlier, Shashoua, Sweeny, and Tietz[2] were the first to note that diisocyanates possessing substituents on a carbon atom in the α position, relative to one of the isocyanate groups, will polymerize only through the sterically unhindered isocyanate group. Thus, it was possible to polymerize 2,4-toluene diisocyanate to yield linear polymer containing pendant isocyanate groups. Since this discovery various groups[78-81] have succeeded in preparing copolymers where an appropriate diisocyanate, e.g., 2,4-toluene diisocyanate, has been added to one or both ends of a polystyrene or polydiene segment. The presence of the unpolymerized isocyanate groups renders these block copolymers eligible for post-polymerization chain extension and crosslinking reactions.

Hergenrother and Ambrose[80,81] have investigated this concept with regard to the preparation of polybutadiene–polyimide block copolymers. These materials were prepared by reacting polybutadienes (containing approximately 90% vinyl units), capped at one end with several units of 2,4-toluene diisocyanate, with a diamine followed by the addition of a dianhydride. Thermal gravimetric analysis of these copolymers (in nitrogen or air) revealed that weight loss did not occur until a temperature of about 450 °C was reached.

These authors also found[80] that the addition of 2,4-toluene diisocyanate to the poly(butadienyl)lithium chain-end can lead, under some circumstances, to chain coupling. The extent of this chain coupling was found to decrease as the molar ratio of 2,4-toluene diisocyanate to active chain-ends increased. It should be noted though that these authors[80] failed to consider the possibility that 2,4-toluene diisocyanate may lead to some branched or star polymer formation as will the use of the isomers of divinylbenzene with poly(styryl)- or poly(dienyl)lithium chain-ends.[82-87] Their method of analysis, gel permeation chromatography, can be relatively insensitive in distinguishing between branched and linear chains where the molecular weights do not differ too dramatically. Hence, a reexamination of these "coupled" polybutadienes using more sophisticated analytical procedures, e.g., osmometry, fractionation, etc., would seem appropriate in order to determine whether or not 2,4-toluene diisocyanate can lead to the formation of branched, star-shaped, polybutadienes.

VI. Physical Properties of Poly(n-alkyl isocyanates)

A. Qualitative Information from Unfractionated Samples

The properties of the poly(*n*-alkyl isocyanates) in solution dominate the physical measurements on this family of polymers because their extended molecular conformation results in unique behavior in solution. The rigid rod character of these polymer molecules is dramatically reflected in solution measurements of dielectric relaxation, intrinsic viscosity, light scattering, Kerr effect, electric dichroism, etc. Such solution measurements are extremely sensitive to the length or molecular weight of a rigid polymer molecule, and, therefore, the distribution of molecular weights becomes an important characteristic of the samples which are used for these experiments. The initial measurements of dielectric constant,[43] intrinsic viscosity,[88,89] and light scattering[89] of poly(*n*-butyl isocyanate) (PBIC) and poly(*n*-hexyl isocyanate) (PHIC) in solution were carried out on unfractionated samples before the extreme sensitivity of the solution properties on the distribution of molecular weight was recognized.[90] Unfortunately, many measurements of solution properties have been made on unfractionated or poorly characterized samples and, therefore, cannot be interpreted quantitatively. Even for the case in which an unfractionated sample is well characterized, an interpretation of the data is difficult because the conformation of the molecule changes from rodlike at low molecular weight to random coil at high molecular weight, so that one is observing a distribution of molecular weight as well as a distribution of molecular conformation. In this review we present only those quantitative data which have been taken on reasonably well-characterized fractions. Although other data numbers will not be presented, important qualitative information from all experiments regarding the molecular conformation of the poly(*n*-alkyl isocyanates) will be discussed.

From Buchard's measurements,[88] the intrinsic viscosity–molecular weight exponent and the sedimentation coefficient–molecular weight exponent for PBIC were observed to be well outside Gaussian behavior. Even though Buchard's samples were unfractionated and his viscosity data apparently obtained under high shear rate conditions, he was justified in concluding that the PBIC molecule was stiff and well extended.

Schneider, Furusaki, and Lenz[89] attempted to fractionate their samples for light scattering and intrinsic viscosity measurements, but their samples still contained a broad distribution of molecular weights. This diminished the usefulness of their numbers, but their measurements showed that PHIC had a large ratio of radius of gyration to $\langle M_w \rangle$ and a large statistical length supporting Buchard's conclusions regarding the rigidity of the molecule. Schneider et al. concluded that the molecular rigidity was an inherent property of the molecule and that it could not be accounted for by considering the polymer as a Gaussian chain swollen by strong interactions with the solvent. They proposed that the rigid conformation arose from a resonance between the nitrogen and carbonyl group which brings about a partial double bond in the main chain. This hypothesis was demonstrated to be incorrect when electric dichroism was measured for PBIC solutions.[91] Below, we will discuss the conformational energy calculations which show that the rigidity of the molecule arises from a combination of a high potential barrier to rotation from a planar amide configuration and steric interference between the *n*-alkyl side chain and the carbonyl group.

Schneider et al.[89] also identified a solvent–solute interaction whereby $[\eta]$ for a sample in CCl_4 decreased from a value of 12.3 to a value of 7.3 dl g^{-1} in chloroform, indicating a solvent–solute interaction by which the more polar chloroform brings about a diminution of the rigid molecular posture.

The initial dielectric measurements of PBIC in benzene solution were carried out by Yu, Bur, and Fetters[43] using unfractionated samples. They observed very large molecular dipole moments, and their measurements of the dielectric relaxation time τ as a function of molecular weight were interpreted in terms of a rigid molecule. One significant observation was that only one mode of molecular relaxation was active in the dielectric dispersion and it corresponded to an end-over-end motion of a rodlike molecule. Absent from the dielectric measurements was a mode of relaxation $\tau \propto M$, from which it could be concluded that there was no mode of motion corresponding to rotation about the long axis of the molecule. In this case, the component of dipole moment perpendicular to the long axis of the rod, $\mu_\perp$, is zero. They concluded that the dielectric dispersion was associated with a dipole moment parallel to the long axis of the molecule and that the symmetry necessary for $\mu_\perp$ = zero was brought about by a helical conformation of the molecule. The molecular dimension and dipole moments which Yu et al.[43] calculated were necessarily incorrect because their samples, being unfractionated, contained not only a distribution of molecular weight, but also a distribution of molecular conformation. A dipole reversal model which they proposed in order to account for their lower than expected dipole moments was shown to have no validity when the experiments were carried out[90] with narrow fractions of PBIC.

Kerr effects and electrooptic experiments on PBIC and PHIC were used by Tsvetkov and coworkers[92] and by Plummer and Jennings[93] to corroborate the parallel direction of the permanent dipole moment. Tsvetkov et al. observed that both shear and electric birefringence of PBIC were positive and large compared with those the *n*-butyl isocyanate monomer. The advantage of these experiments was that conclusions regarding the dipole and rigidity of the poly(*n*-alkyl isocyanate) could be obtained from a *single* sample, i.e., without making measurements as a function of molecular weight.

B. Quantitative Data from Dielectric and Intrinsic Viscosity Measurements on Fractionated Samples

1. Dielectric Measurements

We have insisted on the proper characterization and fractionation of the poly(*n*-alkyl isocyanate) samples used in the solution measurements as a function of molecular weight. In the high polymer molecular weight range 2.0×10^4 to 12×10^6, the

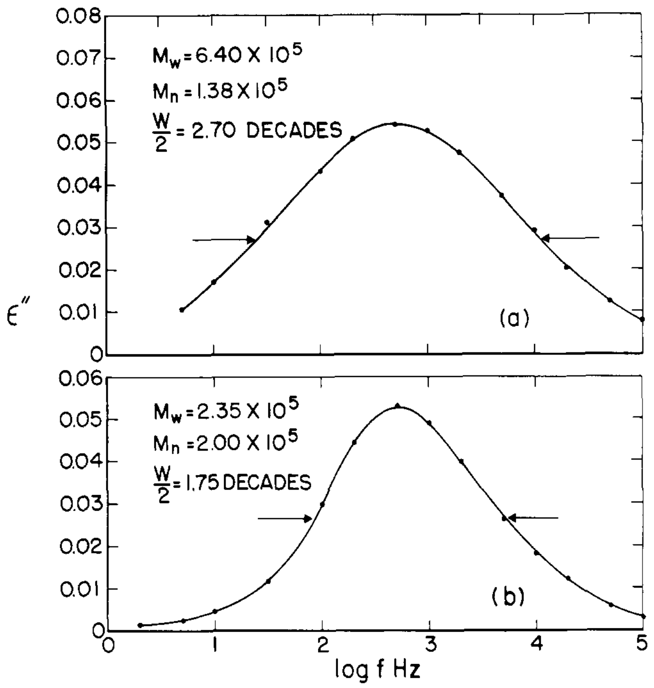


Figure 2. (a) ϵ'' vs. log f for an unfractionated PBIC sample in CCl_4 solution at 23 °C. (b) ϵ'' vs. log f for a fractionated PBIC sample in CCl_4 solution at 23 °C. The half-width, $W/2$, is noted in each case.[90]

poly(n-alkyl isocyanate) molecule changes conformation from rodlike to random coil so that a sample containing a broad distribution of molecular weights also contains a distribution of molecular conformations. For an unfractionated sample, τ and $[\eta]$ will reflect a dual dependence, on the one hand as a function of molecular weight and on the other as a function of conformation. By using well-characterized and reasonably sharp fractions, it is possible to separate these two effects. For this review we have decided that only data taken on reasonably narrow and adequately characterized fractions can be evaluated quantitatively.

References 12, 33, 39, 90, 91, and 94 through 97 contain the bulk of the published data taken on poly(n-alkyl isocyanate) fractions which have been characterized at least by $\langle M_w \rangle$ and $\langle M_n \rangle$. Bur[94] and co-workers[39,90] carried out the most thorough characterization of the poly(n-alkyl isocyanate) fractions by examining not only $\langle M_w \rangle$ and $\langle M_n \rangle$, but also the spectrum of dielectric relaxation times. They established a relationship between the half-width of the dielectric dispersion curve $W/2$ and the ratio $\langle M_w \rangle / \langle M_n \rangle$ for a rodlike molecule. Here $W/2$ is a measurement of the frequency spread in decades of the dielectric loss ϵ'' vs. frequency curve at half-height. This is shown in Figure 2 where ϵ'' vs. frequency is plotted for both an unfractionated and fractionated sample. The unfractionated sample yields a dispersion curve with a distribution of relaxation times, $\phi(\tau)$, much broader than is observed for the fractionated sample. Below, we show data which demonstrate that for a rigid-rod molecule, $\tau \propto M_w{}^{2.7}$ Because of the 2.7 exponent, a distribution $\psi(M)$ in molecular weight is greatly amplified when observed as $\phi(\tau)$. Thus the envelope of the dielectric loss curve is a sensitive reflection of $\psi(M)$.

Bur[94] obtained $\phi(\tau)$ by considering the equations which govern the real ϵ', and imaginary ϵ'' parts of the dielectric dispersion,

$$\epsilon' = \epsilon_\infty + \int_0^\infty \frac{(\epsilon_s - \epsilon_\infty)\phi(\tau)\ d\tau}{1 + \omega\tau} \quad (5)$$

$$\epsilon'' = \int_0^\infty \frac{(\epsilon_s - \epsilon_\infty)\omega\tau\phi(\tau)\ d\tau}{1 + \omega^2\tau^2} \quad (6)$$

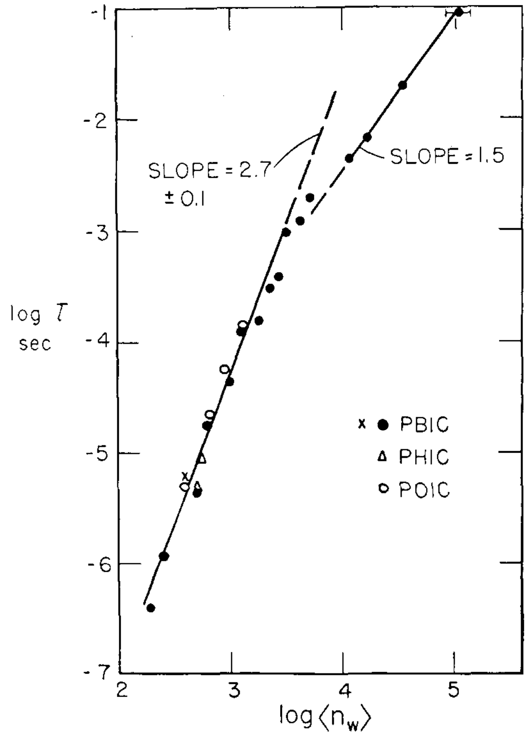


Figure 3. Log τ vs. log $\langle n_w \rangle$ for poly(n-alkyl isocyanate) fractions in solution at room temperature: (●) PBIC data of Bur and Roberts;[90] (○) POIC data of Bur, Roberts, and Fetters;[39,104] (X) PBIC and (△) PHIC data of Lochhead and North.[96]

where ϵ_s and ϵ_∞ are the low- and high-frequency values of the dielectric constant, and ω is the angular frequency of the measuring electric field. For a fraction of rodlike molecules, $W/2$ was found to be related to the ratio $\langle M_w \rangle / \langle M_n \rangle$ by

$$W/2 = 4.40(\langle M_w \rangle / \langle M_n \rangle) - 3.26 \text{ for } \langle M_w \rangle / \langle M_n \rangle < 1.35 \quad (7)$$

The samples used by Bur and coworkers were selected on the basis of the criteria $W/2 < 2.10$ decades, $\langle M_w \rangle / \langle M_n \rangle < 1.2$, and the absence of any low or high molecular weight tails in the sample. Other authors, notably Tsvetkov and coworkers,[92,98-103] have stated that their polymer samples were fractionated, but they do not present adequate characterization data, and they did not apply any criteria for the selection or rejection of "fractionated" samples.

In analyzing the dielectric dispersion for a polymer sample containing a distribution $\psi(M)$ of rigid rod molecules, Bur[94] assumed that there is a one-to-one correspondence between $\phi(\tau)$ and $\psi(M)$ and the dipole moment μ is proportional to the molecular weight or length of the molecules. The results showed that $\psi(M)$ could be obtained from $\phi(\tau)$ and that the maximum of the dielectric loss, ϵ''_{max}, occurred at a frequency corresponding to the relaxation time of the polymer molecule whose molecular weight was slightly larger (no more than 10%) than the $\langle M_w \rangle$ of the samples.

Contrary to this, Jennings and Brown[95] suggested that a plot of τ vs. $\langle M_n \rangle$ was the proper presentation for the PBIC relaxation time data. This suggestion was not based on a theoretical or experimental analysis of the measurement and therefore cannot be given serious consideration. On the other hand, Bur's analysis justifies the view that, within the limits of uncertainty in the measurement of $\langle M_w \rangle$, the dependence of τ on molecular weight can be seen in a plot of τ vs. $\langle M_w \rangle$. Figure 3 is a plot of log τ vs. log $\langle n_w \rangle$ (where $\langle n_w \rangle$ is the weight-average degree of polymerization) which contains dielectric data for the n-butyl,[90,96] n-hexyl,[90,96] and n-octyl[39] homologs in dilute solutions. The solvents were CCl_4, benzene, or toluene. It is to be noted that data for the three homologs lie on the same curve with some differences due to the different solvents used. Thus, τ depends only on the length or degree of polymerization, and is insensitive to the size of the *n*-alkyl side chain or the homolog of the sample. This is also seen in the intrinsic viscosity vs. $\langle n_w \rangle$ data.

In Figure 3, at low molecular weight, τ follows a 2.7 exponential dependence on $\langle n_w \rangle$, but as molecular weight increases this power dependence falls off to 1.5 for $\langle n_w \rangle$ above 2.5×10^3. The 2.7 power is an extreme value, the highest attainable exponent for a linear molecule. Only when a linear molecule is stretched out in a rodlike conformation and the hydrodynamic shielding is minimized will the exponent attain a value of 2.7. At high $\langle n_w \rangle$, the 1.5 exponent is characteristic of a Rouse–Zimm mode of relaxation of a random-coil macromolecule in dilute solution. Over the range of $\langle n_w \rangle$ from 2×10^2 to 12×10^4, the data of Figure 3 reflect the conformation change of the poly(*n*-alkyl isocyanate) from rigid rod at low $\langle n_w \rangle$ to moderate flexibility at intermediate $\langle n_w \rangle$ and finally to random coil at high $\langle n_w \rangle$.

Theories[105–108] of hydrodynamic behavior of rigid rods in solution, dating back to Perrin[105] in 1934, predict the 2.7 exponent. These calculations give a relationship between τ and the rod dimensions for the end-over-end motion as

$$\tau = \frac{\pi N_0 L^3}{6kT(\ln L/b - \gamma)} \tag{8}$$

Here, L and b are the length and radius of the rod, N_0 is the viscosity of the solvent, and γ is a constant[105–107] or a slowly varying function of L and b.[108] For a range of L corresponding to high polymer, and for $L \gg b$, a numerical calculation[43] yielded $\tau \propto L^{2.7}$. From the data of Figure 3, L_0, the projection of the intermonomer distance onto the major axis of the molecule, can be calculated by using eq 8 and by substituting $\langle n_w \rangle L_0$ for L. Values of L_0 in the range 1.1 to 1.3 Å were calculated by several authors,[39,90,95,96,98,103] but these numbers are significantly less than reliable data from x-ray,[109] light scattering,[12,33] and conformation energy calculations[91] which give L_0 in the range 1.8 to 2.0 Å. Bur and Fetters[39] discuss the problems of calculating L_0 from the hydrodynamic experiments and conclude that the theoretical model does not exactly apply to the poly(*n*-alkyl isocyanates) case, because the Oseen tensor which is used to calculate local shielding effects is inappropriate. The 2.7 slope of the log τ — log $\langle n_w \rangle$ is a long-range parameter, and theory and experiment agree regarding the rodlike behavior. It is the absolute value of τ which is not accurately given by eq 8.

From the static dielectric constant, calculations of the dipole moment μ were carried out by Bur and Roberts[90] using the equation

$$\langle \mu^2 \rangle = \frac{9kT}{4\pi N_A} \frac{\langle M_n \rangle}{C} \left[\frac{\epsilon_s - 1}{\epsilon_s + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right] \tag{9}$$

where N_A is Avogadro's number, C is the concentration, and kT has the usual meaning. The results are shown in Figure 4 where $\langle n_w^2 \rangle / \langle \mu^2 \rangle$ is plotted against $\langle n_w \rangle$. For $n_w < 10^3$ it is observed that $\langle \mu^2 \rangle \propto M_w^2$ or that μ is proportional to the length of the molecule. From the τ measurements[90] and from the Kerr effect measurements,[92,93] it was established that μ was large and directed along the long axis of the rod. $\mu \propto L \propto \langle n_w \rangle$ is characteristic of a rigid-rod conformation for which there is no reversal of the dipole moment along the length of the polymer chain. By an extrapolation to the ordinate of Figure 3, the dipole moment per monomer unit directed along the long axis is obtained as $\mu_0 = 1.13$ D. The atomic configuration of the poly(*n*-alkyl isocyanates) considered from the perspective of x-ray[109] and electric dichroism,[91] and from conformational energy calculations,[91] shows that the carbonyl group is favorably directed along the long axis of the chain and that the dipoles of each monomer unit add positively, resulting in large dipoles per polymer molecule.

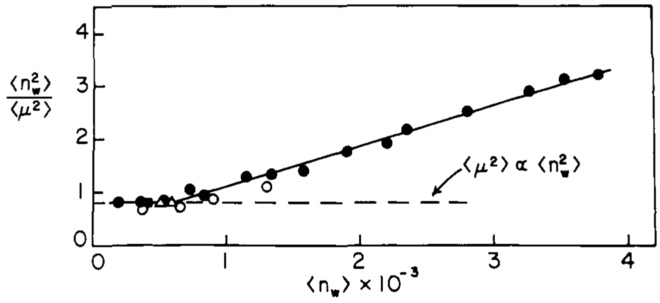


Figure 4. $\langle n_w^2 \rangle / \langle \mu^2 \rangle$ vs. $\langle n_w \rangle$ for PBIC, PHIC, and POIC (at room temperature); (●) PBIC data of Bur and Roberts;[90] (○) POIC data of Bur, Roberts, and Fetters;[104] (■) PBIC and (△) PHIC data of Lochhead and North.[96]

TABLE V. Dipole Moment of High Molecular Weight PBIC[90]

$\langle n_w \rangle$	$\langle \mu^2 \rangle$	$\langle \mu^2 \rangle / \langle n_w \rangle$
0.54×10^4	6.56×10^6	12.1×10^2
1.2×10^4	14.2×10^6	11.8×10^2
1.7×10^4	20.6×10^6	12.1×10^2
3.5×10^4	39.4×10^6	11.3×10^2
12×10^4	12×10^7	10×10^2

Because of these large dipoles, the poly(*n*-alkyl isocyanates) lend themselves to orienting electric field experiments such as electric dichroism and Kerr effect.

The dipole moment data of Figure 4 also show the deviation from rodlike behavior for $n_w > 10^3$; as the flexibility of the molecule increases, $\langle \mu^2 \rangle / \langle n_w^2 \rangle$ decreases. Since μ is the result of a vector summation of dipoles directed along the main chain, it is proportional to the end-to-end distance. The random-coil conformation of PBIC for $n_w > 10^4$ is confirmed by the data in Table V where it is shown that $\langle \mu^2 \rangle / \langle n_w \rangle$ = constant.

With the knowledge that μ is proportional to the end-to-end distance, Bur and Roberts[90] analyzed the PBIC dipole moment data in terms of the Kratky–Porod wormlike polymer chain model. In the Kratky–Porod model the end-to-end distance r is related to the total length L and the persistence length q by the following equation:

$$\langle r^2 \rangle = 2Lq - 2q^2(1 - e^{-L/q}) \tag{10}$$

Recognizing that there is a 1:1 correspondence between the end-to-end distance vector r and μ of a PBIC molecule, we may rewrite eq 10 with suitable dipole moments for each dimensional quantity. Thus,

$$\langle \mu^2 \rangle = 2n_n \mu_0 \mu_q - 2\mu_q^2[1 - \exp(-n_n \mu_0 / \mu_q)] \tag{11}$$

where n_n is the number-average degree of polymerization, and μ_q is called the persistent dipole moment. We have substituted $\langle \mu^2 \rangle$ for $\langle r^2 \rangle$, $n_n \mu_0$ for L, and μ_q for q.

By varying the parameter μ_q, a fit of the Kratky–Porod model to the experimental data was carried out.[90] The results are shown in Figure 5 with μ_q in the range of 790 to 900 D. If we define a new parameter n_q, the number of persistent monomer units,

$$n_q = \mu_q / \mu_0 \tag{12}$$

we obtain $n_q = 700$ which corresponds to a PBIC molecular weight of 70 000. For $L_0 = 2$ Å, $q = 1400$ Å, which is higher than the value obtained from light scattering (500–600 Å),[12] but it must be recognized that different solvents were used for the dielectric (CCl_4) and light scattering ($CHCl_3$) measurements. Jennings and Brown[95] have suggested that the persistence length is a function of the molecular weight and that, if the high molecular weight data are considered alone, then $q = 550$ Å. A close inspection of Figure 5 shows that best Kratky–Porod fit is significantly different from the experimental data. This suggests that the change in conformation from rigid rod to ran-

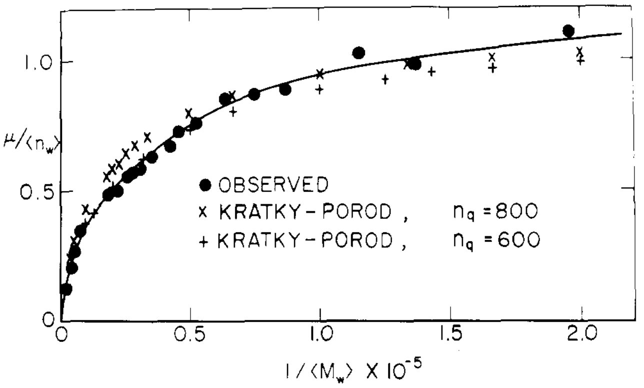


Figure 5. $\mu/\langle n_w\rangle$ is plotted against $1/\langle M_w\rangle$ for PBIC. The observed data are compared with the best fit of the Kratky–Porod wormlike model of polymer chain configuration.[90]

dom coil may be accompanied by structural interruptions such as helix reversals or polymerization through the carbon–oxygen double bond.

Other dielectric measurements have been carried out by Tsvetkov and coworkers,[99,100] but the published dispersion curves show an inconsistency. A close inspection of their ϵ' vs. log f and ϵ'' vs. log f plots reveals that the dispersion is much narrower than that which would be observed for a system having only a single relaxation time. Such behavior does not describe a relaxation process, and therefore the Tsvetkov data cannot be interpreted as end-over-end rotatory diffusion of a rodlike molecule.

An additional inconsistency in Tsvetkov's paper[99] is the misplotting of data. The published plot (Figure 2 in ref 99) of log τ vs. log M shows continuous curvature over the molecular weight range of 1.1×10^4 to 2.86×10^5 g mol^{-1}. However, an examination of the data in Table 1 of ref 99 reveals that the log τ vs. log M plot is actually a *straight* line with a slope of about 2 and not the variable slope of 2.7 to 1.7 as claimed by Tsvetkov and coworkers.[99]

2. Intrinsic Viscosity Measurements

Measurements of intrinsic viscosity have been made by Buchard,[88] Schneider, Furusaki, and Lenz,[89] Tsvetkov and coworkers,[98,101–103] Bur and Fetters,[39] and Berger and Tidswell.[33] Only the latter two publications contain data on well-characterized fractions. Although Tsvetkov et al.[92,98,101–103] stated in their papers that they "fractionated" their samples, no characterization data were presented. Therefore, the Tsvetkov data will not be presented here. In the Bur and Fetters' [39] case, the fractions were characterized by measurements of $\langle M_w\rangle/\langle M_n\rangle$, the dipole moment, dielectric dispersion curves, $W/2$, and in some cases gel permeation chromatography. In the Berger–Tidswell[33] case for PHIC samples, only $\langle M_n\rangle$ and $\langle M_w\rangle$ were measured. However, some question regarding the characterization exists because, for most of the low molecular weight samples, $\langle M_n\rangle$ is greater than $\langle M_w\rangle$. We have presented the Berger–Tidswell data,[33] but we have not included it in the quantitative analysis.

For their intrinsic viscosity measurements, Bur and Fetters[39] confined their attention to low molecular weights and considered the Kirkwood–Auer–Riseman (KAR) model[107] for the solution behavior of rodlike molecules. The KAR equation relating $[\eta]$ to L and b is

$$[\eta] = \frac{4\pi N_A L^3}{9 \times 10^3 M \ln L/b} \tag{13}$$

Equation 13 can be rewritten as

$$M_0[\eta] = \frac{4\pi N_A n_w{}^3 L_0{}^3}{9 \times 10^3 n_w \ln n_w(L_0/b)} \tag{14}$$

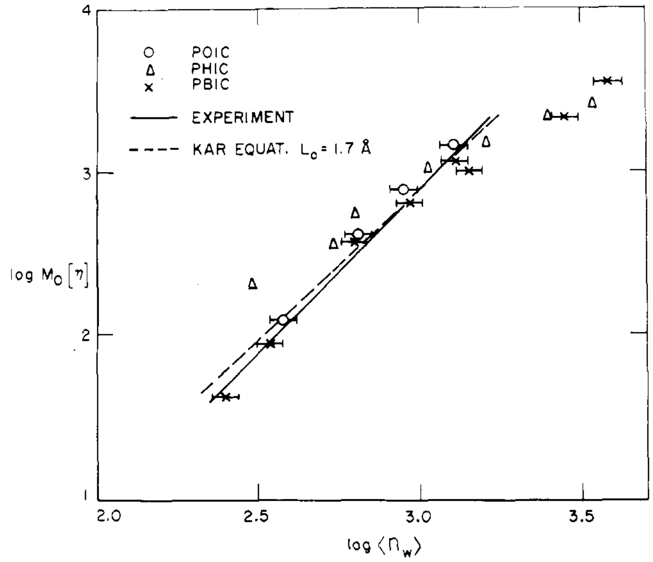


Figure 6. Log $M_0[\eta]$ vs. log $\langle n_w\rangle$ for PBIC, PHIC, and POIC in CCl_4 at room temperature: (X) PBIC and (O) POIC data of Bur and Fetters;[39] (Δ) data of Berger and Tidswell.[33]

where M_0 is the molecular weight of a monomer unit in the chain. If L_0 and L_0/b are constants, the same for all homologs, then the right-hand side of eq 14 does not depend on any quantity which distinguishes one homolog from another. A plot of the Berger–Tidswell[33] and Bur–Fetters[39] data in Figure 6 shows that, within the limits of uncertainty, the data for PBIC, PHIC, and poly(n-octyl isocyanate) (POIC) fall on the same curve. Thus, $M_0[\eta]$ depends only on $\langle n_w\rangle$ or the length of the molecule and is not significantly influenced by changes in the side chain or radius b. The same insensitivity to the homolog was observed in the dielectric relaxation time measurements.

For $\langle n_w\rangle < 1.4 \times 10^3$, a least-squares fit of the Bur–Fetters data[39] of Figure 6 yields the solid straight line with the following empirical form

$$M_0[\eta] = 7.58 \times 10^{-4} n_w{}^{2.0} \tag{15}$$

$$n_w < 1.4 \times 10^3 \qquad M_w/M_n < 1.2$$

Equation 15 is presented as a master equation which gives the intrinsic viscosity–molecular weight dependence for any fraction of poly(n-alkyl isocyanate) as long as $\langle \eta\rangle_w < 1.4 \times 10^3$.

In Figure 6, the slope of the solid straight line, 2.0 ± 0.13 (by least-squares fit), is in reasonable agreement with the 1.85 slope of the KAR equation on such a plot. This agreement is a necessary and sufficient condition that the linear PBIC and POIC molecules are rigid rods over the molecular weight examined. If L_0 is used as a parameter to fit eq 14 to the data of Figure 6, we find the best fit to be the dashed line for which $L_0 = 1.7$ Å. The KAR slope, 1.85, is independent of the value of L_0.

For the calculation of L_0, eq 14 is utilized by letting the ratio L_0/b equal 0.3. Bur and Fetters obtained[39] an average $L_0 = 1.66 \pm 0.12$ from 12 measurements. Thus, while the slope of the curve in Figure 6 agrees with the KAR equation, the absolute value of the calculated L_0 is in conflict with the light scattering[12] and x-ray[109] data. This same conflict arises with the analysis of the dielectric data. A contradiction between the model assumptions and the real physical situation is undoubtedly at the root of the problem. Since the slopes of the log τ − log $\langle n_w\rangle$ and log $M_0[\eta]$ − log $\langle n_w\rangle$ do agree with the model, the source of the problem is probably at the local level, particularly with the form of the Oseen tensor describing near-neighbor hydrodynamic interaction.

Calculations of L_0 by Berger and Tidswell[33] and by Tsvetkov et al.[98,101–103] must be evaluated by considering the poor characterization data on their samples. In the Berger–Tidswell

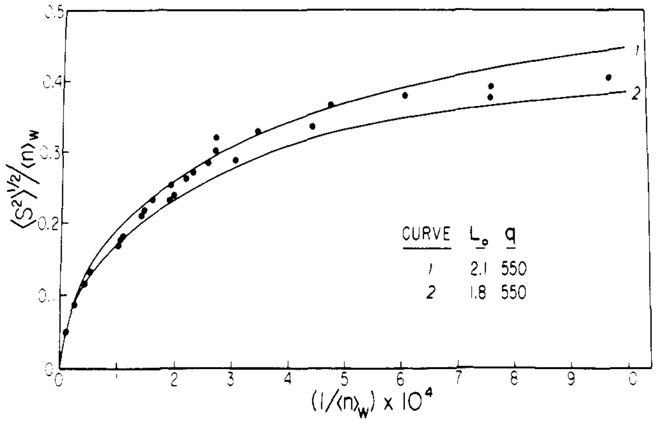


Figure 7. Plot of the observed ratio of the radius of gyration to the weight-average degree of polymerization against the reciprocal of the weight-average degree of polymerization.[12]

case,[33] most of the sample characterizations suffered from a fundamental conflict, i.e., $M_n > M_w$. The samples of Tsvetkov et al.[98,101–103] were not characterized with regard to the breadth of the heterogeneity indices of their fractions.

In Figure 6, the data at high molecular weight ($n_w > 2000$) deviates from the straight-line rigid-rod behavior. This coincides with the log τ – log $\langle n_w\rangle$ plot of Figure 3. Strictly speaking, nonrodlike behavior begins at the degree of polymerization at which the slope becomes less than 1.85 or less than 2.7, respectively. The dynamic data are not sensitive enough to establish this point with precision. By contrast, the static measurements of dipole moment,[90] light scattering,[12] and electric dichroism[91,97] show that the flexibility of the molecule begins at $\langle n_w\rangle = 500$ to 800 depending on the solvent and the sensitivity of the measurement.

If $[\eta]$ data were available over a wider range of molecular weight including the limiting behavior at high molecular weight, then it would be fruitful to consider an analysis of the data using a wormlike coil model.[110–112] Unfortunately, only a few data points exist outside the rodlike region of Figure 6, and we consider this to be insufficient information for applying partially flexible theories. Data collected on high molecular weight (up to 1.2×10^7 g mol^{-1}) PBIC by Ambler, McIntyre, and Fetters[113] will close this gap in information.

A recent paper by Tsvetkov and coworkers[102] has presented intrinsic viscosity data on "fractionated" samples of poly(chlorohexyl isocyanate) in CCl_4 over the molecular weight range of 1.2×10^4 to 3.06×10^5. As before Tsvetkov and coworkers have failed to provide what criteria were used for the selection or rejection of their "fractionated" samples. Unfortunately, this paper of Tsvetkov and coworkers[102] contains a very fundamental conflict; i.e., although their electric birefringence data were taken to demonstrate the change in conformation from rodlike to random coil of the poly(chlorohexyl isocyanate) over the molecular weight range investigated, their intrinsic viscosity data fail to do the same. In fact, a plot of log M_0 $[\eta]$ vs. log $\langle n_w\rangle$ yields a *straight* line with a slope of 1.25, a result similar to their PBIC data.[98,103] This value is markedly different from ours *and* from the theoretical value predicted by the KAR equation. There is no way to evaluate this difference since the experiments of Tsvetkov and coworkers are not well enough defined. In particular, the shear rates used in their viscosity measurements, the characterization data on their "fractions", and information on the distribution of molecular weights in each fraction were not provided. Thus, in view of these deficiencies and the inconsistencies present in their papers, it is our conclusion that the results of Tsvetkov and coworkers[92,98–103] cannot be taken as an accurate reflection of the hydrodynamic behavior of poly(*n*-alkyl isocyanates) of narrow molecular weight distribution.

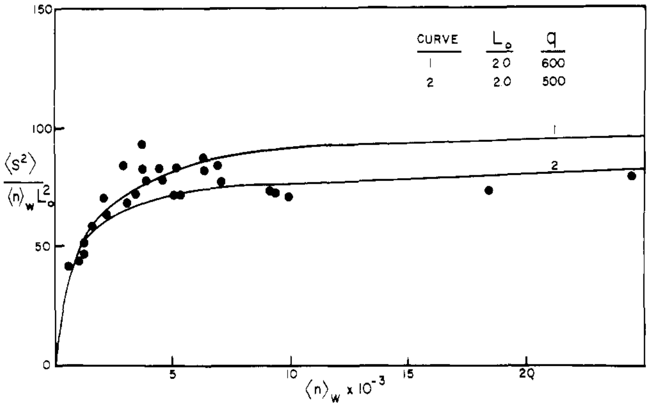


Figure 8. Plot of the observed characteristic ratio, $\langle S^2\rangle/\langle n_w\rangle L_0^2$ vs. the weight-average degree of polymerization.[12]

Parenthetically, it can be noted that the values for the exponent *a* in the Mark–Houwink relation found by Tsvetkov and coworkers[98,101–103] are similar to those found by Buchard[88] for PBIC in tetrahydrofuran ($a = 1.18$) and benzene ($a = 1.11$), by Schneider, Furusaki, and Lenz[89] for PHIC in chloroform ($a = 1.0$), and by Berger and Tidswell[33] for PHIC in a variety of solvents and solvent mixtures ($a = 0.96$ to 1.13). These relatively low values of *a* are, in the main, a consequence of both a distribution of molecular weights and conformations in the samples studied by these workers.

C. Light-Scattering Measurements

In the main, the information obtained pertaining to the chain conformation of the poly(*n*-alkyl isocyanates) has been obtained from the hydrodynamic properties of this family of macromolecules. Fetters and Yu[12] and Berger and Tidswell[33] have studied PBIC and PHIC, respectively, by examining the equilibrium properties of these chains. Using light scattering and osmotic pressure measurements, they demonstrated the nonlinear dependence of the radii of gyration and the virtual independence of the light scattering and osmotic second virial coefficients on molecular weight.

The chain dimensions and geometry of the poly(*n*-alkyl isocyanates) were determined from molecular weight–radius of gyration data analyzed in terms of the worm-like coil model of Porod and Kratky.[110,111] The expression for the mean-square radius of gyration, in the absence of excluded volume effects, was derived by Benoit and Doty[114] as follows:

$$\langle S^2\rangle_0 = q^2[(x/3) - 1 + (2/x) - (2/x^2)(1 - e^{-x})] \qquad (16)$$

with $x \equiv \langle n_w\rangle L_0/q$, where q is the persistence length, $\langle n_w\rangle$ the weight-average degree of polymerization, and L_0 the monomeric projection along the contour direction. The two adjustable parameters in eq 16 are q and L_0, whereas the experimentally accessible quantities are $\langle S^2\rangle_0$ and $\langle n_w\rangle$.

The ready determination of L_0 is not possible from the observation of the asymptotic value of $\langle S^2\rangle_0/\langle n_w{}^2\rangle$ at small $\langle n_w\rangle$. Instead, $\langle S^2\rangle^{1/2}/\langle n\rangle_w$ was plotted[12] against $(1/\langle n\rangle_w)$ (Figure 7), where the two variable parameters were selected to give the best fit to the data. As is apparent, the point where $\langle S^2\rangle^{1/2}/\langle n_w\rangle$ no longer depends on the reciprocal of chain length is not reached. Nonetheless, the range for L_0 was narrowed down to 1.8–2.1 Å for the case where q was chosen to be 550 Å.

A more refined estimate of the persistence length was made from a plot of the characteristic ratio,[115] $\langle S^2\rangle/\langle n_w\rangle L_0^2$, against the chain length (Figure 8). The majority of the experimental points are embraced by the two theoretical curves calculated from persistence lengths of 500 and 600 Å. It should be mentioned that the asymptotic value of the characteristic ratio is more sensitive to the choice of the persistence length than to

TABLE VI. Intrinsic Viscosity Values of Poly(*n*-hexyl isocyanate) Fractions in Various Solvents[33]

PHIC[a] $\langle M_w \rangle \times 10^{-3}$, g mol^{-1}	$[\eta]$, dl g^{-1}						
	CCl_4	$C_6H_5CH_3$	H_4-Furan	$CHCl_3$	CH_3OH/ $C_6H_5CH_3$ (19.5% v/v)[b]	CH_3OH/ CCl_4 (18.5% v/v)[a]	CF_3COOH/ CCl_4 (1.47% w/v)
424	19.5	16.3	16.4	11.8	15.1		10.7
312	17.4	13.9	13.8	10.3	13.05		9.77
204		10.7					
204	12.05	10.35	10.26	8.03	9.55	11.56	7.66
162	9.00	8.17	7.50	6.24	7.18		5.69
135	8.26	7.30	6.85	5.43	6.46		5.31
111	6.04	5.42	5.19	4.51	5.19		4.01
79	4.32	3.79	3.67	2.07	3.50	4.13	2.95
72	3.46	3.11	3.02	2.51	2.93		2.43
68	2.90	2.69	2.51	2.26	2.50	2.88	2.10
38	1.64	1.57	1.49	1.33	1.43		1.30

[a] For all fractions $[\eta]$ varies consistently with solvent. Measurements on one fraction ($\langle M_w \rangle = 2.04 \times 10^5$ g mol^{-1}) in *n*-hexane and *n*-butyl chloride in addition to the above solvents led to the following relationship: $[\eta]_{n\text{-}C_6H_{12}}$ (12.9) > $[\eta]_{CCl_4}$ (12.05) > $[\eta]_{C_6H_5CH_3}$ (10.35) $\simeq$ $[\eta]_{n\text{-}C_4H_8O}$ (10.26) > $[\eta]_{n\text{-}C_4H_9Cl}$ (10.16) > $[\eta]_{CHCl_3}$ (8.03). [b] These mixtures represent θ conditions at 25 °C.

TABLE VII. Temperature Dependence of Dipole Moment for a PBIC Fraction[a] in Trichloroethylene[117]

Temp, °C	$\langle \mu^2 \rangle$, D^2	Temp, °C	$\langle \mu^2 \rangle$, D^2
23.0	0.650	−32.1	0.885
10.8	0.674	−43.2	0.920
−4.0	0.774	−53.8	0.945
−15.5	0.814	−63.0	1.01

[a] $\langle M_w \rangle = 1.03 \times 10^5$ g mol^{-1}; $w/2 = 1.7$; $\langle M_w \rangle / \langle M_n \rangle < 1.1$.

the choice of the monomeric projection. Hence, with the value of L_0 of about 2 Å accepted, the upper boundary of the persistence length, curve 1, cannot be raised without missing the majority of the data. Likewise, the lower boundary, curve 2, cannot be lowered for the same reason. The range for persistence length was thus determined[12] to be from 500 to 600 Å.

Using the approach of Fetters and Yu,[12] Berger and Tidswell[33] determined q for PHIC (where L_0 was taken to be 2.0 Å) in tetrahydrofuran. The best fit for their light scattering data was a value of 425 Å for the persistence length.

The diameter of PBIC in toluene was estimated[12] from osmotic pressure measurements and the application of Zimm's theory[116] for stiff chain molecules. The value for this diameter was found to be about 10 Å.

D. Solvent Effects

The effect of solvent on the molecular conformation of the poly(*n*-alkyl isocyanates) was noted in the early papers by Buchard[88] and by Schneider et al.[89] The latter authors measured $[\eta]$ of PHIC in CCl_4, benzene, tetrahydrofuran (H_4-furan), H_4-furan–dimethylformamide (4:1) mixture, and chloroform. They observed that CCl_4 gave the highest value of $[\eta]$ and chloroform the lowest value; that is, $[\eta]$ decreases for the more polar solvents. Schneider et al.[89] used the $[\eta]$ data to consider the problem: to what extent is the extended conformation of PHIC due to intrinsic chain stiffness or due to long-range solvent interactions which swell the chain? To answer this question, they measured a value of the viscosity–molecular weight exponent for PBIC and PHIC in H_4-furan and found it to be about 1.10, well above the value of 0.8 from the Flory theory for the excluded volume effect of a Gaussian chain swollen by strong interactions with a solvent. If the measurements had been made on near-monodisperse fractions, the exponent would have been higher than 1.10. The value of the exponent is definite evidence that non-Gaussian behavior cannot arise solely from swelling of the polymer by interactions with the solvent. Also, using the Kirkwood–Riseman theory,[107] Schneider et al.[89] calculated an exponent equal to 0.91 for a theta solvent, indicating that, even in the absence of long-range forces, the polymer chain is abnormally expanded. Thus, they concluded that "the observed chain dimensions must be a consequence of short-range restrictions to rotation modified in only a secondary way by long-range effects."

Berger and Tidswell[32,33] did an extensive examination of the solvent effect and observed $[\eta]$ for PHIC under theta conditions. In Table VI their data are presented for various solvents including theta mixtures of methanol/toluene and methanol/CCl_4. The measurements showed that PHIC is insensitive to the addition of a nonsolvent, since, up to the point of precipitation $[\eta]$, K, and α all remain constant. Thus we have a strong indication of the inherent stiffness of the chain.

In the theta solvent strong short-range forces prevent the contraction of the PHIC molecule as will occur with a flexible polymer molecule. The conformation of the polymer in CCl_4, toluene, and in theta mixtures can be considered to be unaffected by long-range forces and dominated by short-range local forces. Any alteration of the conformation of the molecule can only be brought about by solvent–solute interaction which alters the molecular configuration at a specific monomer site. Chloroform could solvate the molecule in a manner which would alter the barrier to rotation or trifluoroacetic acid could protonate the molecule.

The dominance of the short-range forces is also seen in the measurement of intrinsic viscosity[33] and dipole moment[117,118] as a function of temperature. Both $[\eta]$ and $\langle \mu^2 \rangle$ decrease as temperature increases, indicating a contraction with a rise in temperature. It is apparent that the contracted conformation has a higher energy state than the extended conformation. Table VII contains the relationship between the dipole moment and temperature for a PBIC fraction in trichloroethylene.

Parenthetically, it should be noted that Pierre and Desreux[119] have reported that between the temperatures of 298 to 318 K, a reversible "transition" occurs for both PBIC and PHIC "fractions", a transition which manifests itself via a discontinuity in the plot of η_{sp}/c vs. temperature and in the intensity of scattered light at only one angle, 135°! However, the intrinsic viscosity data of Berger and Tidswell[33] over the same temperature range show *no* evidence for the existence of this transition. Furthermore, dipole moment data[117] taken in toluene over the temperature range of 268 to 333 K fail to show the existence of a transition similar to that claimed by Pierre and Desreux.[119]

With this background regarding the dependence of polymer conformation on specific solvent–solute interaction, the drastic effect of the addition of pentafluorophenol (PFP) can be considered. Having shown that PFP does not cause chain scission (as do dichloro- and trifluoroacetic acid), Fetters[31] observed the data of Figure 9 by adding PFP to a PBIC–CCl_4 solution. Here η_{sp} is plotted against the mole ratio PFP to monomer of PBIC. It is seen that η_{sp} decreases monotonically with the addition of PFP; there is no critical concentration at which η_{sp} reflects the existence of a phase transition as was suggested earlier by Bur and Roberts.[90] Fetters concluded that the change η_{sp} is not caused by a cooperative helix-coil transition, but rather by a specific solvent-solute interaction which accumulates with the addition of PFP to solution.

Tsvetkov and co-workers[120] recently verified Fetters[31] observation as to the effect of PFP on the rigidity of PBIC in CCl_4. Intrinsic viscosity, flow birefringence, and electrical birefringence (Kerr effect) measurements showed that a considerable decrease in chain rigidity occurred for solutions with up to 20 vol % PFP. Higher concentrations of PFP apparently led to chain degradation.

The change in chain conformation was ascribed[120] to "the effect of the aromatic component of the solvent on the conjugation in the main chain of the polymer". However, this rationalization cannot be taken seriously in view of the fact that trifluoroacetic acid causes a change in poly(*n*-alkyl isocyanate) conformation similar to that observed for PFP. Protonation of the carbonyl oxygen likely occurs leading to a reduction in the steric restrictions which are responsible for the extended molecular posture of the poly(*n*-alkyl isocyanates). These small local adjustments could permit bending and rotational modes of motion and thus lead to increased flexibility in the poly(*n*-alkyl isocyanate) chain.

Tsvetkov and co-workers have attributed to Fetters[31] statements to the effect that the rigidity of the poly(*n*-alkyl isocyanate) chains are due to steric interactions between *only* the alkyl side groups and that the conformational changes induced in the PBIC chain by PFP are equivalent to the helix-coil transition seen for the polypeptides. Unfortunately, these two claims of Tsvetkov and coworkers[120] are misrepresentations of Fetters' conclusions, as a proper understanding of the paper in question[31] reveals.

E. Electric Dichroism in PBIC Solutions

An extensive theoretical and experimental investigation of electric dichroism (ED) has been carried out on dilute solutions of PBIC as a function of $\langle M_w \rangle$ by Troxell and Scheraga.[91] They found positive dichroism from two absorption bands in the ultraviolet which indicated that the molecule was rigid up to $\langle n_w \rangle = 600$ and that there was no evidence of electron delocalization over the whole of the macromolecule. They concluded that the rigidity in the poly(*n*-alkyl isocyanates) arises from a fortunate combination of effects: from a high potential barrier to rotation from the planar amide form, and severe steric interference between the *n*-alkyl side chain and the carbonyl group.

The absorption of light by matter is an anisotropic process since it depends on the interaction of the electric vector of light with the electric dipole transition vector of the absorber. In the ED experiments, light-absorbing molecules are partially oriented by a strong external field, and the rotation, α, of linearly polarized light is measured. By varying the magnitude of the orienting electric field E and the angle θ between E and the major axis of the outgoing polarized light, Troxell and Scheraga[91] were able to obtain molecular information such as polarization of transitions, orientation of chromophores, and the permanent dipole moment of the oriented molecule. Here, we will summarize the theoretical-experimental approach which Troxell and Scheraga developed.

The rotation α of linearly polarized light by a liquid is simplified by setting $\theta = 45°$ and assuming that the electric field dependence of the circular dichroism $(n_L - n_R)$ is negligible. In this case,

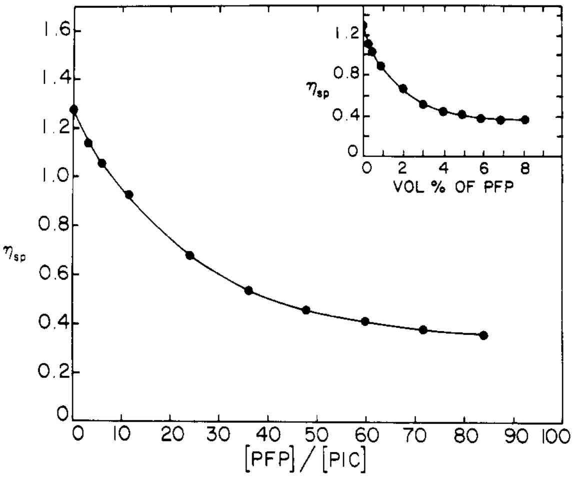


Figure 9. Plot of the specific viscosity vs. the mole ratio of pentafluorophenol to the monomer of PBIC; $\langle n_w \rangle = 1210$. Insert: Plot of the specific viscosity vs. volume percent of pentafluorophenol. PBIC concentration equal to 8×10^{-3} g dl^{-1}.[31]

$$\alpha_{ED,45°} = (\alpha_{E\neq 0} - \alpha_{E=0})_{45°} = 33(\epsilon_{\parallel} - \epsilon_{\perp})/c \quad (17)$$

where α is in degrees, l is the path length in the medium, c is the molar concentration, ϵ is a molar extinction coefficient, and $\parallel$ and $\perp$ indicate linearly polarized light parallel and perpendicular to E. The quantity $(\epsilon_{\parallel} - \epsilon_{\perp})$ is called the electric dichroism, but instead of measuring both $\epsilon_{\parallel}$ and $\epsilon_{\perp}$, Troxell and Scheraga chose the experimentally convenient measurement of $\alpha_{ED,45°}$. $(\epsilon_{\parallel} - \epsilon_{\perp})$ is related to molecular quantities by[91]

$$(\epsilon_{\parallel} - \epsilon_{\perp}) = 3f(x)g(\xi_{0i})\epsilon_{E=0} \quad (18)$$

where $\epsilon_{E=0}$ is the extinction coefficient of the isotropic liquid at $E = 0$, f(x) is an orientation factor for the macromolecule, and g(ξ_{0i}) is a geometric factor for an electric dipole transition moment μ_{0i} of an electronic transition $0 \rightarrow i$. The orientation factor is

$$f(x) = \frac{1}{15}\left[x^2 - \frac{2}{21}x^4 + \frac{1}{105}x^6 - \ldots\right] \quad x = \mu E/kT \quad (19)$$

where μ is the dipole moment of the oriented macromolecule, and E is the internal static orienting field. The geometric factor is

$$g(\xi_{0i}) = (3\cos^2 \xi_{0i} - 1)/2 \quad (20)$$

where ξ_{0i} is the angle between μ_{0i} and μ. μ and g(ξ) are obtained from the ED data by considering α_{45} as a function of E. From eq 17 through 20, α_{45} as a function E has the form

$$\alpha_{ED,45} = A_0E^2 + A_1E^4 \quad (21)$$

where Troxell and Scheraga showed that the E^6 term could be neglected. μ and g(ξ) can be obtained from A_0 and A_1 which are the slope and intercept of a plot of $\alpha_{ED,45}/E^2$ vs. E^2.

Troxell and Sheraga found that the largest macromolecular effects, which they had to consider in their study of PBIC solutions, were main chain flexibility and polydispersity in their fractions. Their samples were well-characterized and reasonably narrow fractions for which $\langle M_w \rangle$, $\langle M_n \rangle$, and the dielectric dispersion were measured. The quantity g(ξ) was found to be a more sensitive indicator of main chain flexibility than were the $\langle \mu^2 \rangle$ data of Bur and Roberts.[90] For a rigid rod, g(ξ) is constant and independent of $\langle \mu_{obsd} \rangle$. In Figure 10 ED data are presented as

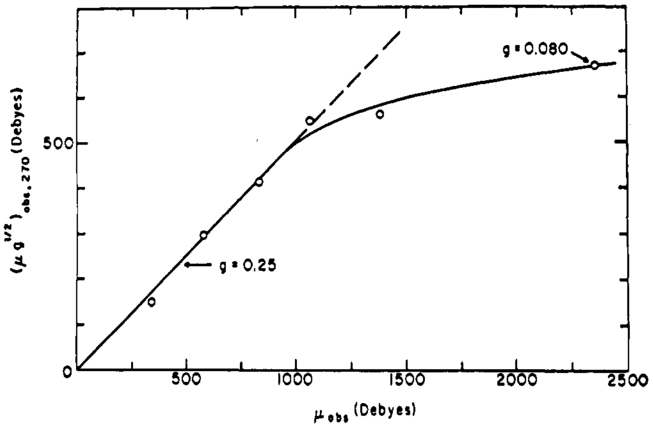


Figure 10. The molecular weight dependence of the PBIC electric dichroism data is presented as $(\mu g^{1/2})_{obsd\ 270}$ vs. μ_{obsd}. For $\mu_{obsd} < 1000$ D, $\mu_{obsd} \propto M_w$. Data of Troxell and Sheraga[91] obtained at 270-mμ wavelength.

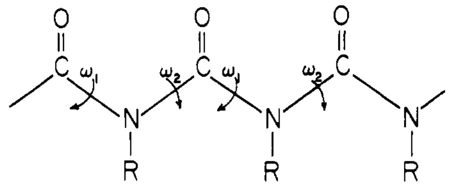
$\mu g^{1/2}$ vs. $\langle \mu_{obsd} \rangle$. The initial constant slope for $\langle \mu_{obsd} \rangle < 600$ is a region of constant g or rigid molecular posture. As $\langle \mu_{obsd} \rangle$ increases molecular flexibility increases and g falls quickly to 0.08 at $\langle \mu_{obsd} \rangle = 2350$. Throughout the measured range of wavelength, the observed value of g was positive and reached a maximum of 0.27. With this information Troxell and Scheraga eliminated the suggestion that electronic delocalization exists over the whole macromolecule. Such delocalization was thought to be due to electron overlap from the partial double bond character of the –NC(=O)– bonds. If delocalization exists, then space group symmetry demands that $\xi = 0$ or 90° for which $g = +1.0$ or -0.5, a situation not observed experimentally. (In spite of these findings, there remain those[101,120] who still ascribe the stiffness of the poly(n-alkyl isocyanate) chains to electronic delocalization).

Two absorption bands were observed,[91] one at 249 mμ and one <203 mμ. The angle ξ for the directions of the polarization of these bands were found to be 53 and 44° for the <203-mμ and 249-mμ band, respectively. Here, ξ is the angle between μ_{0i} and μ. Troxell and Scheraga tentatively assigned the μ_{0i} transitions to primarily along the C=O bond (for the <203-mμ transition) and primarily in the plane of the NC=O group (for the 249-mμ transition).

Using methods developed for conformational energy calculations on the polypeptides,[121] Troxell and Scheraga[91] obtain a helix for the lowest energy configuration. With reference to Figure 11, the helix is described as $(\omega_1, \omega_2) = -40°, 160°$ or 40°, 200°, i.e., left- and right-hand helices of equal energy, where ω_1 and ω_2 equal 0° in the trans configuration. The values of ξ obtained from this helix were 58.5 and 37° which compared favorably with the experimental values of 53 and 44°. The helix is similar to the cis–trans structure of Figure 11, in which the dipole moments perpendicular to the major axis cancel. We discuss the molecular configuration in more detail below.

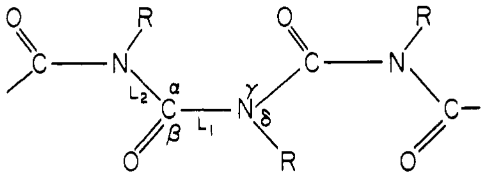
F. Molecular Configuration and Conformational Energy Calculations

The first suggestions regarding the molecular configuration of the poly(n-alkyl isocyanates) were presented by Schneider, Farusaki, and Lenz[89] who speculated that steric interference would eliminate either the planar cis structure or the planar cis–trans structure of Figure 11. In the first case, neighboring alkyl side chains as well as neighboring carbonyl groups are separated by distances much less than is possible by van der Waals radii. Another unfavorable aspect of the trans structure is the repulsive interaction between negatively polarized carbonyl pairs and between pairs of positively polarized nitrogens.



trans configuration

(a)



cis-trans configuration

(b)

Figure 11. Trans and cis–trans configurations of poly(n-alkyl isocyanates).

Considering the cis–trans structure, steric crowding again arises because of the close proximity of the carbonyl oxygen and the methylene carbon of the side chain. One favorable aspect of the cis–trans structure which was noted by Schneider et al.[89] is that the alkyl side chain is in a position to shield the highly polar backbone from the solvent medium, and thereby facilitate the solubility of the polymer in nonpolar solvents.

In order to accommodate the result from dielectric measurements that $\mu_\perp = 0$, Yu, Bur, and Fetters[43] proposed that a helical configuration of the rodlike molecule would produce cancellation of perpendicular dipole elements with a total sum equal to zero. Such a helix could evolve from the planar cis–trans structure by partial rotation about the C–N bonds of the main chain with the result that the steric crowding between carbonyl oxygen and alkyl group is relieved.

The x-ray studies of Shmueli, Traub, and Rosenheck[109] yielded the first definitive evidence of a helix. Although the measurements were made in the crystalline state, an ultraviolet spectrum of a concentrated PBIC solution was observed to be the same as that for a film obtained after evaporation of the solvent. Thus, the equivalence of the atomic configuration in the solid and solution state was established.

X-ray diffraction from oriented and unoriented films of PBIC provided[109] evidence for the hexagonal packing of the molecules. Considering the reflections in terms of helical diffraction theory, Shmueli et al.[109] indexed a meridional reflection at 1.94 Å as (008) which indicated that there are eight monomer units along the c axis. The number of turns per eight monomer units was determined to be three.

While the cell dimensions and helix parameters were obtained directly from the x-ray pattern, Shmueli et al.[109] had less success in calculating atomic coordinates. They found it necessary to make assumptions regarding bonds lengths and bond angles; e.g., the C=O and N—C$_\alpha$ bonds of Figure 11 were assumed to be 1.24 and 1.47 Å and the NCN angle was set at 120°. Other parameters were varied between reasonable limits, and a computer calculation was used to eliminate structures which did not meet their established van der Waals criteria. The result was 31 possible configurations, all of which were very similar and the dimensions of an acceptable configuration are given in Table VIII. The configuration is a helix which can be derived from the cis–trans structure of Figure 11 by slight rotations about the C–N bonds of the main chain so that neighboring amide groups are no longer coplanar.

TABLE VIII. Poly(*n*-alkyl isocyanate) Geometry [a] (See Figure 11)

Author	L_1, Å	L_2, Å	Angle, deg α	β	γ	δ
Han–Yu[122]	1.32	1.32	120	120	106	131
Troxell–Scheraga[91]	1.32	1.32	114	123	114	123
Shmueli et al.[109]	1.41	1.39	120	126	129	112

[a] From A. Tonelli, ref 123.

Another approach to determining the atomic coordinates is via conformational energy and calculations. These have been carried out for the poly(*n*-alkyl isocyanates) by Troxell and Scheraga,[91] Han and Yu,[122] and Tonelli.[123]

Troxell and Scheraga[91] employed the techniques developed for the polypeptides[121] for their calculations. They considered potential energy contributions from nonbonded van der Waals and electrostatic interactions and the intrinsic torsional potential hindering rotation about C–N backbone bonds. They assumed amide geometry and potential constants. The resultant lowest energy conformation was the helix which we referred to above $(\omega_1,\omega_2) = 40°, 160°$ or $40°, 200°$. This helix has eight monomer units per three turns and is very similar to the helix proposed by Shmueli et al.[109] for the crystalline state.

Han and Yu[122] assumed amide-like geometry and permitted nonhelical configurations in their calculations, but they assumed a potential function which contained only steric interactions. This assumption is decidedly weak in view of the experimental observation[31–33] that the rigidity of the molecule is very sensitive to solvent–solute interactions. Polar solvents bring about flexibility in the molecule which could not exist if steric crowding was the sole source of rigidity. The result of the Han–Yu calculations was a helix with two monomer units per turn and rotation angles $(\omega_1, \omega_2) = \pm 95°, \pm 95°$.

Tonelli[123] took a more general approach to the problem and expanded the calculations to include variable geometry, nonhelical configurations, and an estimate of the inherent barrier to rotation about the C–N bonds of the main chain, V_ω. He found that all of the conformational calculations were inconclusive because of the lack of information regarding bond angles, bond lengths, and V_ω. The conformation of the lowest energy helix depends on the assumptions which are made for V_ω and the geometry. Data from suitable model compounds are not available. Because of this, Tonelli[123] proceeded to calculate other conformational properties, radius of gyration and dipole moment, for the proposed helices. The results of his calculations are shown in Tables IX and X. It is seen that the Troxell–Scheraga helix produces the best agreement with experiment. It adequately accounts for the large dipole moment of PBIC in CCl_4, the solvent for which the most rigid posture is observed. The difference between calculated (1.49 D) and experimental (1.13 D) values of μ_0 can be attributed to the distribution of molecular weights in the fractions, to a lack of knowledge regarding the internal electric field of the dielectric experiment, and to uncertainty in the Tonelli computations. When comparing the values of the radius of gyration, $\langle S^2 \rangle$, it must be remembered that the experimental numbers are from light-scattering measurements which were made on $CHCl_3$ solutions. The poly(*n*-alkyl isocyanate) molecule is more flexible in $CHCl_3$ than it is in CCl_4, and the experimental $\langle S^2 \rangle / \langle n_w^2 \rangle$ ratio is expected to be lower than the calculated value. For an ideal rigid rod with $L_0 = 2$ Å, the ratio $\langle S_2 \rangle / \langle n_w^2 \rangle$ would be 0.33 Å^2.

TABLE IX. Helix Parameters

Helix	Monomers/turn	Rotation/monomer (deg)	Translation/monomer (Å)
Tonelli[123]			
$(\omega_1, \omega_2) = \pm 40°$, $\pm 40°$	5[a]	72[a]	2.34[a]
Han–Yu[122]			
$(\omega_1, \omega_2) = \pm 95°$, $\pm 95°$	4	90	1.8
Troxell–Scheraga[91]			
$(\omega_1, \omega_2) = -40°, 160°$ or $40°, 200°$	8/3	141	1.82
Shmueli et al.[109] in crystal	8/3	135	1.94

[a] Geometry of Shmueli et al.[109] was assumed.

TABLE X. Calculated Radii of Gyration and Dipole Moments for Low-Energy Poly(*n*-alkyl isocyanate) Helices [a]

Helix	$\langle S^2 \rangle / n_w^2$, Å^2 [b]	$\mu_0 = \mu / n_w$,[c] D
Tonelli[123]	0.371[d]	0.008[d]
$(\omega_1, \omega_2) =$	0.405[e]	0.007[e]
$\pm 40°, \pm 40°$	0.489[f]	0.32[f]
Han–Yu[122]	0.293[d]	0.006[d]
$(\omega_1, \omega_2) =$	0.318[e]	0.005[e]
$\pm 95°, \pm 95°$	0.405[f]	0.29[f]
Troxell–Scheraga[91]	0.229[d]	2.2[d]
$(\omega_1, \omega_2) = 40°$,	0.256[e]	2.0[e]
$160°$ or $40°, 200°$	0.341[f]	1.49[f]

[a] From A. Tonelli, ref 123. [b] $\langle S^2 \rangle / n_w = 0.14–0.014$ A^2 for PBIC measured in chloroform[12] (see text); for ideal rigid rod with $L_0 = 2$ Å, $\langle S^2 \rangle / n_w^2 = 0.33$ Å^2. [c] $\mu_0 = 1.13$ D for PBIC in CCl_4.[90] [d] Geometry of Han and Yu, ref 122. [e] Geometry of Troxell and Scheraga, ref 91. [f] Geometry of Shmueli et al., ref 109.

The helices of Troxell–Scheraga[91] and Shmueli et al.[109] are similar and can be pictured as close to the cis–trans structure of Figure 11. Slight rotations about the main chain bonds bring neighboring monomer units out of coplanarity but still permit the alkyl side chain to shield the highly polar main chain. The similarity between the molecular conformation in solution and in the crystalline state was borne out experimentally by Shmueli et al.[109] when they observed the same ultraviolet absorption spectra for the solution and the solid film. We conclude that, when the geometry of Shmueli et al.[107] is assumed, the Troxell–Scheraga helix[91] is an accurate representation of poly(*n*-alkyl isocyanate) molecules in solution.

Tonelli[123] also proposed that helix reversal (left to right and vice versa) is the source of flexibility in the higher molecular weight species. He computed an energy for reversal to be 0–3 kcal/mol depending on the magnitude of V_ω. We suggest that, for polar solvents, the solvent–solute interaction produces a large number of reversals in the chain.

G. Solid-State Properties

It appears from the data at hand that the use of the poly(*n*-alkyl isocyanates) in the solid state is limited. This is, in part, because the decomposition temperature is low,[2,47,117] about 140 °C. Dilatometric measurements, which were used to determine this temperature, are shown in Figure 12. As the decomposition products are formed, the volume of the sample increases rapidly. Shashoua et al.[2] attributed this decomposition to impurities such as catalyst residue which will cause depolymerization at these temperatures.

Visual inspection of the dilatometer sample showed that the opaque polymer was being transformed into a clear liquid of low viscosity. Experiments by Iwakura et al.[11] showed that the degradation step involved an unzipping of the polymer chain and that the products were, in the main, monomer and trimer.

Bur and Roberts[117] also carried out dielectric measurements on bulk PBIC. An unfractionated sample was prepared by pressing it in a disk shape at temperatures below 110 °C. The density of the disk at 24 °C was 1.071 g/cm^3 which is somewhat lower than the value[109] of 1.10 g/cm^3, and it indicates that the

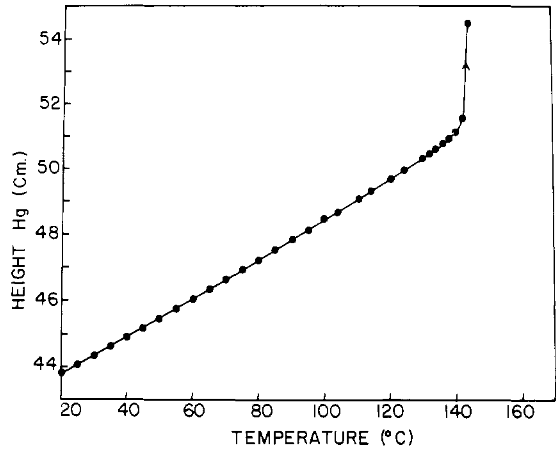


Figure 12. Height of Hg in dilatometer vs. temperature for bulk PBIC. The density of the PBIC sample at 24 °C was 1.0717 g/c^3 and the volume expansion coefficient $\alpha = 5.44 \times 10^{-4}$ °C^{-1} (data of Bur and Roberts[117]).

dielectric sample was highly crystalline with a small amount of voids and/or noncrystalline material. The dielectric loss data at room temperature are shown in Figure 13. There is a well-defined loss peak at 2 MHz with a low-frequency shoulder at 30 kHz. This loss region is tentatively attributed to motion of polar end groups and segmental motion in the region of helix reversal sites. Data as a function of molecular weight and temperature are needed here.

It is well known that solutions of asymmetric biological macromolecules exhibit a liquid crystal phase when the concentration of solute becomes so large that an isotropic distribution of particles costs too much energy.[124] The theory of this phase transition is based on volume exclusion alone; attractive forces between solute molecules are not required. Theory and experiment are in reasonable agreement for the rodlike polypeptides. Bur and Roberts[117] carried out an extensive search for this liquid crystal phase of the asymmetric poly(*n*-alkyl isocyanates) molecules, but they obtained only negative results. Their experiments involved various solvents, concentrations and temperatures of fractions of PBIC. The solvents employed were CCl_4, toluene, chloroform, and trichloroethylenes. Low-angle x-ray, NMR, dielectric, birefringence, and electron microscope measurements were used to search for the liquid crystal phase.

No evidence of aggregation was obtained from room temperature dielectric measurements as a function of concentration (in toluene) on a low molecular weight fraction of PBIC.[117] The measured dipole moment decreased by only 5% over a change in concentration from 10^{-4} to 10^{-2} g/cm^3, and τ was observed to be a continuously increasing function of concentration. However, lowering the temperature of toluene solutions of PBIC brought about an aggregation which formed at −7 °C. The solution became a thixotropic gel containing solvent and PBIC aggregate which melted over a broad temperature range from 33 to 46 °C with the low molecular weight species melting out first. The measurements made on the gel indicated that the aggregate was not a liquid crystal. High-resolution NMR measurements showed that toluene remained in the isotropic liquid state and was not incorporated in a liquid crystal matrix. When observed in a polarizing microscope, the application of a high electric field did not affect the random orientation of the aggregates. This lack of interaction with the electric field suggests that the molecules stack together in pairs with dipole moments pointing in opposite directions.[117] Finally, electron microscope and x-ray measurements confirmed the existence of the crystalline phase. It appears that attractive forces between molecules dominate the transition. It is noteworthy that this crystallization does not occur in trichloroethylene down to a temperature of −65 °C. This is interpreted in terms of the influence of the solvent-solute interaction of the polar trichloroethylene which increases the flexibility of the polymer and thereby produces an increase in entropy of the solution.

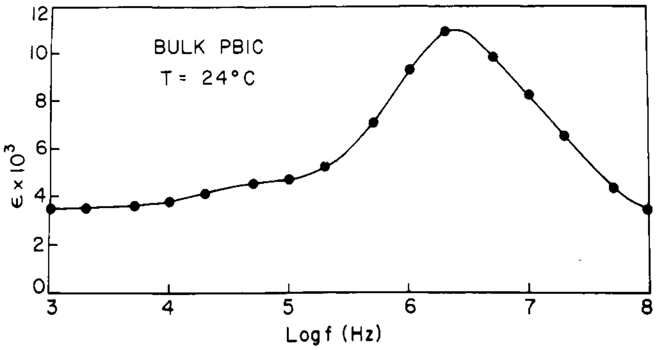


Figure 13. Plot of ϵ'' vs. log *f* for PBIC.[117]

VII. Appendix

Pierre and Marchal[125] have reported that dipole moment data for PHIC and poly(*n*-nonyl isocyanate) samples in carbon tetrachloride ($M_w < 10^5$) show that transitions, i.e., a discontinuity in chain conformation, occur between the temperature of 293 and 313 K. These transitions were deemed to be identical with those previously found from viscosity and light scattering results.[119] As was previously mentioned, the intrinsic viscosity results of Berger and Tidswell[33] fail to show any evidence of such a discontinuous transition. Additional intrinsic viscosity measurements[36] on a low molecular weight PBIC fraction also fail to show the existence of any temperature-dependent transition. It should also be mentioned that the persistence length values, derived from dipole moment data,[126] on a PBIC sample ($\bar{M}_w = 6.5 \times 10^4$, $\bar{M}_n = 2.9 \times 10^4$), show no abrupt "transition" over the temperature range of 293 to 313 K.

The conformation of several poly(aryl isocyanates) has been examined[127] by viscosity and light scattering. Without exception, these polyisocyanates were classified as flexible polymers in a variety of solvents; e.g., the Mark-Houwink exponent, *a*, was found to range from 0.53 to 0.73. These results are similar to those of Tsvetkov[92] pertaining to polyisocyanates with aromatic substituents. No quantitative rationalization currently exists[128] as to how aromatic substituents lead to enhanced flexibility in the polyisocyanate backbone. It should be noted that infrared spectra[129] of poly(*n*-butyl isocyanate) and poly(methylphenyl isocyanate) support the contention that large conformational differences exist between the alkyl and aryl polyisocyanates.

Han and Yu[130] have examined the relaxation processes of PHIC fractions ($\bar{M}_w/\bar{M}_n < 1.1$) in dilute solution by the application of quasi-elastic Rayleigh scattering technique. The relaxation times thus determined were in good agreement with those obtained[90] via dielectric relaxation measurements.

The storage, G', and loss, G'', moduli were measured in dilute solutions for three PHIC samples ($\bar{M}_w/\bar{M}_n < 1.1$) ranging in molecular weight from 9.9×10^4 to 1×10^6. The solvents used were tetralin and tetralin–Aroclor. For the lowest molecular weight sample, the low frequency behavior of the extrapolated intrinsic moduli $[G']$ and $[G'']$ agreed with the Kirkwood–Auer[107] theory for rigid rods. The higher molecular weight samples showed evidence of some chain flexibility. Hence, these viscoelastic measurements coincide with the previously discussed conformational findings for the poly(*n*-alkyl isocyanates).

Utilizing x-ray scattering, Clough has concluded[132] that PHIC in the solid state forms a 12_5 helix. This may be contrasted with the 8_3 helix reported[109] for PBIC. One additional aspect of

Clough's results is that the equatorial spacings apparently showed that the lateral chain packing is not hexagonal as found[109] for PBIC. The translation per monomer was reported[132] to be 1.55 Å These helix parameters are somewhat different from those presented in Table IX for PBIC.

A conformational analysis was carried out[128] for polyisocyanates where the side group was either the methyl, propyl, *n*-butyl, or tolyl group. Regular conformations were found to be plausible for *all* of the polymers. The helical parameters calculated were close to those found for PBIC (Table IX). However, the cause of the difference in the rigidity between the alkyl and aryl polyisocyanates was not found.

Vitovskaya and Tsvetkov[133] have treated the intrinsic viscosity data of Tsvetkov and co-workers[101-103] by the Yamakawa-Fujii theory[135] for the intrinsic viscosity of rigid chain polymers. These results[133] seemingly indicate that the poly(*n*-alkyl isocyanates) can be characterized by a curved rod conformation, even at molecular weights of less than 10^5. This is, of course, at variance with the previously discussed findings pertaining to the conformational characteristics of the poly(*n*-alkyl isocyanates). As a result of their analysis, Vitovskaya and Tsvetkov[133] conclude that the Bur-Fetters interpretation[39] of the dilute solution viscosity properties of PBIC and POIC using the Kirkwood-Auer-Riseman theory[107] was "unjustified". We can only surmise from this comment that Tsvetkov and co-workers[92,98-103,133,134] have yet to recognize and acknowledge both the importance and necessity of working with well-characterized poly(*n*-alkyl isocyanate) fractions of *narrow* molecular weight distributions in order to achieve meaningful insight into the hydrodynamic properties of these polymers. To date, Tsvetkov and co-workers[92,98-103,133,134] have yet to publish complete characterization data pertaining to their polyisocyanate "fractions".

Quantum chemical calculations[136-141] have been carried out for a series of isocyanates with the aim of establishing which atom in the nitrogen-carbon or carbon-oxygen double bond pair would bear the negative charge after anionic attack. It was determined[136-141] that, independent of the identity of the substituent on the nitrogen atom, the anion will reside on the nitrogen atom. This, of course, is in accord with Sashoua's[2] original mechanism. These quantum chemical treatments apparently established that the carbonyl group would not respond to anionic attack. However, this is not in accord with the experimental observations[40,41,50,53,55] where the carbonyl double bond was found to participate in the anionic polymerization of some di- and triisocyanates.

The stabilities of a series of alkyl and aromatic polyisocyanates were examined under electron bombardment.[142] This electron beam (5 keV) induced depolymerization produced only monomer as the degradation product for the aliphatic polyisocyanates. The degradation product for the aromatic polymer was not identified. The mechanism by which this degradation proceeded was not elucidated.

Ambler and McIntyre[143,144] have checked the universality of the universal calibration concept[145] for gel permeation chromatography with a series of PBIC fractions. They have found that high molecular weight PBIC, which is not a true rigid rod but rather a wormlike chain, fits the $M[\eta]$ calibration whereas true rodlike PBIC does not. These results indicate that $M[\eta]$ can serve as a universal calibration only when the molecular conformation of all the species involved are similar, i.e., either flexible Gaussian coils or rigid rods.

Ambler[144] has also shown that the log $\overline{M}_w$ vs. elution count calibration for PBIC fractions is nonlinear over the *entire* molecular weight range of 3×10^4 to 1.2×10^7 g mol^{-1}. This demonstrates that accurate characterization of the poly(*n*-alkyl isocyanates) by gel permeation chromatography cannot be accomplished from calibrations based on the use of Gaussian coils (polystyrene), a procedure which has apparently been used by others.[38,119,125]

VIII. Addendum

As we have noted, the poly(*n*-alkyl isocyanate) molecule changes conformation from rodlike to random coil over the molecular weight range of 2.0×10^4 to 1.2×10^7 g mol^{-1}. A polydisperse sample thus will contain a "dual" distribution, i.e., of molecular weights *and* molecular conformations. Hence, well-characterized, reasonably sharp fractions must be used for any hydrodynamic study in order to obtain data which can be evaluated quantitatively. References 12, 33, 39, 90, 91, 94, 95, 97, 130, 131, and 143 contain all of the data from samples which possessed near monodisperse molecular weight distributions. These fractions were characterized via membrane osmometry, light scattering, and the spectrum of dielectric relaxation times at the National Bureau of Standards. All of these samples were synthesized via anionic polymerization using high-vacuum conditions.[146,147]

We should also note that the PBIC fraction of 36.1 was reported in ref 12 and 90 as having an $\langle M_w \rangle$ of 1.0×10^7 g mol^{-1}. This sample has been recharacterized[113] at the Institute of Polymer Science via low-angle light scattering. The revised $\langle M_w \rangle$ is $1.2\ (\pm 0.05) \times 10^7$ g mol^{-1}.

We also wish to note that samples 1 through 3 and 6 of ref 91 are, respectively, samples 37-2b, 37-4, 37^1-2a, and 1^1-2 of ref 90. Sample 4 of ref 91 is sample KI-2 of ref 39 and 94. Samples 1 through 4 of ref 97 are samples 37-2a, 37-3, 21, and 37-1a of ref 12, 39, and 94. Sample 5 of ref 97 is sample 14-1 of ref 12 and 90.

IX. References

(1) V. E. Shashoua, *J. Am. Chem. Soc.*, **81**, 3156 (1959).
(2) V. E. Shashoua, W. E. Sweeny, and R. F. Tietz, *J. Am. Chem. Soc.*, **82**, 816 (1960).
(3) A. W. Hofmann, *Ber.*, **3**, 761 (1870).
(4) H. L. Snape, *J. Chem. Soc.*, **49**, 254 (1886).
(5) R. G. Arnold, J. F. Nelson, and J. J. Verbane, *Chem. Rev.*, **57**, 47 (1957).
(6) J. H. Saunders and R. J. Slocombe, *Chem. Rev.*, **43**, 203 (1948).
(7) R. G. Arnold, J. F. Nelson, and J. J. Verbane, *J. Chem. Educ.*, **34**, 158 (1957).
(8) J. Idris and N. G. Savill, *J. Chem. Soc.*, 4392 (1957).
(9) E. C. Juence and W. C. Francis, *J. Org. Chem.*, **26**, 3334 (1961).
(10). G. Natta, J. DiPietro, and M. Cambini, *Makromol. Chem.*, **72**, 202 (1964).
(11) Y. Iwakura, K. Uno, and N. Kobayashi, *J. Polym. Sci., Part A-1,* **6**, 1087 (1968).
(12) L. J. Fetters and H. Yu, *Macromolecules,* **4**, 385 (1971).
(13) P. L. Pickard and G. W. Polly, *J. Am. Chem. Soc.*, **76**, 5169 (1954).
(14) E. Lieber, D. Levering, and L. Patterson, *Anal. Chem.*, **23**, 1594 (1951).
(15) R. C. Fuson, W. D Emmons, and J. P. Freeman, *J. Am. Chem. Soc.*, **75**, 5321 (1953).
(16) J. Furukawa, S. Yamashita, M. Maruhashi, and K. Harada, *Makromol. Chem.*, **85**, 80 (1965).
(17) J. Furukawa, S. Yamashita, K. Harada, and H. Satani, *Kogyo Kagaku Zasshi,* **70**, 1013 (1967); *Chem. Abstr.*, **68**, 96183q (1968).
(18) K. Harada, A. Deguchi, J. Furukawa, and S. Yamashita, *Makromol. Chem.*, **132**, 281 (1970).
(19) Y. Iwakura, K. Uno, and N. Kobayashi, *J. Polym. Sci., Part A-2,* **4**, 1013 (1966).
(20) C. G. Overberger, S. Ozaki, and H. Mukamal, *J. Polym. Sci., Part B,* **2**, 627 (1964).
(21) R. C. Schulz and R. Stenner, *Makromol. Chem.*, **72**, 202 (1964).
(22) R. C. Schulz and H. Hartmann, *Makromol. Chem.*, **55**, 227 (1962).
(23) R. Hart, *Bull. Soc. Chim. Belg.*, **65**, 291 (1956).
(24) T. Kashiwagi, M. Hidai, Y. Uchida, and A. Misono, *J. Polym. Sci., Part B,* **8**, 173 (1970).
(25) H. Sobue, Y. Tabata, M. Hiraoka, and K. Oshima, *J. Polym. Sci., Part C,* No. 4, 943 (1964).
(26) Y. Iwakura, K. Uno, and N. Kobayashi, *Bull. Chem. Soc. Jpn.*, **39**, 2551 (1966).
(27) I. Sugawara, E. Marchal, H. Kadoi, Y. Tabuta, and K. Oshima, *J. Macromol. Sci. Chem.*, **A8**, 995 (1974).
(28) G. S. Shapoval, E. M. Skobets and N. P. Markova, *Vysokomol. Soedin.*, **8**, 1313 (1966); *Polym. Sci., USSR,* **8**, 1444 (1965); *Dokl. Akad. Nauk SSSR,* **173**, 392 (1967); *Chem. Abstr.*, **67**, 11894d (1967).
(29) G. S. Shapoval, N. P. Markova, and E. M. Skobets, *Sint. Fiz.-Khim. Polim.*, No. 5, 76 (1968); *Chem. Abstr.*, **70**, 4677u (1969).
(30) M. Goodman and S. Chen, *Macromolecules,* **3**, 398 (1970).
(31) L. J. Fetters, *J. Polym. Sci., Part B,* **10**, 577 (1972).
(32) M. N. Berger, *J. Macromol. Sci. Rev. Macromol. Chem.*, **69**, 269 (1973).
(33) M. N. Berger and B. M. Tidswell, *J. Polym. Sci., Part C,* No. 42 1063 (1973).

(34) M. Goodman and S. Chen, *Macromolecules,* **4,** 625 (1971).
(35) T. Minami, H. Kawai, T. Agawa, and S. Komori, *Kogyo Kagaku Zasshi,* **70,** 222 (1967); *Chem. Abstr.,* **68,** 40163r (1968).
(36) L. J. Fetters, unpublished observations.
(37) H. Mukamal, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1966.
(38) R. A. Godfrey and G. W. Miller, *J. Polym.· Sci., Part A-1,* **7,** 2387 (1969).
(39) A. J. Bur and L. J. Fetters, *Macromolecules,* **6,** 874 (1973).
(40) G. C. Corfield and A. Crawshaw, *J. Polym. Sci., Part A-1,* **7,** 1179 (1969).
(41) G. C. Corfield and A. Crawshaw, *J. Macromol. Sci., Chem.,* **A5,** 3 (1971).
(42) C. G. Overberger and J. A. Moore, *Encycl. Polym. Sci. Technol.,* **7,** 743 (1967).
(43) H. Yu, A. J. Bur, and L. J. Fetters, *J. Chem. Phys.,* **51,** 406 (1966).
(44) M. Szwarc, M. Levy, and R. Milkovich, *J. Am. Chem. Soc.,* **78,** 2656 (1956).
(45) D. H. Richards and M. Szwarc, *Trans. Faraday Soc.,* **55,** 1644 (1959).
(46) M. Morton, A. Rembaum, and E. E. Bostick, *J. Polym. Sci.,* **32,** 530 (1958).
(47) L. A. Wall, private communication from the National Bureau of Standards, 1966.
(48) G. C. Robinson, *J. Polym. Sci.,* **A2,** 3901 (1964).
(49) C. King, *J. Am. Chem. Soc.,* **86,** 437 (1964).
(50) G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.,* **79,** 3128 (1957); C. L. McCormick and G. B. Butler, *J. Macromol. Sci., Rev. Macromol. Chem.,* **C8,** 201 (1972).
(51) Y. Iwakura, K. Uno, and K. Ichikawa, *J. Polym. Sci.,* **A2,** 3387 (1964).
(52) W. L. Miller and W. B. Black, *Polym. Prepr.,* **3,** No. 1, 345 (1962).
(53) G. C. Corfield and A. Crawshaw, *Chem. Commun.,* No. 4, 85 (1966).
(54) A. Oku, T. Shono, and R. Oda, *Makromol. Chem.,* **100,** 224 (1967).
(55) G. B. Butler and G. C. Corfield, *J. Macromol. Sci., Chem.,* **A5,** 37 (1971).
(56) H. Staudinger, F. Felix, and E. Geiger, *Helv. Chim. Acta,* **8,** 314 (1925).
(57) K. Harada, J. Furukawa, and S. Yamashita, *Makromol. Chem.,* **131,** 185 (1971).
(58) Y. Kitayama, H. Ohama, and H. Kobayashi, *J. Polym. Sci., Part A-1,* **7,** 935 (1969).
(59) H. Takida and T. Noro, *Kobunshi Kagaku,* **22,** 463 (1965); *Chem. Abstr.,* **64,** 2174b (1966).
(60) Spencer Chemical Co. British Patent 959 527 (1964).
(61) Japanese Patent 46-10184 (1971).
(62) Y. P. Getmanchuk, Y. L. Spirin, R. I. Dryagileva, and N. P. Doroshenko, *Sint. Fiz.-Khim. Polim.,* No. 5, 84 (1968); *Chem. Abstr.,* **70,** 29353y (1969).
(63) Y. P. Getmanchuk, Y. L. Spirin, and R. I. Dryagileva, *Vysokomol. Soedin.,* **10,** 139 (1968); *Polym. Sci. USSR,* **10,** 162 (1968).
(64) Y. P. Getmanchuk, Y. L. Spirin, and R. I. Dryagileva, *Dokl. Akad. Nauk SSSR,* **171,** 1105 (1966); *Chem. Abstr.,* **66,** 65863r (1967).
(65) M. C. Raes, J. V. Karabinos, and H. J. Dietrich, *J. Polym. Sci., Part A-1,* **6,** 1067 (1968).
(66) G. Odian and L. S. Hiraoka, *J. Polym. Sci., Part A-1,* **8,** 1309 (1970).
(67) G. Odian and L. S. Hiraoka, *J. Macromol. Sci., Chem.,* **A6,** 109 (1972).
(68) K. Hashimoto and H. Sumitomo, *J. Polym. Sci., Part A-1,* **9,** 107 (1971).
(69) K. Hashimoto and H. Sumitomo, *J. Polym. Sci., Part A-1,* **9,** 1747 (1971).
(70) S. Nunomoto and Y. Yamashita, *Kogyo Kagaku Zasshi,* **71,** 2067 (1968); *Chem. Abstr.,* **70,** 47947 (1969).
(71) Y. Yamashita, S. Nunomoto, and S. Miura, *Kogyo Kagaku Zasshi,* **69,** 317 (1966); *Chem. Abstr.,* **66,** 86032 (1967).
(72) H. Higashi and H. Harada, *Kogyo Kagaku Zasshi,* **69,** 2344 (1966); *Chem. Abstr.,* **66,** 105236 (1967).
(73) Japanese Patent 11,140 (1969); *Chem. Abstr.,* **71,** 71176 (1969).
(74) E. Dyer and E. Sincich, *J. Polym. Sci., Polym. Chem. Ed.,* **11,** 1249 (1973).
(75) G. B. Butler and S. B. Monroe, *J. Macromol. Sci., Chem.,* **A5,** 1063 (1971).
(76) G. B. Butler and S. B. Monroe, *J. Macromol. Sci., Chem.,* **A5,** 1057 (1971).
(77) J. Cazes, *J. Chem. Educ.,* **43,** A 567 (1966).
(78) British Patent 987 741 (1965); Japanese Patent 40-12,304 (1965); *Chem. Abstr.,* **62,** 1818a (1965).
(79) M. Morton and L. J. Fetters *Macromol. Rev.,* **2,** 101 (1967).
(80) W. L. Hergenrother and R. J. Ambrose, *J. Polym. Sci., Part B,* **10,** 679 (1972).
(81) W. L. Hergenrother and R. J. Ambrose, *J. Polym. Sci., Polym. Lett. Ed.,* **12,** 343 (1974).
(82) D. Decker and P. Rempp, *C. R. Acad. Sci.,* **261,** 1977 (1965).
(83) D. J. Worsfold, J. G. Zilliox, and P. Rempp, *Can. J. Chem.,* **47,** 3379 (1969).
(84) J. G. Zilliox, *Makromol. Chem.,* **156,** 121 (1972).
(85) A. Kohler, J. Placek, I. Koessler, J. G. Zilliox, and P. Rempp, *Eur. Polym. J.,* **8,** 627 (1972).
(86) L. K. Bi, L. J. Fetters, and M. Morton, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.,* **15,** 157 (1974).
(87) L. K. Bi and L. J. Fetters, *Macromolecules,* **8,** 90 (1975); 732 (1976).
(88) W. Buchard, *Macromol. Chem.,* **67,** 182 (1963).
(89) N. S. Schneider, S. Furusaki, and R. W. Lenz, *J. Polym. Sci., Part A-3,* 933 (1965).
(90) A. J. Bur and D. E. Roberts, *J. Chem. Phys.,* **51,** 406 (1969).
(91) T. C. Troxell and H. A. Scheraga, *Macromolecules,* **4,** 528 (1971).
(92) V. N. Tsvetkov, I. N. Shtennikova, E. I. Rjumtsev, L. N. Andeyeva, Y. P. Getmanchuk, Y. L. Spirin, and R. I. Dryagileva, *Vysokomol. Soedin., Ser. A,* **10,** 2132 (1968); *Polym. Sci. USSR,* **10,** 2482 (1968).
(93) H. Plummer and B. R. Jennings, *Eur. Polym. J.,* **6,** 171 (1970).
(94) A. J. Bur, *J. Chem. Phys.,* **52,** 3813 (1970).
(95) B. R. Jennings and B. Brown, *Eur. Polym. J.,* **7,** 805 (1971).
(96) R. Y. Lochhead and A. M. North, *J. Chem. Soc., Faraday Trans. 2,* **68,** 1089 (1972).
(97) J. B. Milstein and E. Charney, *Macromolecules,* **2,** 678 (1969).
(98) V. N. Tsvetkov, I. N. Shtennikova, E. I. Rjumtsev, and Y. P. Getmanchuk, *Eur. Polym. J.,* **7,** 767 (1971).
(99) V. N. Tsvetkov, E. I. Rjumtsev, F. M. Aliev, and I. N. Shtennikova, *Eur. Polym. J.,* **10,** 55 (1974).
(100) V. N. Tsvetkov, E. I. Rjumtsev, F. M. Aliev, I. N. Shtennikova, and S. M. Savvon, *Vysokomol. Soedin., Ser. A,* **16,** 1401 (1974); *Polym. Sci. USSR, Ser. A,* **16,** 1627 (1974).
(101) V. N. Tsvetkov, T. V. Pekker, Y. P. Getmanchuk, P. N. Lavrenko, and S. V. Bushin, *Vysokomol. Soedin., Ser. A,* **16,** 566 (1974); *Polym. Sci. USSR, Ser. A,* **16,** 655 (1974).
(102) V. N. Tsvetkov, E. I. Rjumstev, N. V. Pogodina, and I. N. Shtennikova, *Eur. Polym. J.,* **11,** 37 (1975).
(103) I. N. Shtennikova, V. N. Tsvetkov, T. V. Pekker, E. I. Rjumtsev, and Y. P. Getmanchuk, *Vysokomol. Soedin., Ser. A,* **16,** 1086 (1974); *Polym. Sci. USSR, Ser. A,* **16,** 1256 (1974).
(104) A. J. Bur, D. E. Roberts, and L. J. Fetters, unpublished observations.
(105) F. Perrin, *J. Phys. Radium,* **5,** 497 (1934).
(106) J. M. Burgers, "Second Annual Report on Viscosity and Plasticity", Nordemann Publishing Co., New York, N.Y., 1938, p 117; *Verh K. Ned. Akad. Wet., Afd. Natuurk., Reeks 1,* **16** (4), 113 (1938).
(107) J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.,* **19,** 281 (1951); J. Riseman and J. G. Kirkwood, "Rheology", Vol. I, F. Eirich, Ed., Academic Press, New York, N.Y., 1956, p 508.
(108) S. Broersma, *J. Chem. Phys.,* **32,** 1626 (1960).
(109) U. Schmueli, W. Traub, and K. Rosenheck, *J. Polym. Sci., Part A-2,* **7,** 515 (1969).
(110) G. Porod, *Monatsh. Chem.,* **80,** 251 (1949).
(111) O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas,* **68,** 1106 (1949).
(112) S. F. Kurath, C. A. Schmitt, and J. J. Bachhuber, *J. Polym. Sci., Part A,* **3,** 1825 (1965).
(113) M. Ambler, D. McIntyre, and L. J. Fetters, submitted for publication.
(114) H. Benoit and P. Doty, *J. Phys. Chem.,* **57,** 958 (1953).
(115) P. J. Flory, "Statistical Mechanics of Chain Molecules", Wiley, New York, N.Y., 1969, p 11.
(116) B. H. Zimm, *J. Chem. Phys.,* **14,** 164 (1946).
(117) A. J. Bur and D. E. Roberts, unpublished observations.
(118) J. S. Anderson and W. E. Vaughn, *Macromolecules,* **8,** 454 (1975).
(119) J. Pierre and V. Desreux, *Polymer,* **15,** 685 (1974).
(120) V. N. Tsvetkov, E. I. Rjumtsev, I. N. Shtennikova, N. V. Pogodina, and T. V. Pekker, *Eur. Polym. J.,* **11,** 315 (1975).
(121) H. A. Sheraga, *Adv. Phys. Org. Chem.,* **6,** 103 (1968); *Chem. Rev.,* **71,** 195 (1971).
(122) C. C. Han and H. Yu, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.,* **14,** 121 (1973).
(123) A. Tonelli, *Macromolecules,* **7,** 628 (1974).
(124) C. Robinson, J. C. Ward, and R. B. Beevers, *Discuss. Faraday Soc.,* **25,** 29 (1958).
(125) J. Pierre and E. Marchal, *J. Polym. Sci., Polym. Lett. Ed.,* **13,** 11 (1975).
(126) S. B. Dev, R. Y. Lochhead, and A. M. North, *Discuss. Faraday Soc.,* **44,** 244 (1970).
(127) L. Lecomte and V. Desreux, *Polymer,* **16,** 765 (1975).
(128) I. S. Milevskaya, T. M. Birshtein, and V. A. Zubkov, *Vysokomol. Soedin., Ser. A,* **16,** 2787 (1974); *Polym. Sci. USSR,* **16,** 3249 (1975).
(129) B. Z. Volchek and V. N. Nikitin, *Dokl. Akad. Nauk SSSR,* **205,** 622 (1972).
(130) C. Han and H. Yu, *J. Chem. Phys.,* **61,** 2650 (1974).
(131) N. Nemoto, J. L. Schrag, and J. D. Ferry, *Polym. J.,* **7,** 195 (1975).
(132) S. B. Clough in "Characterization of Materials in Research: Ceramics and Polymers", J. J. Burke and V. Weiss, Ed., University Press, Syracuse, N.Y., 1975, p 417.
(133) M. G. Vitovskaya and V. N. Tsvetkov, *Eur. Polym. J.,* **12,** 251 (1976).
(134) M. G. Vitovskaya, P. N. Laurenko, I. N. Shtennikova, A. A. Gorbunov, T. V. Peker, E. V. Korneeva, E. P. Astapenko, Yu. P. Getmanchuk, and V. N. Tsvetkov, *Vysokomol. Soedin., Ser. A,* **17,** 1917 (1975).
(135) H. Yamakawa and M. Fujii, *Macromolecules,* **7,** 128 (1974).
(136) V. B. Zabrodin, A. A. Bagatur'yants, and S. G. Entelis, *Zh. Fiz. Khim.,* **42,** 2324 (1968).
(137) S. P. Bondarenko, R. P. Tiger, Ye. V. Borisov, A. A. Bagatur'yants, and S. G. Entelis, *Zh. Org. Khim.,* **10,** 271 (1974).
(138) B. M. Rode, W. Kosmus, and E. Nachbaur, *Chem. Phys. Lett.,* **17,** 186 (1972).
(139) Yu. P. Yegorov, A. A. Kisilenko, and V. V. Pen'kovskii, *Teor. Eksp. Khim.,* **8,** 613 (1972).
(140) A. O. Litinskii, A. I. Shreibert, L.-M. Z. Balyavichus, and A. B. Botolotin, *Teor. Eksp. Khim.,* **8,** 807 (1972).
(141) R. P. Tiger, S. P. Bondarenko, and S. G. Entelis, *Vysokomol. Soedin., Ser. A,* **17,** 605 (1975); *Polym. Sci. USSR,* **17,** 697 (1976).
(142) A W. Levine, M. Kaplan, and J. Fech, Jr., *J. Polym. Sci., Polym. Chem. Ed.,* **11,** 311 (1973).
(143) M. R. Ambler and D. McIntyre, *J. Polym. Sci., Polym. Lett. Ed.,* **13,** 589 (1976).
(144) M. R. Ambler, Ph.D. Thesis, Akron University, 1975.
(145) Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci., Ser. B,* **5,** 753 (1967).
(146) L. J. Fetters, *J. Res. Natl. Bur. Stand., Sect. A,* **70,** 421 (1966).
(147) M. Morton and L J. Fetters, *Rubber Rev., Rubber Chem. Technol.,* **48,** 359 (1975).