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**Crystalline Polymers of Phenyl- and *n*-Butylisocyanates**

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# Crystalline Polymers of Phenyl- and *n*-Butylisocyanates

By G. NATTA, J. DIPIETRO\*, and M. CAMBINI

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## SUMMARY:

By polymerizing phenyl or *n*-butylisocyanate in various solvents in the presence of anionic catalysts such as lithium or sodium alkyls, crystalline polymers were obtained. For both polymers, the I.R. spectra, the X-ray diffraction spectra and other physical properties have been reported. The possible structures of the two crystalline polymers have also been discussed. By cationic catalysts (e.g.  $\text{AlBr}_3$ ) amorphous polymers were obtained from phenylisocyanate, but no polymers from *n*-butylisocyanate.

## ZUSAMMENFASSUNG:

Durch Polymerisation von Phenyl- oder *n*-Butylisocyanat in verschiedenen Lösungsmitteln in Gegenwart anionischer Katalysatoren wie Lithium- oder Natriumalkylen wurden kristalline Polymere erhalten.

Für beide Polymere werden die IR-Spektren, die Röntgenbeugungsspektren und andere physikalische Eigenschaften wiedergegeben. Die möglichen Strukturen der beiden kristallinen Polymeren werden diskutiert. Mit kationischen Katalysatoren (z.B.  $\text{AlBr}_3$ ) wurden im Fall des Phenylisocyanats amorphe Polymere erhalten, während das *n*-Butylisocyanat keine Polymere lieferte.

In a recent publication<sup>1)</sup>, G. NATTA and collaborators have shown that dimethylketene can polymerize to give at least two different types of crystalline polymers. One type results if the ethylenic bond of the ketene molecule opens up in the propagation step, while a second type polymer is obtained if the carbonyl bond opens up. Structural similarity of mono-isocyanates with ketenes has suggested that they may be likewise polymerizable to crystalline polymers. Isocyanates are known to form dimers and trimers when treated with basic substances as catalysts such as triethylamine<sup>2</sup> and pyridine<sup>3)</sup>.

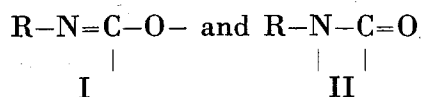
Recently<sup>4)</sup>, isocyanates were reported to undergo homopolymerization to high molecular weight products. The polymerization was carried out at low temperatures and was applicable to both aliphatic and aromatic isocyanates giving prevailingly amorphous polymers. It is of interest to point out that the authors had lack of success with classical anionic catalysts, such as metal alkyls, GRIGNARD reagents and sodamide.

\*) Nato Postdoctoral Fellow.

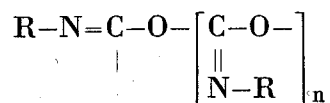
Substances, which possess two double bonds in the molecule, especially those having such bonds in an adjacent position, even if between atoms having the same degree of electronegativity, show great reactivity and stimulate considerable interest.

Following the tradition of these laboratories in the synthesis of new crystalline polymers it was most appropriate to investigate whether crystalline polyisocyanates could be obtained.

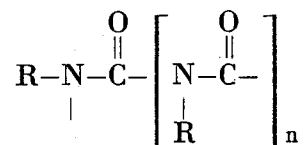
In a possible linear and regular polymerization of isocyanates,  $R-N=C=O$ , where R may be either an aliphatic or aromatic group, two fundamental monomeric structural units are possible:



The regular 1,2-carbonyl type of opening (I) would give origin to macromolecules having a polyacetalic structure:



By the 2,3-carbon-nitrogen double bond opening (II), a disubstituted amidic type of structure would be formed:



In both structures there are no asymmetric atoms in the chains, therefore, only a regularity of the chemical structure can be sufficient for the presence of crystallizability in the polymer.

### *Experimental*

The two monomers, phenyl- and *n*-butylisocyanate, were obtained from commercial sources. Prior to their polymerization, they were fractionally distilled, through a 12-in. helix-packed column, to a purity higher than 99% (determined by gas-chromatography).

All the solvents used in this work were dried with sodium-potassium alloy and distilled before use.

The various catalysts employed in this work were prepared according to standard procedures. The preparation of ethyl-lithium was best performed by the slow addition of ethyl bromide to a wellstirred mixture of lithium and pentane. The reaction product was a precipitate consisting of lithium bromide and ethyl lithium, the latter being only slightly soluble in pentane, 7.6 g./l.

Since ethyl lithium is about ten times as soluble in benzene as in pentane at room temperature, it was separated from lithium bromide by solution in benzene, removed from pentane by distillation followed by crystallization of the ethyl lithium from benzene.

### Preparation of Polymers

Table 1 shows representative reaction conditions for the polymers prepared in this work.

Table 1. Polymerization of Phenyl and *n*-Butyl Isocyanates

Iso-cyanate	Catalyst (ml.)	Sol-vent	Time (hrs.)	Temp. (°C.)	Con- ver- sion (%)	X-ray Exami- nation*)	[ $\eta$ ] (100 ml./g.) in benzene at 30°C.	m.p. (°C.)
phenyl	1 of 10% soln. AlBr <sub>3</sub> in <i>n</i> -heptane	toluene	48	-60	traces	am.	—	148
	1 of 10% soln. AlBr <sub>3</sub> in <i>n</i> -heptane	CS <sub>2</sub>	48	-60	traces	am.	—	—
	1 BF <sub>3</sub> ·Et <sub>2</sub> O 45%	CH <sub>2</sub> Cl <sub>2</sub>	24	-60	traces	am.	—	—
	1 C <sub>2</sub> H <sub>5</sub> Li in benzene (1·10 <sup>-3</sup> mole/ml.)	toluene	3	-78	30	cr.	—	270
	1 C <sub>2</sub> H <sub>5</sub> Li in benzene (1·10 <sup>-3</sup> mole/ml.)	toluene	18	-78	45	cr.	—	270
	1 C <sub>2</sub> H <sub>5</sub> Li in benzene (1·10 <sup>-3</sup> mole/ml.)	CS <sub>2</sub>	3	-78	34.5	cr.	—	—
<i>n</i> -butyl	0.2 Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	toluene	20	-78	—	—	—	—
	1 of 10% soln. AlBr <sub>3</sub> in <i>n</i> -heptane	toluene	48	-78	—	—	—	—
	1 of <i>n</i> -octyl sodium	CH <sub>2</sub> Cl <sub>2</sub>	20	-78	12	cr.	3.9	165
	1 C <sub>2</sub> H <sub>5</sub> Li in benzene (1·10 <sup>-3</sup> mole/ml.)	toluene	20	-78	43	cr.	11.6	—
	1 C <sub>2</sub> H <sub>5</sub> Li in benzene (1·10 <sup>-3</sup> mole/ml.)	CS <sub>2</sub>	20	-78	76	cr.	8.5	165
	1 C <sub>2</sub> H <sub>5</sub> Li in benzene (1·10 <sup>-3</sup> mole/ml.)	THF	20	-78	27	cr.	1.24	—
	1 LiOC <sub>4</sub> H <sub>9</sub>	acetone	3	-78	18	cr.	4.3	—
	1 C <sub>2</sub> H <sub>5</sub> Li in benzene (1·10 <sup>-3</sup> mole/ml.)	CH <sub>2</sub> Cl <sub>2</sub>	20	-78	23	cr.	2.6	—
	0.4 (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Be	toluene	1/2	-78	36	cr.	6.8	—
1 NaCN in DMF	DMF	1/2	-55	25	very slightly cr.	1.4	—	

\*) am. = amorphous, cr. = crystalline.

## Crystalline Polymers of Phenyl- and *n* Butylisocyanates

The following is a typical polymerization procedure: A 100-ml. test tube, equipped with a side arm, was flamed while being for several times evacuated and swept with dry nitrogen. Toluene (50 ml.) was added, then the isocyanate (10 ml.), and the contents were cooled to  $-78^{\circ}\text{C}$ . With the aid of a syringe, 1.0 ml. of the catalyst was rapidly added to the system, while a stream of nitrogen was continuously sweeping over it.

The reaction mixture apparently solidified over a period of 1–2 hrs. The product was allowed to remain at this temperature  $-78^{\circ}\text{C}$ ., for several hrs., then methanol was added, the polymer filtered and washed with 5% HCl water solution and dried at  $50^{\circ}\text{C}$ . *in vacuo*; the yield and intrinsic viscosity of the polymer were then determined.

The characterization of the products was performed by employing the following apparatus:

The BISCHOFF-DESREUX viscometer for the viscosity measurements, which were carried out at  $30^{\circ}\text{C}$ .; the LEITZ polarizing microscope for determining the m.p. The infrared spectra were obtained in a double beam PERKIN-ELMER 221-spectrophotometer. The X-ray analyses were registered on powdered samples by standard methods.

When using the same homogeneous catalytic system, ethyl lithium in toluene or benzene, the intrinsic viscosity and the yield of polymerization increased by increasing the time of polymerization (Tab. 2).

Table 2. The Influence of the Reaction time at  $-78^{\circ}\text{C}$ . on the Yield and Intrinsic Viscosity of Poly-*n*-butylisocyanate  
(Solvent: Toluene; Catalyst: Concentration  $1 \cdot 10^{-3}$  Mole/ml. in Benzene; Temp.  $-78^{\circ}\text{C}$ .)

Time (hrs.)	Yield (%)	$[\eta]$ (100 ml./g.)*
2	16.8	0.31
5	23	1.1
10	33	5.3
20	43	11.6
40	57	15.3

\*) in benzene at  $30^{\circ}\text{C}$ .

### *Solvent Extractions*

The crude products obtained by the polymerization process described above are in the case of *n*-butylisocyanate white, fibrous solids, while those of phenylisocyanate are powders. They were subjected to a method of extraction with boiling solvents; the results obtained from a typical extraction are reported in Table 3.

The extraction process has given two different types of products. One part is the soluble fraction and the other part is the insoluble one having a high molecular weight.

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The extraction process has given two different types of products. One part is the soluble fraction and the other part is the insoluble one having a high molecular weight.



Table 3. Solvent Extraction of a Poly-(*n*-butylisocyanate). Sample Obtained by the Use of Ethyl Lithium in Toluene at  $-78^{\circ}\text{C}$ .

Sample	Acetone extract (wt.-%)	Ether extract (wt.-%)	<i>n</i> -Pentane extract (wt.-%)	<i>n</i> -Heptane extract (wt.-%)	Total extract (wt.-%)
A	20.8	5.7	3.2	22.0	48.3
B	20.6	6.3	3.9	21.0	48.0

*Soluble fraction*

It is interesting to point out that upon extracting the raw polymer of *n*-butylisocyanate with acetone, a soluble small fraction having a low molecular weight was separated. Its I.R.-spectrum proved to be *N,N'*-dibutylurea, which can be justified by the presence of traces of  $\text{H}_2\text{O}$  in the system. The compound was independently prepared, is crystalline and has a sharp m.p. at  $71-72^{\circ}\text{C}$ .

Similarly by using phenyl isocyanate according to the previously described polymerization procedure, we obtained polymers which present the type of crystallinity seen in Fig. 1.

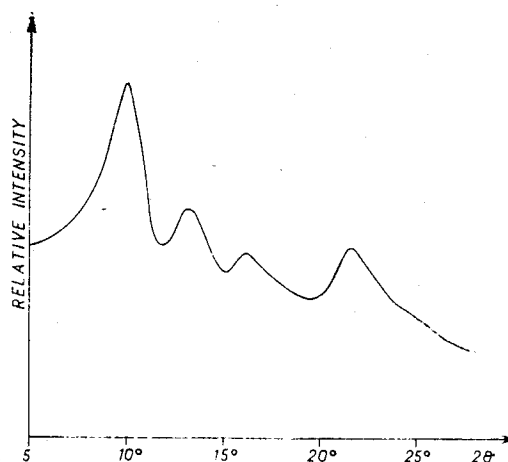


Fig. 1. X-ray GEIGER registration (CuKa) of poly(phenylisocyanate)

By extracting with boiling solvents, it was possible to isolate fractions which resulted more crystalline than the raw polymers, when examined by X-rays. Solvents at their b.p., like acetone, *n*-pentane, ether and methylethylketone were used in the extraction process. Analogously with what was observed in the solvent extraction of poly-*n*-butylisocyanate, a low molecular weight product was obtained from the acetone extraction

## Crystalline Polymers of Phenyl- and *n*-Butylisocyanates

of polyphenylisocyanate. Its I.R.-spectrum was identical to that of a product obtained from phenylisocyanate using as catalyst triethylamine at 50 °C.

It is a crystalline compound, insoluble in benzene and having a m.p. of 274–275 °C.

### *Insoluble fraction*

The extraction residues of poly(*n*-butylisocyanate) are white and possess a higher degree of crystallinity of the type indicated in Fig. 2. The residue to the acetone extraction has the following properties: m.p. (de-

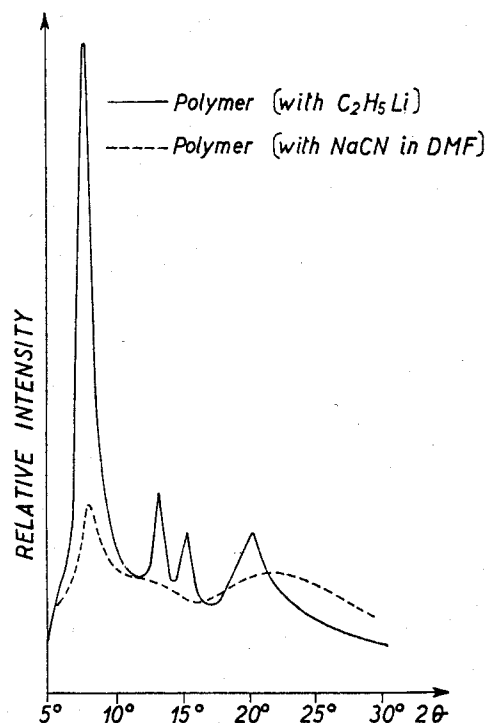


Fig. 2. X-ray GEIGER registration (CuK $\alpha$ ) of poly(*n*-butylisocyanate)

termined by optical methods) = 165 °C.; intrinsic viscosity, determined in benzene at 30 °C. = 5.3; solubility: insoluble in methyl ethyl ketone, dimethyl formamide and carbon tetrachloride. Hot concentrated NaOH or H<sub>2</sub>SO<sub>4</sub> did not hydrolyze the polymer. The residue to the *n*-heptane extraction has the following properties: m.p. (determined by optical methods) = 175 °C.; intrinsic viscosity, determined in benzene at 30 °C. = 8.7; solubility: insoluble in acetone, ether, carbon tetrachloride.

*Discussion of results*

It was of interest to compare those products above described with the poly-phenylisocyanate products obtained by using cationic catalysts which were amorphous by X-ray analysis. Only traces of polymer were obtained when cationic catalysts were employed. When suitable anionic catalysts, like ethyl lithium or *n*-octyl sodium were used, highly crystalline polymer of phenylisocyanates were obtained. The infrared spectrum of the residue to the methylethylketone extraction is shown in Fig. 3.

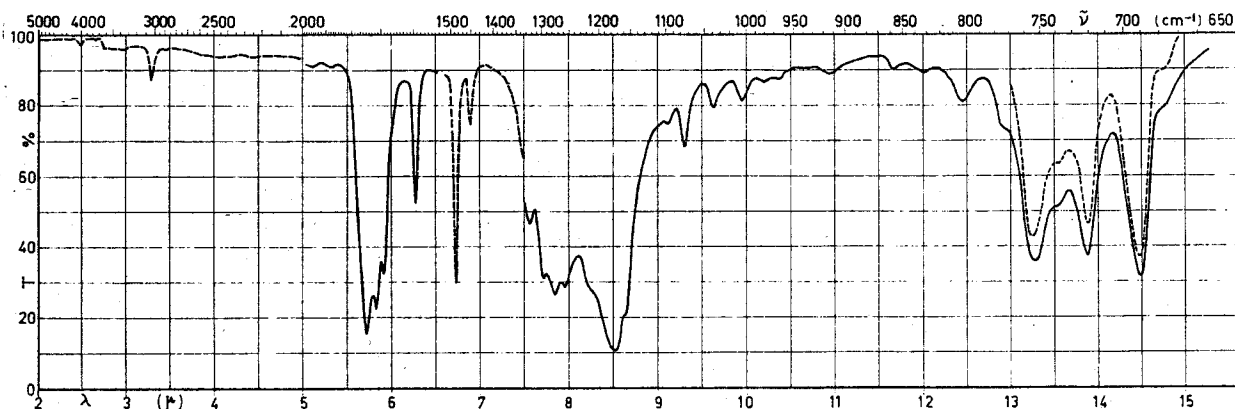


Fig. 3. Infrared spectrum of poly-phenylisocyanate (Methylethylketone residue)  
 - - - - mull in hexachlorobutadiene; — — mull in Nujol

In the case of *n*-butylisocyanate, no polymers were obtained with FRIEDEL-CRAFTS type of catalysts. On the other hand when anionic catalysts, like metallo-organic or alkoxides of metals of group I and II of the periodic table were used in a variety of solvents, crystalline polymers were obtained. In Table I, are reported some results obtained in the polymerization of *n*-butylisocyanate in the presence of ethyl lithium, diethyl beryllium, *n*-octyl sodium, lithium ethoxide and solvents having different dielectric constants. We have generally observed a far lower polymerization rate in cases where CS<sub>2</sub> and tetrahydrofuran were used as solvents, even though the highest conversions were obtained when CS<sub>2</sub> was the solvent in the polymerization. As far as the polymerization conditions are concerned, we kept a low temperature, for instance at -78°C in order to avoid the formation of oligomers, dimers and trimers. For the purpose of comparison we also prepared poly-*n*-butylisocyanate according to the previously described system<sup>4</sup>), which employs, as catalyst, NaCN in dimethylformamide; using the described conditions of polymerization we found that the polymers can be considered practically amorphous with

