

In the case of BCMO grafts, the resulting polymer was extracted with acetone to separate the unreacted or ungrafted PFR; the results are also indicated in Table I. From the decrease in the amount of PFR extracted compared with that of PFR initially used, it might be supported that the graft copolymer was obtained with the apparent efficiencies of grafting as shown in Table I.

Curing the resulting unfractionated polymers, which were a mixture of homopolymer and graft copolymer, was attempted in the presence or absence of hexamethylenetetramine (HMT). The results are shown in Figure 1.

After the curing reaction, the resulting polymers were extracted with acetone and then with cyclohexanone to separate the homopolymers. As seen from Figure 1, the effect of HMT on curing the polymers was not remarkable. However, it was noted that the unfractionated polymers were cured by heating at 170°C. for ten minutes in the absence of HMT. This indicated that unreacted epoxy group in the polymer could also have participated in the cross-linking reaction. The cured polymers thus obtained were completely infusible and insoluble in most organic solvents.

In the case of THF grafts, the separation of pure grafts was unsuccessful, while the unfractionated polymers were easily cured by heating at about 150°C. in the presence or absence of HMT.

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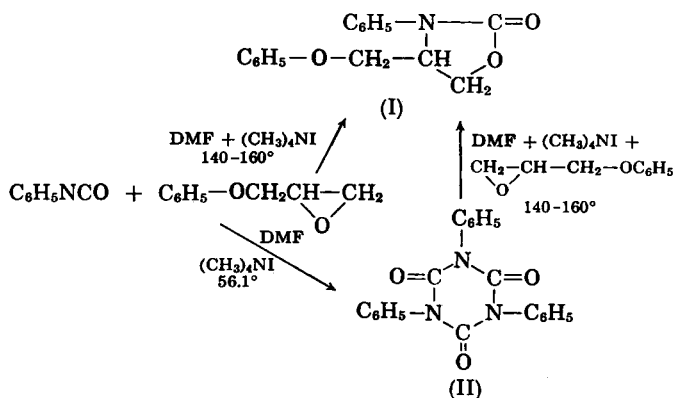
Poly-2-Oxazolidones

Speranza and Peppel¹ recently reported that 2-oxazolidones were formed when mono epoxides and isocyanates are reacted in the presence of tetramethylammonium iodide. They also reported that vinylcyclohexane diepoxide and Epon 828 reacted separately with 2,4-toluenediisocyanate to yield polymeric products which were not further characterized. No other reports have appeared which have described further details on the nature and products of the latter reaction.

This communication outlines an investigation directed toward elucidating the nature of the polymeric products produced when diepoxides react with diisocyanates. In order to obtain information on the conditions and reactions leading to poly-2-oxazolidones, the study of the method of formation of a model compound 3-phenyl-4-phenoxy methyl-2-oxazolidone (I) was first investigated. Heating (0.1 mole) phenylglycidyl ether with

(0.1 mole) phenylisocyanate in 50 ml. dimethylformamide (DMF) in the presence of 0.2 g. tetramethylammonium iodide at 160° for 6 hr. gave a 28% yield of (I), m.p. 137–138° (reported² 137–138°).

The latter material can also be prepared in the absence of a catalyst by heating equivalent amounts at 210° for 15 hr. with no solvent to give an 87.5% yield of (I). However, heating the dimethylformamide solution at 56.1°C. for 24 hr. did not yield (I) but produced the trimer* of phenylisocyanate in 71% yield (II), m.p. 278–280° (reported⁴ 280°). Heating 0.033 mole of the trimer (II) with 0.1 mole phenylglycidyl ether at 160° in 50 ml. DMF in the presence of 0.2 g. tetramethylammonium iodide gave (I) in 16% yield. The latter experiments indicated that 2-oxazolidone formation does not occur at 56.1° but that the trimer (II) is first formed and at elevated temperatures (140–160°) is converted to the 2-oxazolidone (I).

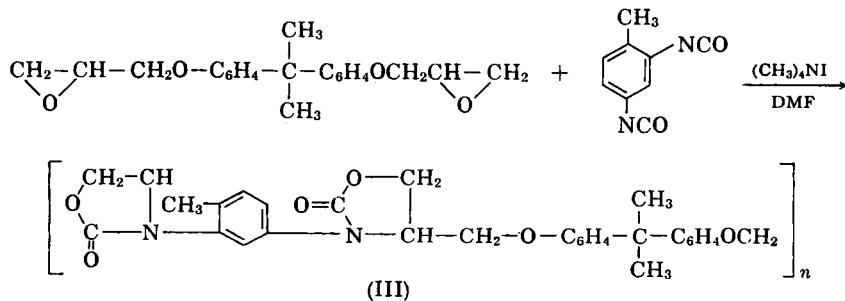


The kinetics of formation of (I) and (II) has also been investigated.

The second order rate constant for the formation of (II) from phenylisocyanate (0.0878 mole) and the equimolar amount of phenylglycidyl ether in DMF using 0.01 mole of tetramethylammonium iodide as catalyst at 56.1° was 6.15×10^{-4} liter/mole-sec. In addition, using the same reactants and concentrations as the above, the reaction yielded (I) when the temperature was raised to 140° at a second order rate of 8.15×10^{-3} liter/mole-sec.

Of particular interest, however, is the reaction of 2,4-toluenediisocyanate and the diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane which under similar conditions as used with phenylglycidyl ether gave the polymer (III) in 91% yield, melting range 175–185°C.

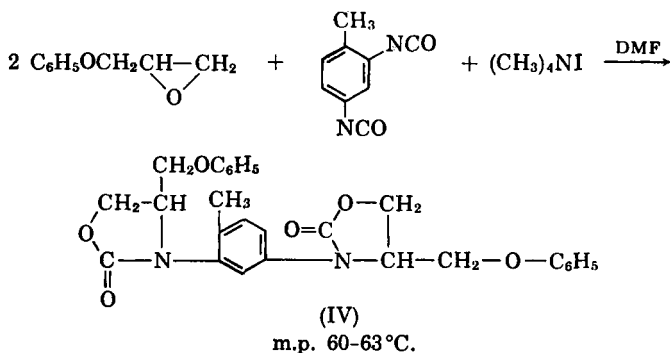
Anal.: Calcd. for (III), as the *n* repeat unit $\text{C}_{30}\text{H}_{30}\text{O}_6\text{N}_2$; % N, 5.45; Found: % N, 5.52.



* Trimerization of phenylisocyanate has been reported to occur in the presence of epoxides at room temperature.³

The infrared spectrum showed strong absorption at 5.65 and 7.10 μ with no absorption at 4.25–4.60 μ , characteristic for free NCO groups. The infrared spectra of 2-oxazolidone and 3-phenyl-4-phenoxyethyl-2-oxazolidone also have carbonyl absorption at about 5.75 μ and a strong absorption at 7.08 μ . The close similarity of the infrared spectrum of polymer (III) to that of the bisoxazolidone (IV) prepared from phenyl glycidyl ether and 2,4-toluenediisocyanate suggests that (III) is a polymer with repeat 2-oxazolidone groups.

Anal.: Calcd. for $C_{27}H_{26}O_6N_2$: % N, 5.90, % C, 68.4, % H, 5.49; Found: % N, 5.04, % C, 67.92, % H, 6.15.



When the catalyst and solvent are omitted in the preparation of (III), a liquid product is obtained which has a large amount of unreacted toluene 2,4-diisocyanate. The addition of the catalyst (tetramethylammonium iodide) to the latter system yielded a brittle polymer (V) with all the isocyanate groups reacted. The softening point of the polymer (V) was in excess of 300° and its infrared spectrum was similar to (III). The polymer (V) probably was crosslinked since it was insoluble in such solvents as DMF, THF, methyl ethyl ketone, xylene, chloroform, and trichloroethylene.

Preliminary studies have indicated that several other poly-2-oxazolidones can be readily prepared from various diepoxides and diisocyanates.

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