We may conclude that this reaction is a normal activated substitution passing through the structure I.

Experimental

Materials.—The diazonium salts were prepared in the usual manner from the corresponding amines, which were commercial materials, and were precipitated by the addition of 10% fluoroboric acid. They were recrystallized by dissolving in ethanol at room temperature, then cooling to −40°. Two recrystallizations usually sufficed to give material which gave ultraviolet spectrum and reaction rates unaltered by further recrystallization. Carbon 14 labeled sodium thiocyanate (obtained in allocation-free quantities from Merck and Co. of Canada) was diluted to a specific activity of about 100 μc. per g. Stock solutions of this were made up in water for the work in water solution and in dimethoxydiethyl ether for all other solvents.

Kinetics.—Solutions of appropriate concentration were made up and placed in the thermostat, which regulated the temperature to better than ±0.2°. Ten-ml. samples were then treated by two different methods to remove unreacted thiocyanate; the resulting solutions were then added to 25 ml. of a solution of excess cuprous chloride in hydrochloric acid. After at least two hours at room temperature, the mixture was extracted with 25 ml. of reagent grade toluene, using a shaking machine for 10 minutes, and the extract was then washed with 25 ml. of water. After drying over calcium chloride, 10 ml. of the solution was mixed with 10 ml. of a solution containing 3 g. of 2,5-diphenyloxazole and 0.1 g. of 1,4-di-(2-(5-phenyloxazolyl))-benzene per liter, then counted in a Packard Tri Carb Scintillation spectrometer using conventional settings. For the slowest reactions at least 1000 counts were recorded, and for most of the runs at least 10,000 counts were recorded. Activities were well above background in all cases so that minor changes in the background could not cause error comparable with that from other sources. Several representative samples were tested for quenching by adding known amounts of radioactive benzoic acid. The rate of counting was indeed lower by about one-quarter than in pure toluene with the standard benzoic acid. This quenching was reproducible and no correction was necessary, since the reactions followed a first-order course. With the *o*-fluoro and *p*-nitro compounds colored by-products were formed, leading also to an optical quenching. Corrections were applied in these cases.

The constant k_d was determined from the counting rates of toluene extracts made before the cuprous chloride treatment. Since it was measured only to show that the correction was small, only about two points were taken and the precision is low.

Neither of the two methods for removing radioactive thiocyanate from the solution gave a quantitative recovery of radioactive diazonium salt, but both were reproducible in this respect. In the first method, 10 ml. of the reaction mixture was diluted with 100 ml. of cold water and 1 millimole of inactive sodium thiocyanate was added. A small excess of silver nitrate was then added and the solution filtered, then treated with cuprous chloride. Only about 45% of the maximum expected number of counts could be obtained by this method. In the second method, a 10-ml. sample of the reaction mixture was diluted with 40 ml. of cold water and passed through a chloride form anion exchange resin (Amberlite IRA-400) in a column cooled from the outside to 6°. The column was washed with 110 ml. of cold water and the solution treated as before with cuprous chloride. This gave about 60% of the expected number of counts. The majority of the runs was done using the second method. Second-order rate constants were calculated by dividing the apparent first-order rate constants by the initial diazonium ion concentration. The apparent first-order rate constants were the slopes of plots of $\ln N_\infty/(N_\infty - N_t)$ *vs.* time, where N_t and N_∞ are the counting rates of samples at time *t* and after many half-lives. Both separation methods gave good straight lines in this plot, and the slopes were the same.

Dielectric constants were measured using a Sargent Oscillometer.[15] A plot of dial reading *vs.* reciprocal of the dielectric constant for several known liquids was linear, so that interpolation was straightforward. Measurements were made at room temperature.

Solubility measurements were made by stirring solid diazonium fluoroborate with the solvent in a thermostat for 20 minutes, then centrifuging to remove the solid; the clear solution was appropriately diluted with water and the concentration determined by measuring the ultraviolet absorbance at the maximum. Since large dilutions were made, no correction for change in spectrum with solvent was made. The values in Table III are the averages of at least three determinations, including some made by adding a saturated water solution with solid salt to the *t*-butyl alcohol solvent so as to approach the equilibrium from the super-saturated side.

Acknowledgment.—We wish to thank the Robert A. Welch Foundation for support of this research.

[15] We thank the Research and Development department of the Humble Oil and Refining Co. for the use of this instrument.

HOUSTON, TEX.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO.]

The Homopolymerization of Monoisocyanates

BY VICTOR E. SHASHOUA, WILFRED SWEENY AND RAYMOND F. TIETZ

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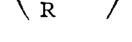
Monoisocyanates were polymerized at low temperatures (−20 to −100°) by anionic catalysts to give linear high molecular weight polymers. These polymers are classified as 1-nylons. The reaction is applicable to both aliphatic and aromatic isocyanates. The scope and limitations of the reaction are defined. The properties of the 1-nylons are described. A proposed mechanism for the reaction is given.

The formation of cyclic dimers and trimers from isocyanates is a well known reaction, promoted by such basic reagents as triethylamine,[1] triethylphosphine[2] and pyridine.[3] In a previous communication[4] from these laboratories the homopolymerization of monoisocyanates to linear film forming products was demonstrated. These studies have now been extended to a host of aliphatic and aromatic isocyanates in an attempt to examine the scope and limitations of this new reaction of isocyanates. To our knowledge the homopolymerization of isocyanates in accordance with the reaction scheme below represents the first example of the polymerization of compounds with $>C=N-$ groups to high molecular weight products. These



$$R-N=C=O \longrightarrow \left(-\underset{\underset{R}{|}}{N}-\overset{\overset{O}{\|}}{C}- \right)_n$$

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[1] D. H. Chadwick and T. C. Allen, U. S. Patent 2,733,254 (1956).

[2] A. W. Hofmann, *Ber.*, **3**, 761 (1870).

[3] H. L. Snape, *J. Chem. Soc.*, **49**, 254 (1886).

[4] V. E. Shashoua, THIS JOURNAL, **81**, 3156 (1959).

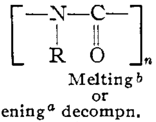
polymers may be classified as N-substituted 1-nylons by analogy to the formation of 6-nylon from caprolactam.

The polymerizations were carried out by treating solutions of monoisocyanates (generally in N,N-dimethylformamide) with anionic catalysts at low temperatures (−20° to −100°). A variety of catalysts and solvents were found suitable for the reaction. These will be described in the Discussion section of this paper. Table I lists the polymers prepared along with some of their properties.

TABLE I

1-NYLON POLYMERS AND THEIR PROPERTIES

Polymer



$$\left[-\underset{\displaystyle R}{\underset{|}{N}}-\underset{\displaystyle O}{\underset{\|}{C}}-\right]_n$$

R =	Softening[a] temp., °C.	Melting[b] or decompn. temp., °C.	Soluble in
Ethyl		250	H_2SO_4, CF_3CO_2H
n-Propyl	180	250	H_2SO_4, CF_3CO_2H
n-Butyl	180	209	Aromatic and chlorinated hydrocarbons
Isobutyl	173	210–220	
n-Amyl	145	209	Same
n-Hexyl	120	195	Same
n-Heptyl	100	180	Same
n-Undecyl	45	155	Same
n-Octadecyl	40	94	Same
Allyl	180	260–290	H_2SO_4, CF_3CO_2H
9-*n*-Decenyl	75	180–240	Aromatic and chlorinated hydrocarbons
Benzyl	..	250	H_2SO_4, CF_3CO_2H
Phenyl	..	197	H_2SO_4
m-Methylphenyl	..	200	N,N-Dimethylformamide
p-Methoxyphenyl	..	212–214	

[a] Temperature at which the polymer first became plastic without sticking on a metal temperature gradient bar. [b] Temperature at which the polymer first left a clear molten trail on a metal temperature gradient bar.

Experimental

Synthesis of Monomers.—Table II summarizes the sources and boiling points of the various isocyanates used in this work. A number of the compounds were synthesized by the Curtius reaction or by the reaction of acid chlorides with silver cyanate. The following methods for the preparation of *n*-heptyl isocyanate and benzoyl isocyanate may be considered as typical of the reaction conditions used. All the monomers were freshly distilled before any polymerization reactions were attempted.

***n*-Heptyl isocyanate** was synthesized by a method similar to that described by Boehmer.[5] One hundred and five milliliters of freshly distilled octanoyl chloride (Eastman Organic Chemicals) was added to 150 ml. of toluene containing 46 g. of activated sodium azide.[6] The mixture was heated under reflux until no further nitrogen was evolved. This took about four hours. The toluene solution was then decanted from the solid residue and distilled through a glass helices-packed column. The residue was fractionated twice, yielding 59.9 g. of a clear white liquid (65%), b.p. 87.5–88.5° (28 mm.).

Anal. Calcd. for $C_8H_{15}NO$: C, 68.1; H, 10.7; N, 9.9. Found: C, 68.5; H, 10.5; N, 9.6.

The phenylurea derivative had a melting point of 64–65°. *Anal.* Calcd. for $C_{14}H_{22}N_2O$: C, 72.4; H, 9.5; N, 12.1. Found: C, 72.3; H, 9.4; N, 11.9.

Benzoyl isocyanate was prepared according to Billitter's[7] method. Benzoyl chloride (58.5 ml.) was added to a mixture of 100 g. of silver cyanate and 150 ml. of dry benzene. The reaction mixture was stirred overnight, and then the mixture was warmed to 60° for one hour. Next the solid suspension of silver chloride was filtered off under nitrogen and the filtrate was fractionated through an 18″ spinning band column at a reflux ratio of 6:1. After removal of the benzene a clear liquid fraction, boiling at 93° (20 mm.), was collected; yield 40 g. The product was extremely water sensitive.

Anal. Calcd. for $C_8H_5NO_2$: N, 9.5. Found: N, 9.3.

Preparation of the Catalysts.—The sodium cyanide solution was prepared by dissolving the dry compound in dry N,N-dimethylformamide (DMF) to give a saturated solution containing 0.68% NaCN. This solution was stored under nitrogen and used as required.

The sodium in DMF solution was prepared by stirring two drops of a 50% sodium dispersion in xylene or white oil (du Pont Electrochemicals Department) in 25 ml. of dry DMF under nitrogen for one hour. The resultant solution was then used directly in the polymerization studies. A fresh solution was prepared for each series of experiments.

The sodium N-methylacetamide catalyst solution was prepared by dissolving 10 g. of dried and distilled N-methylacetamide in 30 ml. of dry triethylamine under an atmosphere of nitrogen. To this, an equimolar amount of sodium was added as a 50% xylene dispersion and the mixture was stirred for a period of 30 minutes. The product precipitated as a pale brown solid. Addition of 10 ml. of N,N-dimethylformamide gave a catalyst solution which was useful in polymerizing ethyl isocyanate.

The sodium benzophenone ketyl solution was prepared by a method similar to that of Bachmann.[8] Dimethoxyethane (50 ml., Eastman Organic Chemicals, dried over sodium and distilled, b.p. 85°) and 0.5 g. of benzophenone was treated with stirring with 5 drops (approximately 1 equivalent) of 50% sodium in xylene. The vigorously stirred mixture slowly turned blue, indicating the formation of the sodium benzophenone ketyl. The solution was kept under nitrogen and used for initiating polymerizations. A fresh solution was prepared for each series of experiments.

The sodium naphthalene was prepared according to the method of Scott, Walker and Hansley.[9]

Purification of the Solvents.—All of the solvents used in this work were dried and distilled before use. In the initial experiments, the dimethylformamide (DMF, Technical grade from Grasselli Chemicals Dept., E. I. du Pont de Nemours & Co.) was purified by distillation from phosphoric anhydride at atmospheric pressure. A forecut of about 600 ml. was discarded from an initial amount of 2 l. and a middle fraction of about 1 l. was collected and used in the polymerization studies.

In subsequent experiments, it was found that simple vacuum distillation of this grade of DMF to remove 10% of the amount charged gave a pot *residue* which was suitable for polymerization studies.

The triethylamine was purified by fractionation. The fraction boiling at 89.6° was used for the polymerization studies.

Preparation of Polymers.—Table III shows representative reaction conditions for each of the 1-nylons prepared in this work. The following is a typical polymerization procedure. A 250-ml. 3-necked flask was equipped with a stirrer and two side-arm adapters. One of these had a calcium chloride tube and a low temperature thermometer for immersion in the reaction medium; the other was fitted with a nitrogen inlet tube and the vertical arm was sealed with a rubber bulb. The flask was then flamed while being swept with nitrogen, DMF (30 ml.) was added, and the contents were cooled to −58°, just about the melting point of DMF. The isocyanate (10 ml.) was added and the contents recooled to −58°. The rubber bulb was then pierced with a hypodermic needle and the catalyst added dropwise from a syringe over a 2–3 minute period while the medium was stirred vigorously. The polymer usually precipitated at once. After stirring for 15 minutes at −58°, methanol (50 ml.) was added, the polymer filtered and washed with

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[5] J. N. Boehmer, *Rec. trav. chim.*, **55**, 379 (1936).

[6] P. A. S. Smith, "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 382.

[7] O. C. Billitter, *Ber.*, **36**, 3218 (1903).

[8] W. E. Bachmann, THIS JOURNAL, **55**, 1179 (1933).

[9] (a) N. D. Scott, J. F. Walker and V. J. Hansley, *ibid.*, **58**, 2442 (1936); (b) N. D. Scott, U. S. Patent 2,181,771 (1939).

TABLE II

SOURCES AND PURITY OF THE ISOCYANATES

Isocyanate	B.p. °C.	B.p. Mm.	Lit. b.p. °C.	Lit. b.p. Mm.	Source
Ethyl	59.5–60		60[a]		Mobay Chemical Co.
Propyl	87		88[b]		Curtius reaction[c]
Isopropyl	75		72[d]		Curtius reaction[c]
n-Butyl	113–115		114–116[b]		Curtius reaction[e]
Isobutyl	102.5–105		104–105[b]		Curtius reaction[e]
n-Amyl	139–140		136–137[b]		Curtius reaction[f]
n-Hexyl	162–163		163–164[g]		Curtius reaction[f]
n-Heptyl	87.5–88.5	28[h]	.....	...	Curtius reaction[i]
n-Undecyl	86–88	1	103	3[j]	Curtius reaction[j]
n-Octadecyl	135.5–137	0.2	190–210	11[b]	Matheson, Coleman and Bell
Allyl	85–88		87–89[b]		Chemicals Procurement Co.
9-Decenyl	56–58.5	0.1[k]	.....		Curtius reaction[l]
Cyclohexyl	63	15[m]	54	11[b]	Curtius reaction[f]
Benzyl	83	5–6	82–84	10[b]	Chemicals Procurement Co.
Phenyl	.....	...	162–163[a]		Eastman Organic Chemicals
m-Methylphenyl	51	3–5	195–198[n]		Grasselli-Chemicals Dept. E. I. du Pont de Nemours & Co.
m-Chlorophenyl	64	2	83–86	10.5[b]	Eastman Organic Chemicals
p-Chlorophenyl	65	2–5	80.6–80.9	9.5[b]	Eastman Organic Chemicals
p-Methoxyphenyl	82	2	97.6–97.8	9.5[b]	Eastman Organic Chemicals
α-Naphthyl	120	2–3	269–270[a]		Eastman Organic Chemicals
Octanoyl	50	1			AgNCO + octanoyl chloride[o]
Benzoyl	93	20	88	10[p]	AgNCO + benzoyl chloride[p]
Carbethoxymethyl	115	15	115–120	14[q]	Eastman Organic Chemicals
3-(α-Isocyanato-ethyl)-phenyl	109–111	2.6	134	11[b]	Organic Chemicals Dept. E. I. du Pont de Nemours & Co.
2,4-Toluene di-	.....	...	.....	...	E. I. du Pont de Nemours & Co.
Trimethylsilyl	91		91[r]		$AgNO_3$ + $(CH_3)_3SiCl$[r]

[a] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, 1953. [b] v. W. Siefken, *Ann.*, **562**, 75 (1949). [c] J. W. Boehmer, *Rec. trav. chim.*, **55**, 379 (1936). [d] T. Curtius, *J. prakt. Chem.*, **125**, 152 (1930). [e] The method of ref. *c* was used with xylene as the solvent. [f] The method of ref. *c* was used with toluene as the solvent. [g] G. Schroeter, *Ber.*, 42, 3356 (1909). [h] N-Phenylurea, m.p. 64–65°. Calcd. for $C_{14}H_{22}N_2O$: C, 72.4; H, 9.5; N, 12.1. Found: C, 72.3, 72.5; H, 9.7, 9.4; N, 11.9, 11.9 [i] Obtained in 68% yield by the method of ref. *c* with toluene as solvent. [j] C. F. H. Allen and A. Bell, *Org. Syntheses*, 24, 94 (1944). [k] Calcd. for $C_{11}H_{19}NO$: C, 72.8; H, 10.6; N, 7.7. Found: C, 72.5, 72.7; H, 10.3, 10.4; N, 7.7, 7.5. [l] Obtained in 62% yield by the method of ref. *j*. [m] Calcd. for $C_7H_{11}NO$: N, 11.2. Found: N, 10.8. [n] L. Gattermann and A. Cantzler, *Ber.*, **25**, 1086 (1892). [o] Obtained 62% yield by the method of ref. *p* with ether as a reaction medium. [p] O. C. Billeter, *Ber.*, **36**, 3218 (1903). [q] A. Morel, *Compt. rend.*, **143**, 119 (1906). [r] G. S. Forbes and H. H. Anderson, THIS JOURNAL, **70,** 1222 (1948).

methanol (300 ml.). The product was dried at 40° under vacuum; the yield and inherent viscosity of the polymer were determined.

Characterization of the Products.—The polymer melt temperatures and softening points were measured on a temperature gradient bar covering the range of 50–350°. Here the temperature at which a polymer sample left a wet molten trace across the surface of the clean metal bar was taken as the polymer melt temperature. The softening points were the temperatures at which the polymers became plastic but did not leave a molten trail along the hot bar. The viscosity measurements were carried out at 30° in an Ostwald–Fenske[10] viscometer. The inherent viscosities (η_{inh} = $(\ln \eta_{rel})/C$) were measured at 30° and at 0.1% concentration for the polymers which were less soluble and at 0.5% concentration for the others. The molecular weights were determined in a Brice–Phoenix[11] apparatus using a 90° turbidity method as described by Debye.[12] The infrared spectra were obtained in a double beam Perkin–Elmer spectrometer using either film samples, or sodium bromide pellets for the powdered polymer samples. The X-ray diffraction analyses were performed on films and powdered samples of these polymers, according to the methods described by Statton.[13]

Studies of the Polymerization Variables.—A number of experiments were carried out with *n*-hexyl isocyanate as a model compound for the study of the influence of temperature, monomer concentration and catalyst concentration on the yield and inherent viscosity of polymer. Figures 1, 2 and 3 summarize the results for 0.1 molar runs in N,N-dimethylformamide using sodium cyanide as the catalyst. In each case the yield and the inherent viscosity of only the methanol-insoluble polymer was determined. The quantity of trimer formed concurrently with the polymer was not measured.

Results and Discussion

Evidence for Polymer Formation.—The fact that polymers are formed *via* the low temperature anionic polymerization of monoisocyanates is clearly proved by the viscosity measurements (see Table III) and the molecular weight determinations on the products. In some cases, inherent viscosities as high as 15.7 at 0.1% concentration were obtained (example 5, *n*-butyl 1-nylon). The molecular weight determinations on the ethyl 1-nylon in trifluoroacetic acid solutions gave a result of 1600–3000, corresponding to a degree of polymerization (D. P.) of 23–42. Similar low values were obtained for all determinations in strong acids because degradation occurred, whereas extremely high values were obtained for those polymers

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[10] M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

[11] (a) Brice–Phoenix Precision Instrument Co., 3805 N. Fifth St., Philadelphia 40, Penna.; (b) B. A. Brice, M. Halwer and R. J. Speiser, *J. Opt. Soc. Amer.*, **40**, 768 (1950).

[12] P. Debye, *J. Appl. Phys.*, **15**, 338 (1944).

[13] W. O. Statton, *ibid.*, **28**, 1111 (1957).

TABLE III

POLYMERIZATION OF THE ISOCYANATES

Expt.	Isocyanate	Amount of RNCO	DMF, ml.	Initiator, ml.	Temp., °C.	Polymer yield, %	η_{inh}	Solvent
1	Ethyl	25 g.	25^a	10^c	−100	41	0.3^f	TFA
2	Ethyl	9 g.	25	2^d	−50	48	...	...
3	*n*-Propyl	10 ml.	30	2^e	−58	70	0.02^g	H_2SO_4
4	Isopropyl	10 ml.	30	2^e	−58	None		
5	*n*-Butyl	10 ml.	30	1^e	−55	75	15.7^g	Benzene
6	Isobutyl	10 g.	41	7^d	−50	18	0.2^g	H_2SO_4
7	*n*-Amyl	10 ml.	20	5^d	−50	67	8.6^g	Benzene
8	*n*-Hexyl	8 ml.	30	4^e	−58	85	2.9^g	Benzene
9	*n*-Heptyl	8.6 g.	41	5^d	−51	59	2.4^g	Benzene
10	*n*-Undecyl	8.5 g.	50	1^d	−30	70	4.8^g	Benzene
11	*n*-Octadecyl	10 ml.	30	1^e	+20	2	0.4^f	Benzene
12	*n*-Octanoyl	10 ml.	30	3^e	−40	None	...	...
13	Allyl	8 g.	30	2^e	−40	10	0.6^g	H_2SO_4
14	9-*n*-Decenyl	10 ml.	30	2^e	−58	75	5.2^g	Benzene
15	Carbethoxymethyl	10 ml.	30^b	3^e	−70	70	0.4^f	H_2SO_4
16	Cyclohexyl	10 ml.	30	3^e	−40	None	...	...
17	Phenyl	25 g.	25	1^c	−40	28	...	...
18	*m*-Tolyl	10 ml.	30	8^e	−58	60	0.3	DMF
19	*p*-Tolyl	5 ml.	50	1^e	−50	25	1.1^f	^{h}
20	*m*-Chlorophenyl	10 ml.	30	8^e	−20	None	...	...
21	*p*-Chlorophenyl	10 ml.	30	4^e	−30	None	...	...
22	*o*-Methoxyphenyl	10 g.	30	4^e	−40	None	...	...
23	*p*-Methoxyphenyl	35 ml.	100	12^e	−58	35	0.7^f	Benzene
24	Benzyl	12.5 ml.	30	1^e	−40	50	0.04^f	H_2SO_4
25	Benzoyl	10 ml.	30	3^e	−40	None	...	...
26	α-Naphthyl	10 ml.	30	3^e	−40	None	...	...
27	α-(3-Isocyanatoethyl)-phenyl	10 ml.	45	2.25^e	−58	11	...	...
28	2,4-Toluene di-	10 ml.	30^a	3^e	−100	30	...	...
29	Trimethylsilyl	10 ml.	30	4^e	−40	None		

DMF = N,N-dimethylformamide, DMA = N,N-dimethylacetamide, TFA = trifluoroacetic acid. [a] Triethylamine used as solvent. [b] DMF/DMA (70/30 by vol.) used as solvent. [c] Sodium in DMF. [d] Sodium benzophenone ketyl. [e] NaCN in DMF. [f] At 0.5% concn. [g] At 0.1% concn. [h] *sym*-Tetrachloroethane–phenol (66:100 by wt.).

which could be dissolved in hydrocarbon solvents. For example, a sample of *n*-heptyl 1-nylon (expt. 9) had a weight average molecular weight of 69,000, *i.e.*, D.P. 450, as measured by light scattering in chloroform and a sample of 9-*n*-decenyl 1-nylon (expt. 14) gave a result of 387,000 in benzene, *i.e.*, D.P. 2140. In addition to the molecular weight evidence, the properties of the products were characteristic of high polymers. Thus, clear, flexible films were obtained from the aliphatic 1-nylons when benzene solutions were evaporated to dryness. These films had an appearance similar to polyethylene, especially when the *n*-alkyl substituent was a long chain.

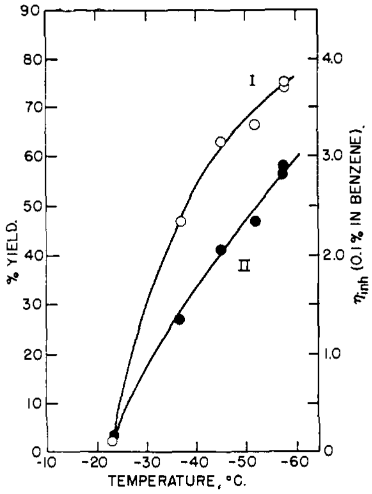

Fig. 1.—Influence of initial reaction temperature on the yield (curve I) and inherent viscosity at 0.1% concentration in benzene (curve II) of N-hexyl 1-nylon.

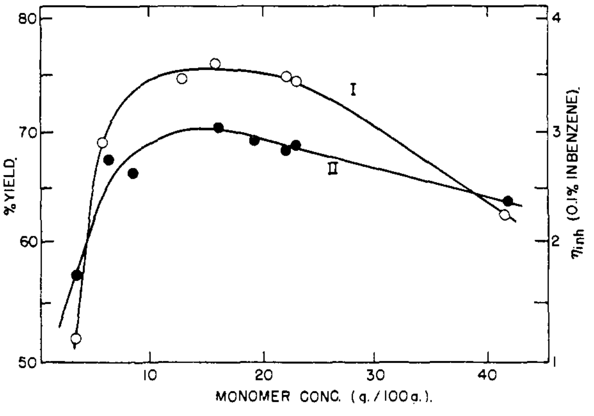

Fig. 2.—Effect of monomer concentration on the yield (curve I) and inherent viscosity at 0.1% concentration in benzene (curve II) of N-hexyl 1-nylon.

Evidence for the assigned 1-nylon structure of the polymers from the monoisocyanates lies mainly in the elemental analysis and the interpretation

TABLE IV

ELEMENTAL ANALYSIS OF 1-NYLON POLYMERS

			Composition, %					
			Calcd.			Observed		
Expt.	Polymer	Formula	C	H	N	C	H	N
1	Ethyl	$(C_3H_5NO)_n$	50.7	7.1	19.7	50.8, 50.4	6.9, 6.9	19.1, 19.3
14	9-*n*-Decenyl	$(C_{11}H_{19}NO)_n$	72.8	10.5	7.7	72.6, 73.0	10.0, 10.2	7.6, 7.6
10	*n*-Undecyl	$(C_{12}H_{23}NO)_n$	73.0	11.8	7.1	73.4	11.7	7.3

of the infrared spectra. Table IV shows the analyses for three of the polymers. The results correspond to the analysis for the monomer molecule, indicating an addition type of polymerization.

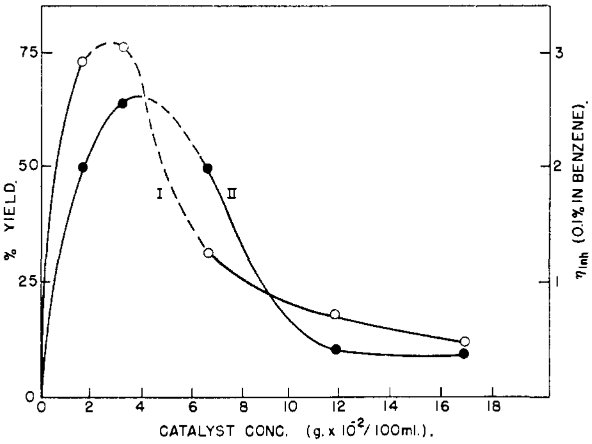

Fig. 3.—Influence of catalyst concentration in N,N-dimethylformamide on the yield (curve I) and inherent viscosity at 0.1% in benzene (curve II) of the methanol-insoluble N-hexyl 1-nylon formed.

The infrared spectra, in all of the polymers, showed a characteristic carbonyl absorption at about 5.85 μ and a band at 7.8 to 7.2 μ, corresponding to a disubstituted amide. In all polymers, there was a conspicuous absence of absorption bands corresponding to NH and isocyanate groups. In the case of ethyl 1-nylon and phenyl 1-nylon, the absorption spectra of the polymers were shown to be quite distinct from trimer, and trimer and dimer, respectively. The postulated structure seems a reasonable one, especially in view of the known tendency of the carbon–nitrogen double bond of an isocyanate to open up and give cyclic dimers and trimers in a head-to-tail type addition.

Synthesis of the Polymers.—A variety of anionic initiators was found suitable for the preparation of the 1-nylons. This is illustrated in Table V. The catalyst of choice was a solution of NaCN in N,N-dimethylformamide[14] because it was less sensitive to traces of moisture and air; but others, such as sodium benzophenone ketyl, sodium napthalene, sodium in N,N-dimethylformamide,[15] and sodium in N-methylacetamide were also effective in promoting the polymerization. The lack of success with classical anionic reagents, such as metal alkyls, Grignard reagents and sodamide, can probably be ascribed either to side reactions, with the isocyanate and/or the solvent, or to insolubility in the reaction medium. That the catalyst must be in solution to be useful as an initiator was demonstrated for sodium cyanide in two ways: (1) Sodium cyanide was found to be insoluble in triethylamine and did not give polymers in this medium, however, by adding enough DMF to the mixture so that some of the cyanide dissolved, an immediate polymerization took place. (2) An anionic exchange resin was charged with cyanide ion. This insoluble form of the cyanide was found to be ineffective as an initiator in DMF.

It is of interest to note that free-radical catalysts, such as potassium persulfate and azo-compounds, are ineffective in initiating the polymerization of the isocyanates. Also, catalysts such as triethylphosphine and triethylamine which are known to catalyze the dimer and trimer formation at higher temperatures are not effective in initiating the polymerization to linear 1-nylons.

A variety of solvents was found useful as the polymerization medium. These fulfill the requirements of an inertness to the isocyanate and a capacity to dissolve the catalyst, presumably with dissociation to give anions. Table V shows some of the results obtained. The most useful solvents were N,N-dimethylformamide and a mixture of N,N-dimethylformamide and N,N-dimethylacetamide (7/3 by vol.). The latter medium had the advantage of freezing at −70° instead of −58° for the N,N-dimethylformamide. It is of interest that such solvents as methylene chloride and 1,2-dimethoxyethane are useful for the polymerization of *n*-hexyl and *p*-tolyl isocyanates, whereas hydrocarbons such as toluene are not useful.

Several variables were found to influence the polymer formation. These are the initial polymerization temperature, concentration of the monomer and concentration of the catalyst. In an attempt to study the importance of these factors in polymer synthesis, a series of experiments was carried out using *n*-hexyl isocyanate as a model with sodium cyanide as the catalyst. It is important to note that the yields do not take into account any trimer formed. Figure 1 shows a plot of the inherent viscosity and yield of methanol-insoluble polymer as a function of the initial polymerization temperature. The graph shows an increase in yield and molecular weight with a decrease in the initial polymerization temperature.

Figures 2 and 3 depict the influence of monomer concentration and catalyst concentration on the yield and molecular weight of the *n*-hexyl 1-nylon. It is seen that there is an optimum concentration range for both monomer and catalyst for highest yield and molecular weight. At high

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[14] This catalyst was shown to be useful for polymerizing vinyl monomers; L. D. Grandine, private communication, E. I. du Pont de Nemours & Company.

[15] This catalyst was shown to be an anionic type for vinyl monomers; L. D. Grandine, private communication, E. I. du Pont de Nemours & Company

TABLE V

POLYMERIZATIONS ILLUSTRATING THE USE OF DIFFERENT SOLVENTS AND CATALYSTS

Expt.	Monomeric isocyanate, ml.	Solvent, ml.	Initial temp., °C.	Catalyst	Yield, %	ηinh (0.5%) benzene
30	8 Hexyl	30 Acetonitrile	−58	4 ml. NaCN soln. in DMF	0	..
31	7.5 Hexyl	30 Triethylamine	−70	3 drops triethylphosphine	0	..
32	8 Hexyl	30 Methylene chloride	−58	4 ml. NaCN soln. in DMF	10	0.3
33	8 Hexyl	30 DMA[b]	−20	4 ml. NaCN soln. in DMF	30	1.1
34	8 Hexyl	30 Toluene	−30	4 ml. NaCN soln. in DMF	0	..
35	7.5 Heptyl	30 Hexane	−70	3 ml. 0.1 *M* lithium butyl in decalin	0	..
36	8 Decenyl	35 DMF/DMA (7/3)	−70	10 ml. of 3 *M* EtMgBr in ether	0	..
37	8 Propyl	30 DMF/DMA (7/3)	−70	0.05 g. sodamide	0	..
38	25 *p*-Tolyl	25 Methylene chloride	−50	2 ml. NaCN in DMF	30	0.45[a]
39	25 *p*-Tolyl	7 Glycol dimethyl ether	−50	2.5 ml. sodium naphthalene soln.	20	0.97[a]
40	25 Phenyl	25 DMF[c]	−40	3 ml. sodium naphthalene soln.	60	..

[a] This was measured in *sym*-tetrachloroethane- phenol (66:100 by wt.). [b] DMA = N,N-dimethylacetamide. [c] DMF = N,N-dimethylformamide.

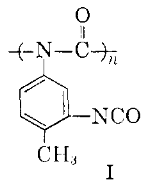
catalyst concentrations a decrease in yield and molecular weight occurs, presumably because of the initiation of a large number of polymer chains leading to cyclic trimers and possibly other methanol-soluble products.

Limitations to Polymer Formation.—An examination of the results in Table III shows that some monomers did not polymerize under the given experimental conditions to yield 1-nylons, indicating that there are certain limitations to polymer formation. These requirements can be classified as due either to the experimental problems or to steric factors influencing the mode of reaction.

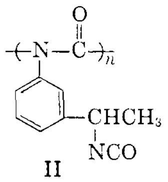
The main experimental limitation on a potentially polymerizable isocyanate is the necessity for solubility (usually more than 1%) in the reaction medium at a low temperature (*i.e.*, less than about −20°). It is believed that this factor prevented the polymerization of the *m*- and *p*-chlorophenyl isocyanates under the conditions examined (see Table III, experiments 19 and 20). This solubility limitation was also responsible for the low yields obtained with *n*-octadecyl isocyanate (see expt. 11, Table III). Here the high polymerization tendency of the monomer is clearly evident from the fact that high polymers (η_{inh} = 0.4 in benzene) could be obtained in low yield even at +20°.

In the aliphatic series the steric factors which influence the polymerizability of a given isocyanate appear to be associated with the α-carbon atom. If the isocyanate group was attached to a primary aliphatic carbon atom, then polymerization occurred readily (see Table III). Attachment to a secondary carbon atom, even if it was contained in a ring, prevented polymerization, *e.g.*, cyclohexyl isocyanate and isopropyl isocyanate.

In the aromatic series, substitution *ortho* to the isocyanate group appeared to inhibit polymerization (for example, see expt. 21, *o*-methoxyphenyl isocyanate, and expt. 25, α-naphthyl isocyanate). The influence of these steric requirements is further illustrated by the fact that one can selectively polymerize the unhindered isocyanate group in the compounds 2,4-toluene diisocyanate and 3-(α-isocyanatoethyl)-phenyl isocyanate (expts. 27 and 28 in Table III). The products from these diisocyanates give viscous solutions in DMF indicating the formation of a polymeric material. Infrared analysis confirmed the presence of the isocyanate groups in the polymer side chains as shown by the formulae I and II. Moreover, the



I



II

polymers were readily crosslinked with water, diamines, etc., indicating the presence of the reactive isocyanate groups.

Properties of the Polymers.—The solubility and melting point (see Table I) behavior of the 1-nylons is very dependent upon the nature of the side chain. N-Alkyl 1-nylons having three carbon atoms or less as the N-substituent are soluble only in concentrated sulfuric acid and trifluoroacetic acid. In these solvents, degradation takes place. For example, a freshly prepared solution of ethyl 1-nylon in trifluoroacetic acid gave an inherent viscosity value of 0.3. Overnight, the inherent viscosity of the solution dropped to 0.04. When the alkyl group is butyl or longer, the polymers are soluble in a variety of aromatic and chlorinated aliphatic solvents, such as benzene, carbon tetrachloride, toluene and chloroform, but only to a limited extent (usually less than 5%). The melting points of the N-alkylated aliphatic 1-nylons decrease with the length of the side-chain substitutent. Figure 4 shows this decrease in melting point as a function of the length of the alkyl substituent. Figure 4 also shows the softening point of these polymers. Most of the polymers exhibited a softening point of 30° or more below the actual melting point of the polymer.

In the aromatic series, N-phenyl 1-nylon is soluble only in concentrated sulfuric acid in which it degrades to the trimer, so that it is difficult to establish its polymeric nature. Substituents on the phenyl group, however, confer an increasing solubility in N,N-dimethylformamide on these aromatic 1-nylons. The polymers are not soluble, however, in toluene or carbon tetrachloride. One of the most soluble aromatic polymers prepared was the *p*-methoxyphenyl 1-nylon. An interesting observation was made on the stability of this

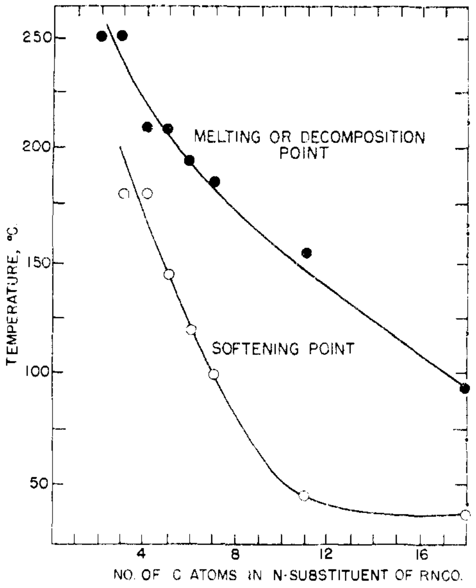


Fig. 4.—Thermal properties of the N-alkyl 1-nylon as a function of the number of carbon atoms in the N-substituent.

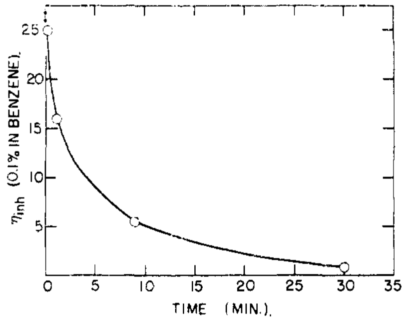


Fig. 5.—Thermal decomposition of N-butyl 1-nylon at 180°; *i.e.*, its softening point.

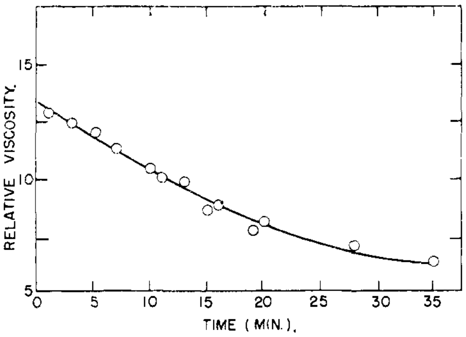


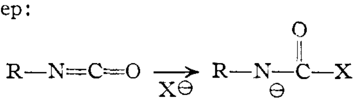
Fig. 6.—Decomposition of N-hexyl 1-nylon at 138° in xylene solution (concn. 0.1%) (relative viscosity denotes the ratio of solution to solvent flow rates).

polymer. It was found that when a solution in N,N-dimethylformamide was allowed to stand overnight at room temperature without removal of the sodium cyanide catalyst, the initially viscous polymer solution containing a high molecular weight product changed to an extremely fluid solution containing no linear polymer. This points to a catalytic depolymerization reaction favored by the higher room temperature conditions as opposed to the polymerization reaction favored at low temperatures, *i.e.*, < −40°. The thermal behavior of solid 1-nylons also shows these depolymerization tendencies. For example, when ethyl 1-nylon was heated to its melting point a distinct odor of an isocyanate was noted together with the formation of a white crysalline solid which melted at the same point as the trimer. A similar behavior was observed for *n*-butyl 1-nylon. Here the change in inherent viscosity was measured for a number of samples heated at 180° (*i.e.*, the polymer softening point) for varying lengths of time. Figure 5 shows the results obtained. The rapid thermal degradation of the polymer is clearly evident. Figure 6 shows the thermal decomposition of N-hexyl 1-nylon in xylene solution at 138°. Again thermal instability is observed.

X-Ray diffraction studies on films prepared by evaporating polymer solutions showed that most of the *n*-alkylated 1-nylons had a low order of crystallinity with the exception of allyl 1-nylon where a high crystallinity was observed. In addition, the X-ray diffraction patterns showed that there was developed high lateral order, especially when the alkyl substituent was a long chain.

Mechanism of the Polymerization.—The polymerization of isocyanates to 1-nylons is thought to be a new example of anionically polymerizable systems requiring basic catalysis and low temperatures. Thus, the initiation step can be considered as the attack of the anion at the isocyanate group as shown in the equation where $X^{\ominus}$ is the initiating anion.

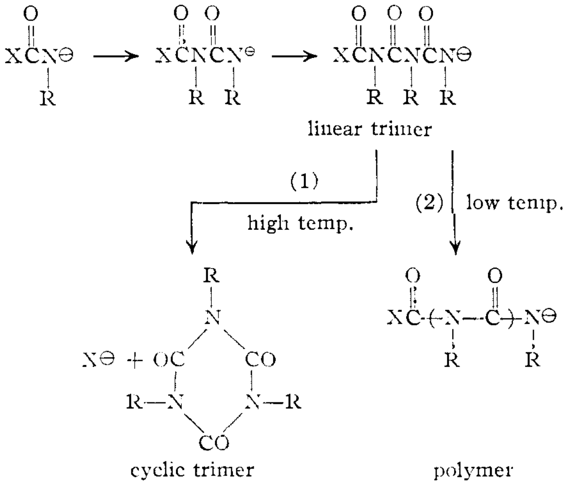
Initiation step:



$$\mathrm{R{-}N{=}C{=}O} \xrightarrow[X^{\ominus}]{} \mathrm{R{-}\underset{\ominus}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}X}$$

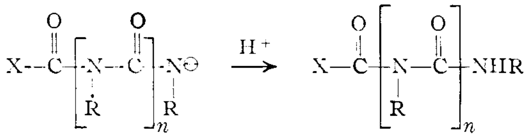
This is analogous to the reaction of nucleophilic reagents such as water, alcohols, etc., with isocyanates. The propagation step is believed to be continued by the nitrogen anion until the linear trimer stage. Then, there are two courses of reaction open: (1) cyclization with the release of the initiating anion to give a trimer, or (2) reaction with more monomer to give polymer.

propagation step:



From a study of the polymerization conditions, it is observed that both these reactions do occur. The trimerization reaction is favored at high concentrations of initiator and high temperature. The polymerization reaction is favored by low temperatures, high monomer concentrations and low concentrations of initiator. These facts are consistent with the postulate that the amount of polymer formation is governed by the relative rate of cyclization. By decreasing the temperature the cyclization rate can be rendered small, to favor the linear polymer formation. The reaction is probably more complex than indicated here, since the depolymerization of 1-nylon as illustrated by the case of *p*-methoxyphenyl 1-nylon can also occur in solution.

The termination step most probably occurs during the isolation of the polymer and/or by reaction with adventitious water present in the reaction medium in a similar manner to the reaction termination step:



$$X-\overset{O}{\overset{\|}{C}}-\left[-\underset{R}{N}-\overset{O}{\overset{\|}{C}}-\right]_n-\underset{R}{N}^{\ominus} \xrightarrow{H^+} X-\overset{O}{\overset{\|}{C}}-\left[-\underset{R}{N}-\overset{O}{\overset{\|}{C}}-\right]_n-NHR$$

In this regard, it is of interest to note that the addition of 5% ethyl succinate, 10% acetonitrile or 5% methylene chloride does not markedly influence the polymerization. However, the addition of 1% formamide completely inhibited the polymerization.

Acknowledgment.—We wish to thank Drs. D. Akeley and R. Zbinden, both of Pioneering Research, E. I. du Pont de Nemours & Co., for their assistance in the light scattering molecular weight determinations and the measurement and interpretation of the infrared spectra, respectively.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Alkylation of Nitriles: Ketenimine Formation[1]

BY MELVIN S. NEWMAN, T. FUKUNAGA[2] AND T. MIWA

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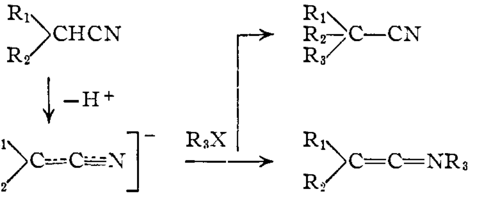
The alkylation of alkylacetonitriles to trialkylacetonitriles by reaction with alkali amides followed by treatment with alkylating agents is described. In the case of diisopropylacetonitrile, alkylation with isopropyl iodide yields moderate amounts of ketenimine as indicated by isolation after hydration as N-isopropyldiisopropylacetamide. In the case of *t*-butylisopropylacetonitrile, only ketenimine was obtained.

The alkylation of nitriles by (1) conversion to an ambident anion[3] with a strong base and (2) reaction of this anion with an alkyl halide, or other alkylating agent, has often been effected.[4-6] To our knowledge, only carbon alkylation has been reported, except for nitrogen alkylation in the case of trimethylchlorosilane.[7]

In connection with a program of synthesis and study of reactions of highly hindered nitriles[8] we had occasion to study the alkylation of highly branched nitriles with a variety of alkylating agents. We now report the formation of substituted ketenimines on alkylation of highly branched nitriles along with the more common carbon alkylation products.



(1a)

(1b)

The results of our alkylation studies are summarized in Table I.

In discussion of the factors involved in predicting and controlling the position at which an ambident anion reacts, several factors were mentioned[3] but steric factors were not stressed. The N-alkylation involved in silicoalkylation was explained mainly on steric grounds.[7] We agree that steric factors are largely responsible. Although we have not studied enough cases to define accurately the conditions for controlling the ratio of carbon to nitrogen alkylation of nitriles, it seems obvious that steric factors are important. In no case did N-alkylation occur when the disubstituted nitrile involved had a *six number*[9] of less than 12. For example, alkylation of *t*-butylmethylacetonitrile (expt. 20) with methyl bromide, *t*-butylethyl-

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[1] This research was supported largely by the United States Air Force under Contract No. AF33(616)-3412, monitored by the Aeronautical Research Laboratory, Wright Air Development Center. Early support from the Research Corporation, 1956–1957, is gratefully acknowledged.

[2] Part of the material herein presented was taken from the Ph.D. Thesis, Ohio State University, 1959, of T. Fukunaga.

[3] We support the use of the term "ambident" for an anion capable of undergoing alkylation at two (or more) positions. See (a) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, THIS JOURNAL, **77**, 6269 (1955); (b) D. Y. Curtin, R. J. Crawford and M. Wilhelm, *ibid.*, **80**, 1391 (1958); (c) N. Kornblum and A. P. Lurie, *ibid.*, **81**, 2705 (1959).

[4] For reviews see (a) A. C. Cope, H. L. Holmes and H. O. House, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1957, Vol. IX, p. 107; and (b) F. W. Bergstrom and W. C. Fernelius, *Chem. Revs.*, **20**, 451 (1937).

[5] C. R. Hauser and W. R. Brasen, THIS JOURNAL, **78**, 494 (1956).

[6] R. L. Jacobs and G. L. Goerner, *J. Org. Chem.*, **21**, 837 (1956).

[7] M. Prober, THIS JOURNAL, **78**, 2274 (1956), termed this alkylation "silicoalkylation."

[8] L. Tsai, T. Miwa and M. S. Newman, *ibid.*, **79**, 2530 (1957).

[9] For definition and discussion of the *six number* see M. S. Newman, *ibid.*, **72**, 4783 (1950), and M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 4, p. 203 ff.