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Robert W. Stackman[a]
[a] Celanese Research Company, Summit, New Jersey

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Addition Polymers of Cyclohexyl Isonitrile

ROBERT W. STACKMAN

Celanese Research Company
Summit, New Jersey

Summary

The preparation of homopolymers of cyclohexyl isonitrile by cationic initiators has been investigated.

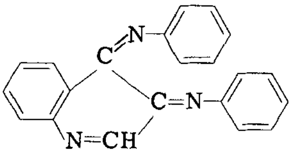
The polymers obtained, using $BF_3 \cdot$ etherate initiator, were insoluble, high-melting solids. Attempts to polymerize the isonitrile with anionic and free radical initiators were unsuccessful. The structure of the polymer could not be determined, but some of the possible structures are discussed.

Attempts to prepare copolymers with various types of monomers using cationic, anionic, and free radical initiators were also unsuccessful. Only mixtures of homopolymers could be obtained from copolymerization experiments using cyclohexyl isonitrile and trioxane with BF_3 etherate initiator.

Organic isonitriles have been known for 100 years, since their preparation in 1866 by Gautier [1] and by Hoffman [2]. Although it has been observed, almost from the first synthesis, that the isonitriles gave highly colored products, which are usually referred to as polymers, on standing or attempted distillation, few attempts were made to characterize these polymers.

Guillemard [3] in 1906 stated that "the polymerization of ethylisonitrile in a sealed tube begins at 120°C and disappeared at 220°C. The isomerization to the nitrile began at 140°C and was complete at 240°C." He further stated that the isomerization proceeded through the trimer. This trimer was, however, not isolated.

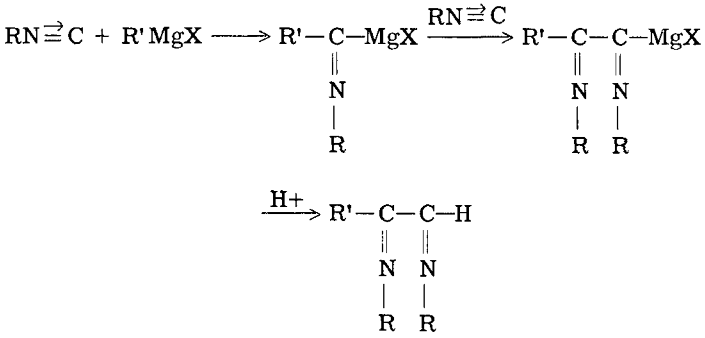
Passerini and Zite [4] described the reaction of phenyl isonitrile with nitrosobenzene and isolated a red compound which analyzed as the trimer of phenyl isonitrile. The structure assigned to the trimer was



A series of para-substituted phenyl isonitriles was synthesized [5] in an attempt to elucidate the nature of the N—C bond. It was found that the p-chlorophenyl isonitrile polymerized rapidly, even in solution, to a dark-colored material. The p-methyl compound polymerized more slowly and the p-methoxy showed still slower reaction. The polymers were not characterized. Similarly, Ugi and Meyr [6] note that the ortho- and para-chlorophenyl isonitriles are unstable and turn green in a few minutes on standing. The green products were not isolated.

Recently Millich and Sinclair [7] have reported on the polymerization of α-phenylethyl isonitrile in the presence of acid-treated powdered glass. The polymers obtained were soluble in aromatic and haloaliphatic hydrocarbons and had number-average molecular weights between 30,000 and 130,000.

Ugi and Fritzer [8] have reported the reaction of cyclohexyl isonitrile with phenyl Grignard reagent. It was found that when equimolar quantities of the isonitrile and Grignard were used, a small amount of a dimer is formed as follows:



$$\mathrm{RN}\overset{\rightarrow}{\equiv}\mathrm{C} + \mathrm{R'MgX} \longrightarrow \mathrm{R'}-\begin{array}[t]{c}\mathrm{C}\\ \| \\ \mathrm{N}\\ | \\ \mathrm{R}\end{array}-\mathrm{MgX} \xrightarrow{\mathrm{RN}\overset{\rightarrow}{\equiv}\mathrm{C}} \mathrm{R'}-\begin{array}[t]{c}\mathrm{C}\\ \| \\ \mathrm{N}\\ | \\ \mathrm{R}\end{array}-\begin{array}[t]{c}\mathrm{C}\\ \| \\ \mathrm{N}\\ | \\ \mathrm{R}\end{array}-\mathrm{MgX}$$

$$\xrightarrow{\mathrm{H}+} \mathrm{R'}-\begin{array}[t]{c}\mathrm{C}\\ \| \\ \mathrm{N}\\ | \\ \mathrm{R}\end{array}-\begin{array}[t]{c}\mathrm{C}\\ \| \\ \mathrm{N}\\ | \\ \mathrm{R}\end{array}-\mathrm{H}$$

No attempts were made to extend this reaction to polymer formation.

EXPERIMENTAL

Materials

Cyclohexyl isonitrile was prepared by the method of Ugi and Meyr [6]. Gas-liquid chromatographic analysis showed only one component present. Trioxane and methyl acrylate were obtained from the Celanese Chemical Co. and purified before use.

Acetaldehyde, acetone, styrene, vinyl butyl ether, and borontrifluoride ethyl etherate were purchased from Matheson Coleman and Bell and were purified before use.

Butyllithium was purchased from Foote Mineral Co. as a heptane–pentane solution. Nitrogen was Airco Prepurified Grade (0.0005 ± 0.0002% oxygen).

Homopolymerizations of Cyclohexyl Isonitrile

Anionic Initiators. Attempts to prepare polymers using butyl Grignard, butyllithium, and triethylaluminium gave no solid polymer.

Thermal and Free Radical Initiators. A sample of cyclohexyl isonitrile was heated at reflux for 25 hr. The liquid turned brown but no viscosity increase was noted. No solid material could be isolated from the dark solution.

Attempts to initiate polymerization with benzoyl peroxide, azobisisobutyronitrile, and dichlorobenzoyl peroxide were also unsuccessful.

Cationic Initiators. Fifty milliliters of anhydrous ether and 4.6 g of cyclohexyl isonitrile (0.042 mole) were charged to a dry, nitrogen-swept reaction flask. The solution was cooled to —10°C with an ice-salt bath and 1.5 ml of a 4.7% BF_3 solution in ethyl ether (0.0012 mole BF_3) was added. A large amount of a cream-colored solid formed immediately. The mixture was stirred for 3 hr at —10°C. At the end of this period the catalyst was neutralized with 2 ml of triethylamine. The solid was removed by filtration and washed thoroughly with methanol and with methylene chloride and dried overnight in a vacuum oven. The yield was 4.5 g (97.8%) of a cream-colored solid which flowed at 329–345°C and showed no birefringence under a hot stage polarizing microscope.

Analysis: Calcd. for $(C_7H_1N)_x$: C 77.0%, H 10.1%, N 12.84%
Found: C 76.7%, H 10.2%, N 12.9%

Other polymerizations under various conditions are summarized in Table 1.

None of the polymers obtained was soluble in any of the solvents tested. The solvents included 97% H_2SO_4, 50% aqueous NaOH, m-cresol, p-chlorophenol, DMF, DMSO, DMAc, trichlorophenol, nitrobenzene, formic acid, acetonitrile, aromatic and aliphatic hydrocarbons, and chlorinated aliphatic hydrocarbons.

Copolymerizations with Cyclohexyl Isonitrile

Trioxane. Attempts to prepare copolymers of trioxane with cyclohexyl isonitrile are summarized in Table 2. No copolymers could be isolated in any of these experiments.

Carbonyl Compounds. The attempted copolymerizations of cyclohexyl isonitrile with acetone and acetaldehyde are summarized in Table 3.

Vinyl Monomers. The copolymerization attempts using styrene, methyl acrylate, and vinyl butyl ether are summarized in Table 4. Other attempts to copolymerize the isonitrile with styrene, butyl methacrylate, and methyl acrylate using free radical initiators in solution and emulsion were also unsuccessful.

TABLE 1. Cationic Homopolymerizations of Cyclohexylisonitrile

						Polymer		
Expt.	Solvent, ml	Cyclohexyl isonitrile, g	Catalyst, mM	Time, hr	Temp., °C	g	% Yield	Appearance
7125-24	Ether, 50	10.7	$BF_3\cdot$ etherate, 1.0	3	25–30	2.0	18	Hard, brown
7125-41	Ether, 300	4.6	$BF_3\cdot$ etherate, 0.6	5	25–30	Trace	—	Yellow solid
7125-44	Ether, 150	4.6	$BF_3\cdot$ etherate, 2.0	7	−10 to 20	Trace	—	Tan solid
7125-48-A	Ether, 100	4.6	$BF_3\cdot$ etherate, 1.5	3	−10	2.1	46	Cream solid
7125-48-B	Ether, 50	4.6	$BF_3\cdot$ etherate, 1.2	3	−10	4.5	98	Cream solid
7125-42	Ether, 300	4.6	$AlCl_3$, 0.6	4	25–30	Trace	—	Yellow solid
7125-50	Ether, 50	4.6	$AlCl_3$, 1.0	2	−10	Trace	—	Tan solid
7169-26	Ether, 50	4.6	$BF_3\cdot$ etherate, 1.2	1/60	−10	3.3	72	Cream solid
7316-26	Cyclohexane	3.7	$BF_3\cdot$ etherate, 1.2	1.5	−10	3	81	Tan solid

TABLE 2. Copolymerization of Trioxane with Cyclohexyl Isonitrile

							Product		
Expt.	Solvent, ml	Cyclohexyl isonitrile, g	Trioxane, g	BF_3 mM	Time, hr	Temp., °C	g	Appearnce	Results of analysis
7125-45	Tetrachloroethane, 100	4.6	9	0.8	3	25–30	0.6	Tan solid	Polyisonitrile
7125-46	Ethylene chloride, 100	4.6	9	1.6	3	−10	2.5	Tan solid	Polyisonitrile
7243-7	Ethylene chloride, 100	4.6	20	1.6	2.5	−10	4.4	Tan solid	Polisonitrile
7246-38	Cyclohexane, 50	2.8	9	4.8	1.5	60–30	0.2	Tan solid	Polyisonitrile
7246-39	Cyclohexane, 50	2.8[a]	9	4.8	1.5	60–30	1.4	Brown-white solid	Polyisonitrile
7246-40	Cyclohexane, 50	2.8[b]	9	4.8	1.5	60-30	8.5	Tan fluffy solid	78% Polyoxymethylene, 22% polyisonitrile
7246-42	Cyclohexane, 50	2.8[c]	9	4.8	1.5	60	6.5	White powder	60% Polyoxymethylene, 40% polyisonitrile
7246-43	Cyclohexane, 50	2.8[d]	9	4.8	1.5	60–30	3.4	Tan fluffy solid	90% Polyoxymethylene, 10% polyisonitrile
7598-7	—	0.9	20	4.8	1.5	80	0	—	

[a] Cyclohexyl isonitrile added after BF_3.
[b] Cyclohexyl isonitrile added after 70 min.
[c] Cyclohexyl isonitrile added after 40 min.
[d] Cyclohexyl isonitrile added after 60 min.

TABLE 3. Copolymerization of Cyclohexyl Isonitrile with Carbonyl Compounds

Expt.	Solvent, ml	Cyclohexyl isonitrile, g	Carbonyl compound, g	Initiator, mM	Time, hr	Temp., °C	Polymer	
							g	Appearance
7125-43	Ether, 300	4.6	Acetaldehyde, (9)	BF_3· etherate, 0.6	5	—10	Trace	White solid
7125-47	Ether, 100	4.6	Acetaldehyde, (4.5)	BF_3· etherate, 1.6	3	—10	1.5	Tan solid
7246-14	Ether, 50	4.6	Acetaldehyde, (9)	Butyllithium, 0.25	5	—70	0	—
7246-4	—	9.2	Acetone, (90)	BF_3· etherate, 4.8	18	25	—	Yellow oil
7246-8	CH_2Cl_2, 100	9.2	Acetone, (9)	BF_3· etherate, 4.8	4.5	—10	—	Yellow oil
7246-9	—	1.8	Acetone, (48)	—	48	70	—	Yellow oil

TABLE 4. Copolymerization of Cyclohexyl Isonitrile with Vinyl Monomers

Expt.	Solvent, ml	Cyclohexyl isonitrile, g	Vinyl monomer, g	Initiator, mM	Time, hr	Temp., °C	Polymer		Results of analysis
							g	Appearance	
246-5	Ether, 100	4.6	Styrene, 9	$BF_3\cdot$ etherate, 3.6	2	–70	4.1	Cream solid	Polyisonitrile
246-6	Acetone, 50	4.6	Styrene, 4.5	$BF_3\cdot$ etherate, 3.2	3	–70	—	Yellow grease	—
246-10	Ether, 50	4.6	Styrene, 9	Butyllithium, 0.1	4.5	–70	0	—	—
246-12	—	1.8	Styrene, 18	—	48	90	0	—	—
246-11	Ether, 50	4.6	Methyl acrylate, 9	Butyllithium, 0.2	4.5	–70	0	—	—
246-13	Ether, 50	4.6	Methyl acrylate, 9	Butyllithium, 0.1	5	–70	0	—	—
246-19	Petroleum ether, 40	4.6	Vinyl butyl ether, 9	$BF_3\cdot$ etherate, 1.8	2	–70	0.2	Yellow	—

DISCUSSION

Anionic Initiation. In view of the results reported by Ugi and Fritzer on the reaction of isonitriles with Grignard reagents [8] it was believed that it might be possible to obtain some polymers by the use of anionic initiators. No reaction was noted, however, in the presence of butyllithium, butyl Grignard, or triethylaluminum. In the presence of 0.7 mole % butyllithium at room temperature for 54 hr no solid material could be isolated. Similar results were found for even higher concentrations of the initiators used. No attempts were made to isolate any liquid products which may have been present.

Attempts to prepare isonitrile copolymers with carbonyl compounds and with vinyl monomers using anionic initiators were also not successful. While control experiments in the absence of isonitrile gave polymer from the vinyl monomers, no polymerization could be detected in the presence of isonitrile. The initiator is therefore probably reacting rapidly with the isonitrile to give a stable species which is noninitiating.

Thermal and Free Radical Initiation. Unlike the aromatic isonitriles, which are reported to undergo ready polymerization on standing or attempted distillation, it was found that cyclohexyl isonitrile could not be homopolymerized with free radicals or by refluxing for 25 hr.

As was the case with anionic initiators, copolymers with vinyl monomers are not formed, and the isonitrile acts on an inhibitor of homopolymerization for styrene and for methyl acrulate, in both solution and emulsion systems.

Cationic Initiation. Cationic initiators such as $BF_3\cdot$ etherate were found to be effective in producing solid polymeric products from cyclohexyl isonitriles. The polymers produced were in all cases high-melting, insoluble materials.

Owing to the lack of solubility, no determination of molecular weights of the polymers obtained could be made.

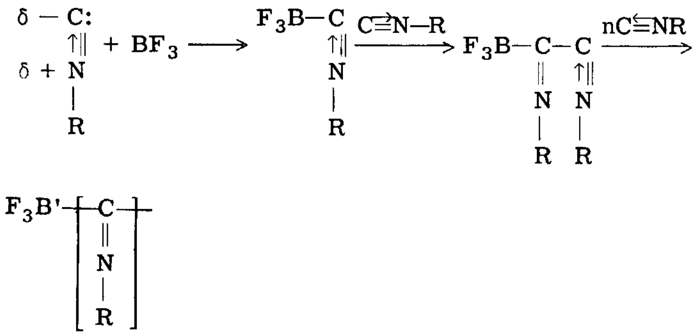
These solid materials are, however, truly of a polymeric nature. The elemental analysis prositively eliminates the possibility that they are any type of simple addition compound of BF_3 and/or ethyl ether with the isonitrile. The empirical formula of the solid products, calculated from the elemental analyses, $(C_7H_{11}N)_x$, is identical to that of the starting cyclohexyl isonitrile.

The extreme insolubility also suggests that these products are more than cyclic trimers or tetramers.

In the polymerizations performed using cyclohexyl isonitrile and $BF_3\cdot$ etherate, a ratio of 34:1 to 18:1 of isonitrile to BF_3 was used. Assuming that each molecule of BF_3 initiates one chain and considering the amount of isonitrile which reacts based on the yield obtained the DP's of the polymers should be 18–34, which corresponds to a molecular weight of 1900–3700.

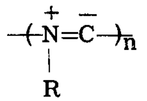
No evidence could be found for assigning a structure to these polymeric isonitriles. Infrared spectra of the polymers sheds little if any light on their structures. No clear-cut absorptions were found which could help elucidate the structure. Owing to the nonreactivity and insolubility, no chemical evidence of structure could be obtained.

One can, however, speculate on what the structure may be for these polymers. Owing to the polarization of the isonitrile group, in which the carbon carries a partial negative charge and a lone pair of electrons, attack at this position by a Lewis acid could lead to polymerization as follows:



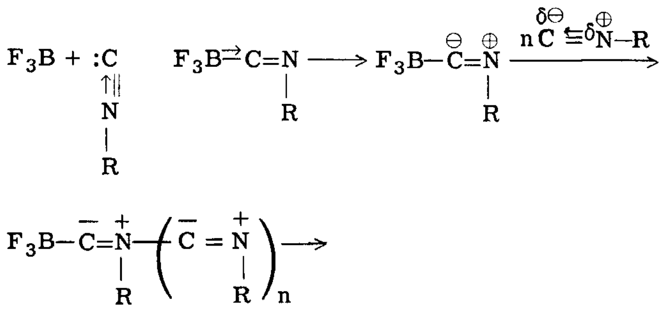
This unusual structure, while appearing sterically difficult to form, can be constructed with space-filling models even when R— is the bulky t-butyl group, as pointed out by Millich and Sinclair [7].

Another possible structure of these polymers suggested by Millich, is

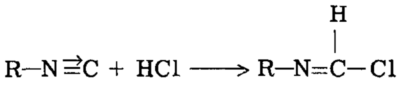


$$-\!\left(\overset{+}{\underset{R}{\underset{|}{N}}}=\overset{-}{C}\right)_{\!n}\!-$$

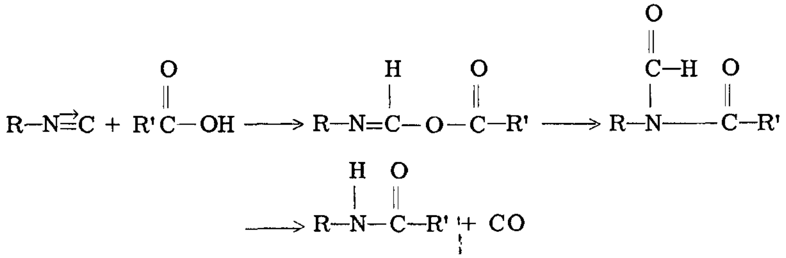
This structure could be formed as follows:



The literature shows that additions to isonitriles proceed generally such that both fragments are added to the carbon of the —N=C group [9]. Such acids as HCl and organic acids give a product arising from α addition:



$$R{-}N\overset{\rightarrow}{\equiv}C + HCl \longrightarrow R{-}N{=}\overset{\overset{\displaystyle H}{|}}{C}{-}Cl$$



$$R{-}N\overset{\rightarrow}{\equiv}C + R'\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \longrightarrow R{-}N{=}\overset{\overset{\displaystyle H}{|}}{C}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R' \longrightarrow R{-}\overset{\overset{\overset{\displaystyle O}{\|}}{C-H}}{\overset{|}{N}}{-\!-\!-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'$$

$$\longrightarrow R{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R' + CO$$

The fact that in the additions the products are the result of α addition would seem to favor the polymerization by the first mechanism to give the C—C chain polymer. The existence of the —C=N— chain polymer cannot, however, be ruled out as a possible structure.

The reaction of $BF_3\cdot$ etherate with the cyclohexyl isonitrile proceeds very rapidly. After 1 min reaction time a 72% yield of solid polymer was obtained. When aluminium chloride was used in place of $BF_3\cdot$ etherate the reaction was much slower and only small amounts of polymer (<10%) were found. No polymer was formed when stannous chloride or ferric chloride were used as initiators.

Solvents were found to have no effect upon the polymerization. Use of either ethyl ether or cyclohexane gave essentially the same yield of polymer. The polymers obtained were identical regardless of which of these solvents were used.

Concentration of isonitrile had a large effect upon the polymerization. When the concentration of isonitrile in ethyl ether was 5% or less, little polymer was obtained. At concentrations of 10% or greater, 90% yields of polymers could be obtained. Addition of $BF_3\cdot$ etherate to pure cyclohexyl isonitrile resulted in immediate formation of solid polymer around the droplet of initiator and therefore isolation of the initiator from the monomer and poor conversions.

Copolymers of isonitriles could not be obtained using $BF_3\cdot$ etherate initiators. The isonitrile was homopolymerized rapidly and preferentially to the exclusion of the comonomer. The results obtained on attempted copolymerization of the isonitrile with trioxane are of interest in this respect. Using a conventional trioxane polymerization procedure, with cyclohexane as the solvent, only polyisonitrile could be isolated if cyclohexyl isonitrile was present before the $BF_3\cdot$ etherate was introduced. If, however, the isonitrile was added at some point after the $BF_3\cdot$ etherate, mixtures of homopolymers were obtained. The homopolymers could be separated by extraction with hot tetrachlorethane. Analysis of the extracted polyoxymethylene showed only about 0.17% N and rapid decomposition at about 130°C.

The lack of formation of any polyoxymethylene when the $BF_3\cdot$ etherate was added to the mixture of trioxane and isonitrile again points up the fact that the isonitrile polymerizes very rapidly and effectively ties up all the BF_3 added. Analyses of the solids obtained in these cases show exclusively polyisonitrile. Even running the polymerization in molten trioxane only polyisonitrile could be isolated.

The only attempted copolymerizations which showed any promising results were the experiments involving acetone. When acetone and isonitrile were allowed to react with $BF_3\cdot$ etherate, a small amount of yellow oil or grease was formed. No characterizations of these oils were attempted.

The experimental evidence thus points to the formation of a polymer from the reaction of $BF_3\cdot$ etherate with cyclohexyl isonitrile. The polymers formed are insoluble in all the solvents investigated and are high melting. No structural determinations could be made on these polymers, owing to their intractability and lack of reactivity.

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Zusammenfassung

Die Darstellung von Homopolymeren aus Cyclohexylisonitril mittels kationischer Initiatoren wurde utersucht.

Die mit BF_3· Atherat als Initiator erhaltenen Produkte waren unlösliche, hochschmelzende Festkörper. Versuche das Isonitril mittels anionischer oder Radikalinitiatoren zu polymerisieren, waren erfolglos. Die Struktur des Polymers konnte zwar nicht bestimmt werden, es werden jedoch mögliche Strukturen diskutiert.

Ebenfalls erfolglos waren Versuche unter Verwendung von kationischen, anionischen oder Radikalinitiatoren copolymere mit verschiedenen Monomeren herzustellen. Lediglich Mischungen aus Homopolymeren wurden bei der Copolymerisation von Cyclohexylisonitril mit Trioxan unter Verwendung von BF_3-Ätherat erhalten.

Résumé

On a étudié la preparation d'homopolymères d'isonitrile de cyclohexyle par des initiateurs cationiques.

Les polymères obtenus avec l'éthérate de BF_3 comme iniateur, étaient des solides insolubles, fondant à température élevée. Les éssais de polymérisation de l'isonitrile avec des iniateurs anioniques et radicalaires libres sont restés sans succès. On N'a pas pu déterminer la structure du polymère, mais on discute quelques structures possible.

Les éssais de preparation des copolymères avec des différents types de monomères à l'aide des iniateurs cationiques, anioniques et radicalaires libres étaient aussi infructueux. On n'a pu obtenir que des mélanges d'homopolymères des essais de copolymérisation de l'isonitrile de cyclohexyl avec le trioxanne en présence de l'éthérate de BF_3 comme iniateur.