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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

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## The Nature of the Cross-linking Reaction in Polymers of Unsaturated Isocyanates\*

GEORGE B. BUTLER AND STUART B. MONROE†

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

### SUMMARY

Copolymers of vinyl isocyanate,  $\beta$ -allyloxyethyl isocyanate, and 9-decenyl isocyanate having low mole fractions of isocyanate monomer were soluble, linear structures. However, at high mole fractions of the isocyanate monomer in the copolymer, the copolymers were insoluble and cross-linked. Evidence has been obtained which supports the postulation that the cross-links are formed at high isocyanate ratios by a mechanism similar to that by which isocyanates are converted to dimers, the uretidenedione structure, or to trimers, the isocyanurate structure.

During an investigation of the polymerization and copolymerization of some unsaturated isocyanates, it was found that all polymers and copolymers having a high ratio of the isocyanate monomer exhibited properties of cross-linked polymers. For instance, all homopolymers of vinyl isocyanate were

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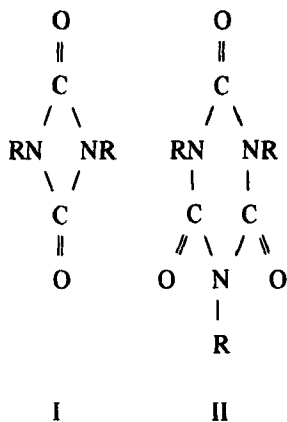
\*Taken from the Ph.D. Dissertation of Stuart B. Monroe, University of Florida, February, 1962.

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

insoluble and did not melt at temperatures up to 300°C. This observation has been reported by others [1, 2]. Furthermore, copolymers from vinyl isocyanate and methyl acrylate or styrene, which contained the isocyanate monomer in the mole fraction range of 0.33 to 0.5, were also insoluble and would not melt at 300°C. On the other hand, copolymers of vinyl isocyanate and styrene or methyl methacrylate, which contained the vinyl isocyanate monomer in the mole fraction range less than 0.1, were soluble and melted in the range of 110-128°C. Corresponding intrinsic viscosities were 0.44 and 0.22 dl/g.

$\beta$ -Allyloxyethyl isocyanate and 9-decenyl isocyanate did not undergo free radical initiated polymerization. Copolymers from one or the other of these materials and methyl acrylate, styrene, or methyl methacrylate, which contained the isocyanate monomer in the mole fraction range less than 0.1, were soluble and possessed intrinsic viscosities of 0.13 to 0.78. Melting ranges varied from 80 to 150°C. However, copolymers from these same monomers and methyl acrylate or dimethyl maleate, which contained the isocyanate monomer in the mole fraction range of 0.15 to 0.5, were insoluble and did not melt at 300°C.

Infrared spectra of insoluble poly(vinyl isocyanate) exhibited no evidence of unsaturation in the region of 1000-800  $\text{cm}^{-1}$ , thus indicating polymerization through the vinyl group. While these same spectra showed strong absorptions characteristic of  $-\text{NCO}$ , there were also bands in the region between 1800 and 1700  $\text{cm}^{-1}$  like those exhibited by isocyanate dimers [3] (uretidenediones) (I) and trimers [4] (isocyanurates) (II).



The spectra of poly(vinyl isocyanate) also contained weak to strong absorption bands in the region  $1655\text{-}1640\text{ cm}^{-1}$ . While these may have been due to residual unsaturation, they could also have been caused by an amide function such as would be found if the polymer had been cross-linked through urea linkages by reaction with water, e.g., atmospheric moisture. However, in preparing poly(vinyl isocyanate), as well as other copolymers, the greatest care was taken to exclude water from the time of final distillation of the isocyanate until the resulting polymer was purified. This included handling of materials in a nitrogen atmosphere, transporting and storing them in vacuum desiccators, and thorough drying of apparatus.

Infrared spectra of insoluble, infusible copolymers also showed absorptions typical of substituted ureas, e.g.,  $1650\text{-}1630\text{ cm}^{-1}$ . However, other characteristic absorptions of the suspected amide linkage were absent. For example, there were no amide II bands which should be found between  $1615$  and  $1555\text{ cm}^{-1}$  according to Moelants and Hart [5] or in the region of  $1630\text{-}1580\text{ cm}^{-1}$  according to Boivin and his co-worker [6]. Absorption bands were present between  $1800$  and  $1700\text{ cm}^{-1}$ . These were assigned to carbonyl absorptions like those found in isocyanate dimers and trimers. Infrared spectra of all copolymers exhibited varying degrees of isocyanate intensities at  $2266\text{-}2256\text{ cm}^{-1}$ . They also showed absorption bands characteristic of the comonomer used during preparation.

Those copolymers which are soluble and which contained unreacted isocyanate functions, as indicated by characteristic infrared absorption, were allowed to react with a stoichiometric amount of water (equivalents of  $\text{-NCO}$  calculated from N analysis) to yield insoluble, infusible products. Infrared spectra of these products showed complete absence of  $\text{-NCO}$  absorption in addition to new bands in the regions of  $1640\text{-}1600$  and  $1600\text{-}1550\text{ cm}^{-1}$ . The former were attributed to amide band I and the latter to amide band II and NH deformation. Otherwise, infrared spectra of the products were the same as those of the noncross-linked polymers.

Poly(vinyl isocyanate) was found to have the same elemental composition as the monomer. If a substituted urea had been formed, the carbon, hydrogen, and nitrogen content should have been higher than that of the monomer. Further,  $\beta$ -allyloxyethyl isocyanate, which would not homopolymerize, could not be made to react with water to yield a solid derivative. However, when placed under simulated polymerization conditions, this compound reacted to form a soluble, low melting, white solid with an intrinsic viscosity of  $0.037\text{ dl/g}$ . Infrared analysis revealed unsaturation ( $\text{-CH=}$  at  $995\text{ cm}^{-1}$ ), and a strong absorption at  $1715\text{ cm}^{-1}$ , but no evidence of isocyanate. The band at  $1715\text{ cm}^{-1}$  is definitely characteristic of isocyanate trimers. This

compound also gave the same elemental analysis as did the liquid, monomeric isocyanate.

The above information is offered as evidence that the unsaturated isocyanates, referred to herein, have been either polymerized or copolymerized to yield cross-linked structures. In products wherein the comonomer to isocyanate ratio was 7:1 or less, cross-linking took place through the NCO group in a manner not unlike that in which isocyanates dimerize or trimerize to form uretidenediones and isocyanurates, respectively. Cross-linked products did not result from reaction of the NCO moieties with water unless the latter was purposely made available.

## EXPERIMENTAL SECTION

### Equipment and Data

All temperatures are uncorrected and reported in degrees Centigrade. Pressures are expressed in millimeters of mercury, having been determined by means of a Zimmerli gauge. Refractive indices were obtained with a Bausch and Lomb Abbe 34 refractometer fitted with an achromatic compensating prism. Infrared spectra were obtained on either a Perkin-Elmer Infracord or a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet radiation was supplied by a Blak-Ray long-wave ultraviolet lamp, model XX-15. Melting point determinations of monomeric compounds were carried out in open capillary tubes in an electrically heated block, while those of polymeric materials were performed on a Kofler micro hot-stage and viewed through a Unitron polarizing microscope. Intrinsic viscosities were calculated from efflux times of solutions through a Cannon-Ubbelohde semimicro dilution viscometer set in a constant temperature bath. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

### 9-Decenyl Isocyanate

Thionyl chloride, as obtained from stock, was treated according to the method of Fieser [7] to give the colorless liquid, bp 75-76°; reported [7] bp 78.8°.

Thionyl chloride, 300 g (2.52 moles), was allowed to react with 394 g (2.14 moles) of 10-undecylenic acid, according to the procedure reported by Kapp and Knoll [8], to yield 327 g (76%) of 10-undecenoyl chloride, bp 78-80° (0.5 mm); reported [8] bp 128° (13 mm).

9-Decenyl isocyanate was prepared by following the procedure outlined by Allen and Bell [9] for synthesizing undecyl isocyanate. Into a 3-liter, three-necked flask, equipped with a reflux condenser, mechanical stirrer, thermometer, and addition funnel, were placed 147 g (2.26 moles) of purified sodium azide (Fisher) and 500 ml of water. The reaction vessel was immersed in an ice-water bath, and a mixture of 327 g (1.62 moles) of 10-undecenyl chloride and 500 ml of acetone was added at such a rate that the reaction temperature remained at 10-15°. The mixture was then cooled to 0° and stirred for 1 hr. The organic layer was removed and added slowly to 1.6 liter of prewarmed (60-70°) benzene in an open beaker, and the solution was held at this temperature, with occasional stirring, until effervescence had ceased. The benzene was removed by distillation at atmospheric pressure, and the residue was distilled through a 12 in., helix-packed column to yield 110 g (38%) of 9-decenyl isocyanate, bp 92-94° (2 mm),  $n_D^{20}$  1.4485. Infrared analysis revealed the following absorption bands  $\text{cm}^{-1}$ : 3010, 2940, 2900 (C-H); 2265 (HCO); 1640 (C=C); 1470, 1355 ( $\text{CH}_2$  deformations); 997 (=CH-); 912 ( $\text{CH}_2$ =).

Analysis calculated for  $\text{C}_{11}\text{H}_{19}\text{NO}$ : C, 72.90; H, 10.56; N, 7.73. Found: C, 73.26; H, 10.30; N, 7.73.

### $\beta$ -Allyloxyethyl Isocyanate

The procedure for preparing 10-undecenyl chloride was used in preparation of  $\beta$ -allyloxypropanoyl chloride. Reaction of 235 g (1.98 moles) of thionyl chloride with 194 g (1.40 moles) of  $\beta$ -allyloxypropanoic acid produced 150 g (68%) of  $\beta$ -allyloxypropanoyl chloride, bp 40-45° (1-2 mm).

Using the same method as for the preparation of 9-decenyl isocyanate, 110 g (0.74 mole) of  $\beta$ -allyloxypropanoyl chloride was caused to react with 74.4 g (1.14 moles) of sodium azide to yield 55 g (56%) of  $\beta$ -allyloxyethyl isocyanate, bp 59° (12 mm),  $n_D^{20}$  1.4320. Infrared analysis revealed the following absorption bands ( $\text{cm}^{-1}$ ): 3120, 3000, 2930 (C-H); 2260 (NCO); 1650 (C=C); 1430, 1350 ( $\text{CH}_2$  deformations); 1280, 1250, 1110 (ether); 995 (=CH-); 930, 868, 820 (CH deformations). This compound was a strong lachrymator.

Analysis calculated for  $\text{C}_5\text{H}_9\text{NO}_2$ : C, 56.70; H, 7.15; N, 11.01. Found: C, 56.93; H, 7.35; N, 11.22.

### Vinyl Isocyanate

Vinyl isocyanate was prepared according to the procedure previously reported [10].

**Preparation of Polymers**

The polymers were prepared as previously reported [10].

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