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Anionic Copolymerization of Aldehydes with Isocyanates

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SUMMARY

The anionic copolymerization of various aldehyde-isocyanate comonomer systems was studied. The order of reactivity for the aldehyde monomers was found to be chloral = formaldehyde > n-butyraldehyde; that for the isocyanates was phenyl isocyanate > n-butyl isocyanate. The observed reactivity of the aldehyde monomer increases as the anionic propagating ion and its gegenion are more tightly bound. This is observed when copolymerization is carried out either in a poor solvent or when the gegenion is lithium instead of sodium. Under these conditions, the aldehyde monomer preferentially solvates the propagating center and its observed reactivity is enhanced.

INTRODUCTION

Some work has been reported on the anionic copolymerization of aldehydes and isocyanates. Takida and Noro [1] studied the copolymerizations of acetaldehyde, n-butyraldehyde, and chloral with ethyl and phenyl isocyanates. The copolymerization of chloral and phenyl isocyanate has been studied by several workers [2, 3]. The copolymerization of small amounts of an isocyanate with formaldehyde for endcapping purposes has been reported in the patent literature [4, 5]. We have studied the anionic copolymerization of various aldehyde-isocyanate systems from the viewpoint of ascertaining information on monomer reactivities and the effects of solvent and initiator on copolymerization behavior. The monomers chosen for study were n-butyl and phenyl isocyanates and formaldehyde, chloral, and n-butyraldehyde. The initiators used were n-butyllithium, potassium cyanide, and sodium naphthalene; the solvents were n-hexane, diethyl ether, tetrahydrofuran, and dimethylformamide.

EXPERIMENTAL

Materials

Chloral and n-butyl isocyanate (Eastman Chemicals Co.) were dried by treatment with 4Å molecular sieves and calcium sulfate, respectively. n-Butyraldehyde (Eastman Chemicals Co.) was treated with sodium carbonate for drying purposes and to eliminate butyric acid (a strong inhibitor in anionic polymerization). These monomers were distilled under nitrogen. Phenyl isocyanate (Matheson, Coleman and Bell Co.; bp 60-62°C/20 mm) was used without further purification. Formaldehyde was obtained by heating paraformaldehyde (Matheson, Coleman and Bell Co.) under dry nitrogen and condensing the vapors at -75°C. Most monomers were used immediately after purification or were stored under conditions whereby they were stable. (The isocyanates were stable at -20°C.)

The solvents used were all Certified Reagent grade. Anhydrous diethyl ether was used without purification. n-Hexane and tetrahydrofuran were dried with metallic sodium and dimethylformamide with potassium hydroxide pellets prior to distillation under nitrogen.

n-Butyllithium, obtained from Alfa Inorganics Co. as a 20 wt-% solution in n-hexane, was diluted by a 25-fold addition of n-hexane to produce an 0.084 M solution. An 0.29 M solution of sodium naphthalene in tetrahydrofuran was prepared by reacting sodium with naphthalene in tetrahydrofuran. Potassium cyanide was dissolved in dimethylformamide to form a saturated solution (0.0318 M) at room temperature.

Polymerization

Polymerizations were carried out in ground-glass stoppered test tubes. The test tubes and various transferring devices (pipets, syringes) were oven dried and then flushed with dry nitrogen; most of the manipulations were carried out in a dry-box which was continuously flushed with nitrogen. Reaction temperatures of -40, -65, and -75°C were studied by using mixtures of Dry Ice with chlorobenzene, chloroform, and acetone (or methanol), respectively. The comonomer mixture (8 ml) and solvent (10 ml) were added to the reaction vessel, thermally equilibrated in a Dewar flask containing the coolant bath, and then 2-3 ml of the initiator solution (which was separately cooled to the reaction temperature) was added and the reaction vessel capped. The solvent of the initiator solution was often not the same as that of the reaction mixture but it constituted a small concentration (ca. 10% by volume of the reaction mixture) and did not affect our studies from the viewpoint of obtaining relative results.

In all cases the polymer formed was insoluble in the reaction mixture. Monomer conversions were kept to less than 10%; the reaction times were usually less than 1 hr. Polymerization was quenched with either a 5% hydrochloric acid solution in methanol or an 8:1 mixture (by volume) of acetic acid and acetone. Quenching was carried out overnight (18 hr) at -75°C to ensure that encapping was complete and to prevent possible depolymerization. The insoluble copolymer was filtered, washed with methanol and/or acetone, and dried at room temperature under vacuum. (Reactions with phenyl isocyanate in dimethylformamide yielded the cyclic trimer of phenyl isocyanate as a minor by-product. This by-product is soluble in methanol and acetone and is removed by the washing procedure.)

Analysis of Copolymers

The compositions of the various isocyanate-aldehyde copolymers were determined by IR spectroscopy. Infrared spectra were taken using suspensions of the copolymers in Nujol. Typical of the spectra obtained are those in Fig. 1 for the phenyl isocyanate and n-butyraldehyde copolymer and homopolymers. Quantitative analysis was performed using the carbonyl absorption at 5.8-5.9 μ for the isocyanate component of the copolymers and the C-O-C absorption in the 10-11 μ region for the aldehyde component. Mixtures of the

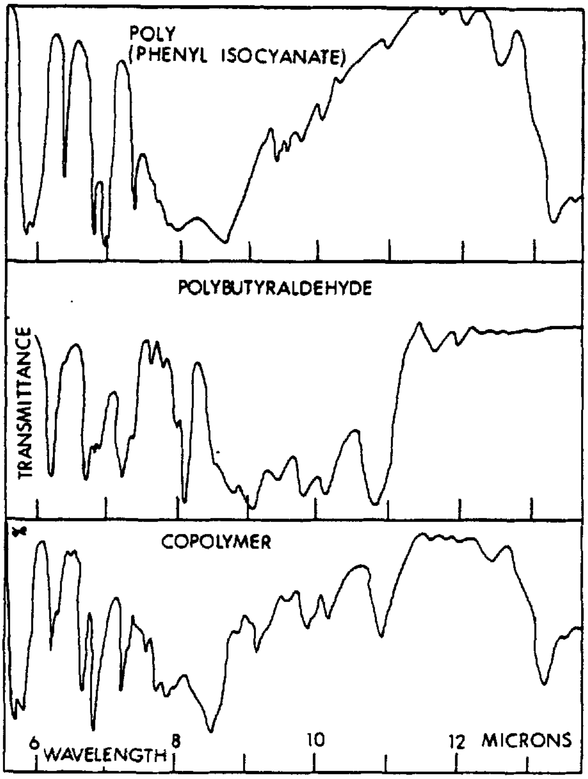

FIG. 1. Infrared spectra of Nujol mulls of phenyl isocyanate and n-butyraldehyde homopolymers and copolymer.

two homopolymers were prepared, their IR spectra obtained, and then a calibration curve of F_1 vs. $A_1/(A_1 + A_2)$ obtained (where F_1 is the mole fraction of aldehyde in the copolymer, and A_1 and A_2 are, respectively, the absorbances of the IR peaks for the aldehyde and isocyanate components). A typical calibration curve, that for the n-butyraldehyde—n-butyl isocyanate system, is shown in Fig. 2. The compositions of the various aldehyde-isocyanate copolymers were obtained by determining their $A_1/(A_1 + A_2)$ values and then referring to the appropriate calibration curve. The general accuracy of the analyses for copolymer composition was considered to be within ±10%.

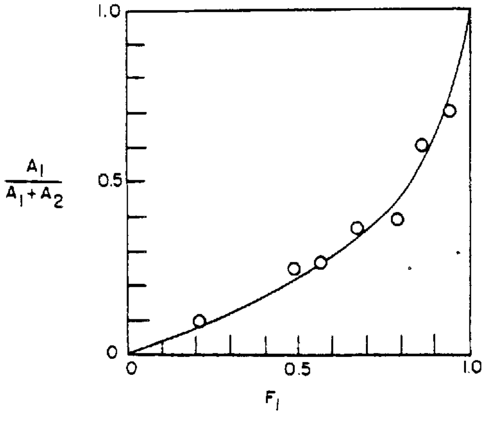

FIG. 2. Infrared calibration curve for the n-butyraldehyde (M_1)—n-butyl isocyanate (M_2) system.

Infrared spectroscopy established the presence of both monomer components in the products obtained from the polymerization of various aldehyde-isocyanate comonomer mixtures. Differential thermal analysis or solubility characteristics were used to show that the products were copolymers and not mixtures of homopolymers or mixtures of a copolymer and a homopolymer. Except for the n-butyraldehyde—n-butyl isocyanate copolymers which were not tested by DTA, the products in all of the other comonomer systems showed a single sharp melting point.

A typical differential thermogram is shown in Fig. 3. The presence of a single melting point is indicative of a copolymer; a mixture of either two homopolymers or of a copolymer with a homopolymer would generally be expected to yield a thermogram with two melting points. The solubility characteristics of the various products substantiated their designations as copolymers:

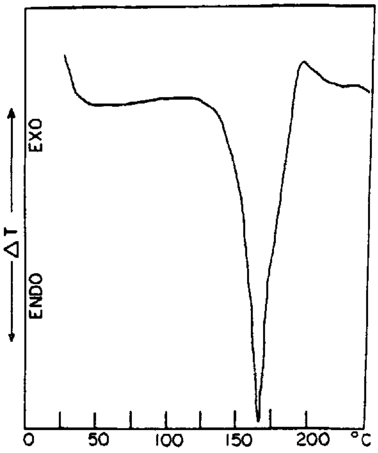

FIG. 3. DTA curve for a n-butyraldehyde—phenyl isocyanate copolymer.

1) Poly(n-butyl isocyanate) is soluble in chloroform while poly (n-butyraldehyde) and the copolymer are insoluble. The solubility characteristics are the only determinants of the copolymer nature of the products in this system.

2) Polychloral, poly(n-butyl isocyanate), and the copolymer are, respectively, insoluble, soluble, and moderately soluble in chloroform.

3) Poly(n-butyl isocyanate) is soluble in chloroform while polyformaldehyde and the copolymer are insoluble.

4) Poly(n-butyraldehyde) is soluble in boiling trichloroethylene while poly(phenyl isocyanate) and the copolymer are insoluble.

5) Polychloral and poly(phenyl isocyanate) are insoluble in chloroform while the copolymer produced using n-butyllithium

as the initiator is soluble. The KCN initiated product is insoluble in chloroform; in this case, DTA serves as the sole method of analyzing the copolymer. (The difference in solubilities between the KCN and n-butyllithium initiated copolymers is ascribed to high and low degrees of stereoregularity, respectively, in the two products.)

6) No useful solubility tests were found for the formaldehyde-phenyl isocyanate copolymer. The DTA data are the sole determinant of the copolymer nature of the products in this system.

RESULTS AND DISCUSSION

Reaction Conditions Free of Depropagation

In order to obtain meaningful data on monomer reactivities and the effects of solvent and initiator in the various aldehyde-isocyanate systems, it was necessary to establish polymerization conditions of temperature and monomer concentration which were free of depropagation. Literature data on ceiling temperatures indicate that n-butyraldehyde is the most prone of all the aldehyde monomers studied toward depropagation. It was found in our studies that the two isocyanate monomers were less prone toward depropagation than n-butyraldehyde. The n-butyraldehyde—phenyl isocyanate system was then chosen for study to determine the effects of temperature and monomer concentration on copolymerization behavior. Table 1 shows data for various copolymerizations carried out with comonomer mixtures of varying concentration at a constant n-butyraldehyde composition of 23 wt-% with n-butyllithium and diethyl ether as the initiator and solvent, respectively. The results show that depolymerization is occurring to different extents at reaction temperatures of -65°C and higher. Polymerization did not occur at -40°C over a range of monomer concentrations from 0.66 to 2.0 M. At -65°C only poly(phenyl isocyanate) was obtained at low monomer concentrations; copolymer was obtained at higher monomer concentration. The copolymer composition was free of depropagation only at -75°C over the concentration range of 0.3-3 M in aldehyde. These reaction conditions were subsequently used for most of the polymerizations in this study except for copolymerizations in DMF solution. A reaction temperature of -68°C was used in the latter case as that was the temperature attained by DMF solutions immersed in Dry

TABLE 1. Effect of Temperature and Monomer Concentration on the Copolymerization of n-Butyraldehyde—Phenyl Isocyanate[a]

Temperature (°C)	Concentration of n-butyraldehyde[b] (M)	n-Butyraldehyde in copolymer (mole-%)
-40	0.66-2.0	No polymer
-65	0.66	Only ØNCO homopolymer
-65	2.0	37
-75	0.32	72
-75	0.71	72
-75	1.19	67
-75	3.14	76

[a] Initiator = n-butyllithium; solvent = diethyl ether.
[b] Comonomer composition is constant at 23 wt-% n-butyraldehyde.

Ice-acetone mixtures. The -68°C copolymerizations were separately shown to be free of depropagation.

Effect of Monomer Structure

A comparison of appropriate sets of copolymerization data allowed a determination of monomer reactivities. For example, Fig. 4 shows the copolymerization behavior of phenyl and n-butyl isocyanates which each copolymerized at -75°C with n-butyraldehyde using n-butyllithium as the initiator and ether as the solvent. The monomer reactivity ratios and the curves are those that best fit the experimental data. By inverting the n-butyraldehyde reactivity ratios (r_1), one obtains the monomer reactivities ($1/r_1$) as 1/70 or 0.0143 for phenyl isocyanate and 1/500 or 0.002 for n-butyl isocyanate. These values of monomer reactivities allow a

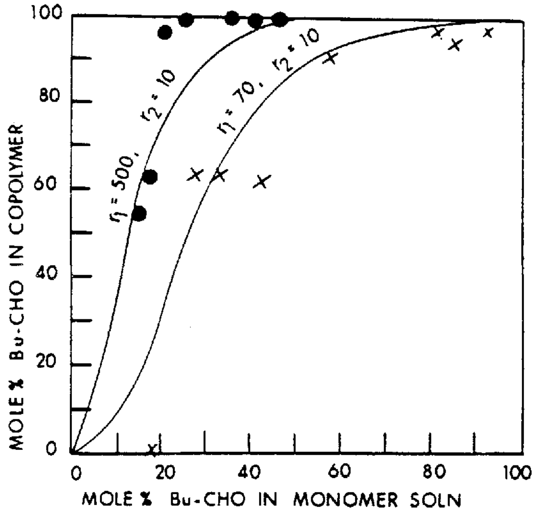

FIG. 4. Copolymer composition curves for the copolymerization of n-butyraldehyde with phenyl isocyanate (●) and n-butyl isocyanate (×). Initiator, n-butyllithium; solvent, diethyl ether; T = -75°C.

comparison of the reactivities of the two isocyanate monomers toward the n-butyraldehyde anion. Phenyl isocyanate is the more reactive isocyanate—not unexpectedly since the phenyl group is much better able to stabilize an anionic propagating center compared to the butyl group. The same order of monomer reactivities is obtained when the two isocyanates are copolymerized with chloral using the above reaction conditions. Data [6] for the chloral-phenyl isocyanate system (n-butyllithium initiation and ether as the solvent) show values of $r_1 \sim 0.5$ and $r_2 \sim 0$. The copolymer composition data in the chloral—n-butyl isocyanate system is shown in Table 2. The small amounts of n-butyl isocyanate in the copolymer make it difficult to calculate precise r_1 and r_2 values. r_1 is in the range 2-50 and $r_2 \sim 0$. The monomer reactivities for phenyl and n-butyl isocyanates toward the chloral anion are 2 and approximately 0.5-0.02, respectively.

The relative order of reactivity for the aldehyde monomers was determined from data on their copolymerizations with phenyl isocyanate (r_2) using n-butyllithium as the initiator with diethyl ether

TABLE 2. Copolymerization of Chloral (M_1) with n-Butyl Isocyanate (M_2)[a]

Mole fraction of M_1 in comonomer	Mole fraction of M_1 in copolymer
0.15	0.91
0.47	0.85
0.72	0.96
0.83	0.99

[a]Initiator = n-butyllithium; solvent = ether; T = -75°C.

as the solvent at -75°C. In the formaldehyde-phenyl isocyanate system, no copolymer was obtained; polyformaldehyde was the sole product, i.e., $r_1 \sim \infty$ and $r_2 \sim 0$. The monomer reactivity ratios for the n-butyraldehyde—phenyl isocyanate system are $r_1 = 70$ and $r_2 = 10$ (from Fig. 4), while those for the chloral-phenyl isocyanate were noted earlier as $r_1 \sim 0.5$ and $r_2 \sim 0$. From these results, one obtains $1/r_2$ values of ∞, ∞, and 0.1 for chloral, formaldehyde, and n-butyraldehyde, respectively, toward the phenyl isocyanate anion. These monomer reactivity values indicate that chloral and formaldehyde are more reactive than n-butyraldehyde. The greater reactivity of chloral is explained by stabilization of an anionic propagating center by the strong electron-pulling effect of the $-CCl_3$ group. The greater reactivity of formaldehyde relative to n-butyraldehyde is due to two factors: lowered steric hindrance at the carbonyl group and the lack of an electron-pushing alkyl group (which destabilizes a propagating anion). The $1/r_2$ values indicate that chloral and formaldehyde are of equal reactivity. The same conclusion is obtained from data on the copolymerizations of these two monomers with phenyl isocyanate at -68°C using KCN as the initiator and DMF as the solvent (Table 3). The monomer reactivity ratios are the same in the two copolymerizations ($r_1 = 0.6$ and $r_2 = 0.2$); the $1/r_2$ values for chloral and formaldehyde are the same.

TABLE 3. Copolymerizations of Phenyl Isocyanate (M_2) with Chloral (M_1) and Formaldehyde (M_1)[a]

Mole fraction of M_1 in comonomer	Mole fraction of M_1 in copolymer
A. Chloral-Phenyl Isocyanate	
0.16	0.36
0.49	0.52
0.50	0.68
0.81	0.74
B. Formaldehyde-Phenyl Isocyanate	
0.42	0.55
0.49	0.56
0.72	0.72

[a] Initiator = KCN; solvent = DMF; T = -68°C.

Effects of Solvent and Gegenion

To examine the effect of solvent on monomer reactivity, the n-butyraldehyde—n-butyl isocyanate system was studied in different solvents—hexane, diethyl ether, THF, and DMF—using n-butyllithium initiation and a reaction temperature of -75°C. In the nonpolar solvent n-hexane, only homopolymerization of n-butyraldehyde occurred even when the comonomer mixture contained up to 90% n-butyl isocyanate. Copolymerization occurred in ether and THF over a wide range of comonomer compositions (Fig. 5). The monomer reactivity ratios were calculated and are shown in Table 4. Similar results were obtained for the chloral-phenyl isocyanate and chloral—n-butyl isocyanate systems. In n-hexane only the homopolymer of chloral was obtained while copolymerization occurred in diethyl ether (Table 5). In all cases the reactivity of the aldehyde monomer decreases and that of the isocyanate monomer increases as the solvating power of the solvent increases. This indicates that the

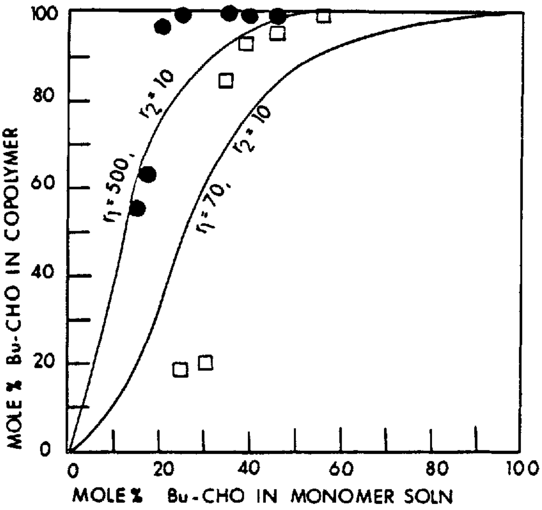

FIG. 5. Effect of solvent on the copolymerization of n-butyraldehyde—n-butyl isocyanate with n-butyllithium at -75°C. Solvents: diethyl ether (●) and THF (□).

TABLE 4. Effect of Solvent on Copolymerization of n-Butyraldehyde(M_1)—n-Butyl Isocyanate (M_2)[a]

Solvent	r_1	r_2
n-Hexane	∞	0
Diethyl ether	500	10
THF	70	10

[a] n-Butyllithium initiation; T = -75°C.

observed reactivity of the aldehyde monomer is enhanced by its preferential coordination with the propagating center when the latter is a relatively tightly-bound ion-pair as it would be in a poor solvent such as n-hexane. The greater coordinating ability of the aldehyde monomer compared to the isocyanate monomer corresponds to the

TABLE 5. Effect of Solvent on Copolymerizations of Chloral (M_1) with Phenyl Isocyanate (M_2) and n-Butyl Isocyanate (M_2)[a]

Solvent	r_1	r_2
Chloral-Phenyl Isocyanate		
Hexane	∞	0
Diethyl ether	~ 0.5	~ 0
Chloral—n-Butyl Isocyanate		
Hexane	∞	0
Diethyl ether	2-50	0

[a] n-Butyllithium initiation; T = -75°C.

differences observed in the dielectric constants of such monomers. For example, benzaldehyde and phenyl isocyanate have dielectric constants of 17.8 and 8.8, respectively, at 20°C [7].

When polymerization is carried out in relatively polar media such as diethyl ether or THF, the propagating ion-pair is not as tightly bound and there is less of a need for its solvation by the aldehyde monomer. The observed reactivity of the aldehyde monomer decreases as its concentration at the site of propagation decreases. This explanation is supported by the results obtained when the effect of gegenion on monomer reactivity was studied. n-Butyraldehyde and n-butyl isocyanate were copolymerized in diethyl ether at -75°C using n-butyllithium and sodium napthalene as the initiators. The copolymer composition curves and monomer reactivity ratios are shown in Fig. 6. The reactivity of the aldehyde monomer decreases as the gegenion changes from lithium to sodium. Since Li^+ is more tightly bound to the anionic propagating center than Na^+ (due to its smaller size), this corresponds to a decrease in aldehyde reactivity as the tightness of the ion-pair decreases. Thus the effects of solvent and gegenion on monomer reactivity are in the same direction.

An interesting side observation was the complete absence of polymerization when copolymerization was attempted with the n-butyraldehyde—n-butyl isocyanate system in dimethylformamide, using n-butyllithium initiation at -75°C. This was surprising since homopolymerization of n-butyl isocyanate readily occurs when that monomer is present alone in DMF under these reaction conditions.

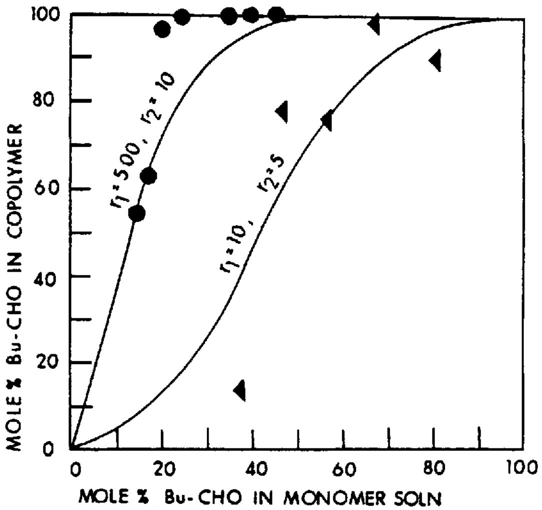

FIG. 6. Effect of gegenion on the copolymerization of n-butyraldehyde—n-butyl isocyanate in diethyl ether at -75°C. Initiators: n-butyllithium (●) and sodium napthalene (◀).

However, it has been reported that n-butyraldehyde does not polymerize in DMF solution [8], perhaps by the propagating anions being solvated so strongly by DMF that monomer is unable to add. The absence of polymerization in the n-butyraldehyde—n-butyl isocyanate can then be explained as an inhibition of the growth of the n-butyl isocyanate propagating species by the addition of n-butyraldehyde to it before propagation is much past the telomer stage. Since the n-butyraldehyde anion does not propagate in DMF, further reaction ceases.

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