

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Some Reactions of Vinyl Isocyanate and Its Copolymers\*

George B. Butler<sup>a</sup>; Stuart B. Monroe<sup>ab</sup>

<sup>a</sup> Department of Chemistry, University of Florida Gainesville, Florida <sup>b</sup> Department of Chemistry, Randolph Macon College, Ashland, Virginia

**To cite this Article** Butler, George B. and Monroe, Stuart B.(1971) 'Some Reactions of Vinyl Isocyanate and Its Copolymers\*', *Journal of Macromolecular Science, Part A*, 5: 6, 1063 – 1070

**To link to this Article:** DOI: 10.1080/00222337108061090

**URL:** <http://dx.doi.org/10.1080/00222337108061090>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Some Reactions of Vinyl Isocyanate and Its Copolymers\*

GEORGE B. BUTLER and STUART B. MONROE†

*Department of Chemistry  
University of Florida  
Gainesville, Florida 32601*

### SUMMARY

Linear, soluble copolymers of vinyl isocyanate with styrene and methyl methacrylate were obtained when the comonomer:vinyl isocyanate ratio in the copolymer was greater than 9:1. When the comonomer to isocyanate ratio was less than 2:1, the copolymers were insoluble. Infrared evidence indicated that spontaneous cross-linking through the isocyanate function occurred by a mechanism similar to the known reaction by which isocyanates undergo dimerization and trimerization. The soluble copolymers retained the reactive isocyanate moiety as was shown by their reactivity with *n*-butylamine and ethanol to produce, respectively, the corresponding polyurea and poly-carbamate, and with ethylenediamine and water to produce cross-linked polymers. The intrinsic viscosity  $[\eta]$  for the 9:1 methyl methacrylate:vinyl isocyanate copolymer was 0.22 dl/g while that for the corresponding ethyl carbamate was 0.24 dl/g.

\*Taken from the Ph.D. Dissertation of Stuart B. Monroe, University of Florida, February, 1962.

†Present address: Department of Chemistry, Randolph Macon College, Ashland, Virginia 23005.

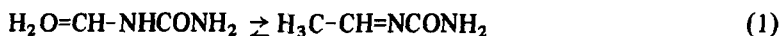
## INTRODUCTION

In 1950 the suggestion was made that copolymers of l-alkenyl isocyanates, e.g., vinyl isocyanate, might be prepared [1]. Iwakura, Sato, Tamikado, and Mizoguchi [2], Hart [3], and others [4] carried out low conversion copolymerizations of vinyl isocyanate as well as reactions of vinyl isocyanate with ammonia and amines to yield unsaturated ureas which were then polymerized to low-molecular weight products. Recently, Overberger, Ozaki, and Mukamal prepared ladder polymers from vinyl isocyanate by reacting the monomer first through the isocyanate group, followed by reaction through the double bond, and vice versa [5].

This investigation involved addition polymerization and copolymerization of vinyl isocyanate through the double bond to yield polymers with reactive isocyanate side groups. The reactions of these products with mono- and difunctional active hydrogen-containing materials were then examined.

## RESULTS AND DISCUSSION

Vinyl isocyanate was synthesized by means of the Curtius rearrangement following the reaction between sodium azide and acrylyl chloride. The corresponding N-vinylurea was prepared by reacting the isocyanate with ammonia. Instability of this derivative was apparent upon heating or standing at atmospheric conditions. Similar results have been observed by others [3, 6], and the instability has been attributed to tautomerism of the N-ethylene compounds into imine forms: e.g.,



would be expected to be quite susceptible to hydrolysis by atmospheric moisture.

Vinyl isocyanate was polymerized in bulk and in solution to yield insoluble, infusible products. These results were consistent with those obtained by Overberger [5] and Hart [7]. Infrared spectra of the insoluble polymers exhibited no evidence of unsaturation in the region of  $1000\text{-}800\text{ cm}^{-1}$ ; but showed strong absorptions characteristic of  $-\text{NCO}$  ( $2265\text{ cm}^{-1}$ ), thus indicating polymerization through the vinyl group. There were also bands in the region between  $1800$  and  $1700\text{ cm}^{-1}$  which are believed to be due to absorptions representative of dimer and trimer formation. Copolymers of vinyl isocyanate, which contained comonomer to isocyanate ratios of less than 2:1, were also insoluble. Again, infrared absorption bands between  $1800$  and  $1700\text{ cm}^{-1}$  were prominent.

Linear, soluble copolymers with reactive isocyanate moieties (strong  $\text{-NCO}$  absorptions in infrared) were prepared from vinyl isocyanate and styrene or methyl methacrylate. These were isolated and caused to react with either *n*-butylamine, ethanol, or ethylenediamine to yield polymeric products with different properties than those of the starting materials. Infrared spectra of these products showed complete absence of  $\text{-NCO}$  absorption in addition to new absorptions in the regions 1640-1600 and 1600-1550  $\text{cm}^{-1}$ . The former were attributed to amide band I and the latter to amide band II and NH deformation. The product of the reaction between the soluble, low melting, vinyl isocyanate-styrene copolymer and ethylenediamine exhibited limited solubility and increased melting temperature, thus indicating that cross-linking had taken place. Representative data and results pertaining to polymerizations and reactions of copolymers are given in Table 1, 2, and 3.

## EXPERIMENTAL

All temperatures are uncorrected and reported in degrees Centigrade. Melting point determinations of polymeric materials were performed on a Kofler micro hot-stage and viewed through a Unitron polarizing microscope. Infrared spectra were obtained on a Perkin-Elmer Infracord or a Perkin-Elmer Model 21 Spectrophotometer. Intrinsic viscosities were calculated from efflux times of benzene of *N,N*-dimethylformamide solutions through a Cannon-Ubbelohde semimicro dilution viscometer set in a 25° constant temperature bath. Ultraviolet radiation was supplied by a Black-Ray long-wave ultraviolet lamp, model XX-15. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

### Vinyl Isocyanate

Into a 1-liter, three-necked flask, equipped with a reflux condenser fitted with a calcium chloride drying tube, mechanical stirrer, thermometer, and additional funnel, were placed 106 g (1.6 moles) of purified sodium azide (Fisher), 300 ml of water, and 1.0 g of hydroquinone. The reaction vessel was immersed in an ice-water bath, and a mixture of 100 g (1.1 moles) of acrylyl chloride and 300 ml of benzene was added at such a rate that the reaction temperature remained at 10-15°. The mixture was cooled at 0° and stirred for 6 hr. The organic layer was removed and dried over calcium chloride for 24 hr. The azide solution and 1.0 g of hydroquinone were added to 1.0 liter of dry benzene in a 2-liter, three-necked flask equipped with a magnetic stirring bar, thermometer, and Dry Ice-acetone reflux con-

Table 1. Polymerizations and Copolymerizations of Vinyl Isocyanate

Polymer No.	Comonomer	Wt comonomer (g)	Wt isocyanate (g)	$\frac{M_2^a}{M_1}$	Initiator (%)	Solvent (ml)	Reaction time
1	None	-	0.90	-	0.5	None	2.0 days
2	None	-	0.29	-	3.2	2.0	3.0 hr
3	Styrene	0.47	0.62	0.5	0.5	None	1.0 week
4	Styrene	0.90	0.22	2.7	0.9	1.0	1.2 days
5	Methyl methacrylate	0.50	0.31	1.1	0.5	1.0	5.0 hr
6	Methyl acrylate	0.59	0.51	0.9	0.5	None	1.0 week
7	Methyl acrylate	0.91	0.22	3.3	0.9	1.0	0.5 hr
8	Fumaritrile	0.78	0.32	2.1	0.9	5.0	1.5 hr

<sup>a</sup> $\frac{M_2}{M_1} = \frac{\text{Moles of comonomer}}{\text{Moles of isocyanate}}$  in feed.

Table 2. Polymers and Copolymers of Vinyl Isocyanate

Polymer No.	Comonomer	Yield (g)	Conversion (%)	Description of product	Melting range (°C)	Intrinsic viscosity (dl/g)	% Elemental analysis	$\frac{M_2}{M_1}$ <sup>a</sup>
1	None	0.90	100	Insoluble, hard white solid	> 300	-	C = 51.96 H = 4.21 N = 19.96	-
2	None	0.18	62	Insoluble, soft white solid	> 300	-	-	-
3	Styrene	0.90	83	Insoluble, white solid	> 300	-	N = 4.70	2
4	Styrene	0.20	18	Soluble, colorless solid	110-125	0.44	N = 1.26	10
5	Methyl methacrylate	0.12	15	Soluble, colorless solid	115-128	0.22	N = 1.42	9
6	Methyl acrylate	0.67	61	Insoluble, rubbery solid	> 300	-	N = 10.13	1
7	Methyl acrylate	0.22	19	Insoluble, rubbery gel	> 300	-	N = 6.03	2
8	Fumaronitrile	0.28	25	Insoluble, yellow-white solid	> 300	-	-	-

$$\frac{2M_2}{M_1} = \frac{\text{Moles of comonomer}}{\text{Moles of isocyanate}} \text{ in copolymer.}$$

**Table 3.** Reactions of Soluble Copolymers of Vinyl Isocyanate

Polymer No.	Reactant	Description of product	Melting range (°C)	Intrinsic viscosity (dl/g)
4	n-Butylamine	White, chalky solid	130-140	0.38
	Ethylenediamine	Partially soluble white solid	> 300	
5	Ethanol	White, powdery solid	120-130	0.24

denser guarded by a calcium chloride drying tube. The reaction mixture was heated, with stirring, to 70-80° until the evolution of nitrogen was nil and then distilled through a 12-in. Vigreux column fitted with an ice-water condenser backed by a Dry Ice-acetone trap. The latter was guarded by a calcium chloride drying tube. Distillation was continued until a vapor temperature of 80° was reached. The distillates in the receiving flask and Dry Ice-acetone trap were combined and redistilled from 1.0 g of hydroquinone through a 12-in., helix-packed column into a receiving flask that contained 200 ml of dry benzene and 1.0 g of hydroquinone. The receiving flask was immersed in a Dry Ice-acetone bath. The product was 40 g (53%) of vinyl isocyanate, bp 39°,  $n_D^{20}$  1.4180; reported [6] bp 39°,  $n_D^{20}$  1.4188. Infrared analysis revealed the following absorption bands ( $\text{cm}^{-1}$ ): 3100 (C-H); 2270 (NCO); 1630 (C=C); 1460, 1380, 1310 (CH deformations); 957 (=CH-); 895 ( $\text{CH}_2=$ ); 835 (CH deformation). This compound was a severe lachrymator.

Analysis calculated for  $\text{C}_3\text{H}_3\text{NO}$ : C, 52.16; H, 4.38; N, 20.26. Found: C, 51.93; H, 4.31; N, 19.91.

### N-Vinylurea

To 2.0 ml of dry benzene in an open vial was added 0.50 g (0.072 mole) of vinyl isocyanate. Gaseous ammonia was immediately bubbled into the solution to yield a gelatinous, white precipitate which was separated by filtration and dried under vacuum (25 mm) at 50°. The product was 0.50 g (80%) of vinylurea, mp 68-70°: reported [3] mp 80-81°. The melting point reported by Hart [3] was determined by means of a Kofler hot-stage. Using this technique for the vinylurea prepared above also revealed a melting point of 80-81°. Infrared analysis revealed the following absorption bands

( $\text{cm}^{-1}$ ): 3250 (N-H); 1665 (-CONH<sub>2</sub>); 1600 (-CONH-); 1550 (NH deformation); 1410, 1325, 1225, 1135, 1075 (CH deformations); 980 (=CH-); 915 (CH<sub>2</sub>=); 850, 840 (CH deformations).

Analysis calculated for C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>O: C, 41.86; H, 6.98; N, 32.56. Found: C, 41.56; H, 7.25; N, 32.34.

Two separate preparations of vinylurea gave products with the respective melting points of 72-73° and 73-74°. Attempts at recrystallizing the product from ethanol resulted in a loss of the material. Vinylurea crystals were converted to a viscous, yellow liquid while standing at room temperature in a screw-capped vial for several weeks.

### Preparation of Polymers

Polymerization reactions were carried out in 40 X 15 mm glass tubes which had constricted necks to allow sealing by means of a gas-air flame. The open end of a reaction tube was fitted with a rubber policeman and weighed to the nearest milligram. Predetermined amounts of initiator, comonomer (where applicable), and solvent (where applicable) were added to the tube, and the tube and contents were weighed after each addition. The isocyanate was distilled through a stainless steel spinning-band column directly into the tube; the tube was capped and again weighed. The tube was cooled in a Dry-Ice bath in a nitrogen atmosphere. The policeman was removed, and the tube was flushed with nitrogen and promptly sealed. Polymerizations were accomplished in the presence of ultraviolet light at room temperature; benzoyl peroxide was used as initiator.

After the polymerization period, the tube and its contents were cooled in a Dry-Ice bath, and the contents removed by breaking the tube. Insoluble polymers were triturated with nonsolvent, and the solid was removed by filtration. Solutions of soluble polymers were poured with stirring into 3 volumes of reagent grade petroleum ether (Fisher) to precipitate the polymer. The polymer was washed and reprecipitated twice more. All polymers were dried at 15 mm of mercury and 50-100°.

### Characterization of Polymers

Polymer solubilities were determined by addition of 5-10 mg of polymer to 0.5-1.0 ml of solvent. If solution did not take place within a matter of minutes, the mixture was heated to reflux and allowed to resume room temperature. If no degree of solubility was observed in N,N-dimethylformamide,



benzene, acetone, tetrahydrofuran, chloroform, carbon tetrachloride, methylene chloride, ethyl acetate, dioxane, or dimethylsulfoxide, the polymer was classified as insoluble.

Melt temperatures of polymers were determined by heating until they were liquified or until a temperature of 300° was reached. Infrared studies were made on potassium bromide disks. Elemental analysis provided a means of calculating the ratio of the number of comonomer units to isocyanate units within a copolymer.

### Reactions of Copolymers.

A sample of 25 mg of copolymer was dissolved in 0.5-1.0 ml of reagent grade p-dioxane (Eastman) in a screw-cap vial, and either 0.1 ml of n-butylamine (Matheson, Coleman and Bell) or absolute ethanol or a calculated equivalent amount of ethylenediamine (0.2% in p-dioxane) was added. The reaction vessel was flushed with dry nitrogen, and 1 drop of a 5% solution of triethylamine in p-dioxane was added. The vial was immediately capped and placed in an oven at 70-90° for 24 hr. The reaction mixture was brought to room temperature and added to 3 volumes of water. The resulting solid was removed by filtration and dried under vacuum (15 mm) at 50°. Products were characterized in the same manner as the polymers.

### REFERENCES

- [1] A. S. Nyquist, C. Cos and E. L. Kropa, U.S. Patent 2,503,209 (April 4, 1950), to American Cyanamid Company.
- [2] Y. Iwakura, M. Sata, T. Tamikado and T. Mizoguchi, *Chem. High Polym.* (Japan), **13**, 390 (1956).
- [3] R. Hart, *Bull. Soc. Chim. Belg.*, **66**, 229 (1957).
- [4] Gevaert Photo-Producten N.V., Belgium Patent 540,975 (January 2, 1956); *Chem. Abstr.*, **52**, 5033 (1958).
- [5] (a) Anon., *Chem. Eng. News*, **41**(52), 33 (1963). (b) C. G. Overberger, S. Ozaki, and H. Mukamal, *J. Polym. Sci., Part B*, **2**, 627 (1964).
- [6] M. Sato, *J. Org. Chem.*, **26**, 770 (1961).
- [7] R. Hart, *Bull. Soc. Chim. Belg.*, **65**, 291 (1956).

Accepted by editor April 9, 1971

Received for publication April 12, 1971