

Isocyanate–Epoxy Reactions in Bulk and Solution

J. S. SENGER, I. YILGOR, and J. E. McGRATH, *Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*
and R. A. PATSIGA, *Indiana University of Pennsylvania, Indiana, Pennsylvania 15705*

Synopsis

The reaction between diisocyanates and diepoxides can produce polyoxazolidones. However, the reaction may be accompanied by concurrent cyclization of isocyanate to produce trimeric isocyanurate. Studies were performed with pure phenyl isocyanate or diphenylmethane-4,4'-diisocyanate (MDI) and the diglycidyl ether of bisphenol-A (DGEBA). Reactions were followed by FT-IR and differential scanning calorimetry in order to determine relative rates of conversion to polyoxazolidone and isocyanurate. Various catalysts were utilized, with the most effective being 2-ethyl-4-methylimidazole (EMI). Bulk reactions between MDI and DGEBA at 150°C resulted in considerable amounts of trimerization, thus giving crosslinked polymers. Solution reactions at 180–185°C in dry *N*-methylpyrrolidone using 0.1% EMI gave soluble and moldable polyoxazolidones.

INTRODUCTION

Following the initial publication in 1958 by Speranza and Peppel,¹ there have been numerous reports on the preparation of polyoxazolidones. A variety of catalysts have been claimed to be effective. These range from neutral salts such as tetramethylammonium iodide^{1,2} and magnesium chloride in hexamethylphosphoramide³ to alkoxides,⁴ diethyl zinc,⁵ and ferric chloride.⁶ Although polyoxazolidones are usually prepared by reaction of isocyanates with epoxides, other, less direct, routes have also been explored.^{7,8} A short but thorough review of polyoxazolidone syntheses has been published.⁹

The oxazolidone ring has good thermal stability⁵ and also mechanical properties of polymers with this structure have been found to be improved.³ Oxazolidone repeat units have been built into polymers containing isocyanurate crosslinks.¹⁰ These polymers have shown promise as components in heat-resistant varnishes. Thus, the oxazolidone structure appears to impart certain superior properties to polymeric materials, and this has led to a sustained interest in finding improved methods for their synthesis.

The various approaches to the preparation of polyoxazolidones cited above have left some questions concerning structural integrity (for example, extent of isocyanurate branching), role of catalyst, effect of impurities, effect of temperature on competing reactions, and properties of the final polymers. We wish to describe a series of studies on the isocyanate–epoxide system in which was examined the reaction of highly purified starting materials including the monomers, diphenylmethane-4,4'-diisocyanate (MDI) and the diglycidyl ether of bisphenol-A (DGEBA). Reactions were conducted in bulk and solution

while monitoring processes by Fourier transform infrared and, in some cases, by differential scanning calorimetry (DSC). A number of catalysts were examined but preference was given to 2-ethyl-4-methylimidazole (EMI), which is soluble in the reaction medium and was found by us and others^{10,11} to be effective.

EXPERIMENTAL

The MDI was vacuum distilled from commercial material (Mobay Chemical) to give a white, crystalline, solid with a mp of 36°C and molecular weight of 250 determined by isocyanate titration using dibutyl amine. DGEBA was crystallized from Epon-825 using 40/60 MIBK/2-ethoxyethyl ether giving a white solid (mp 42°C). Reaction solvents were distilled from calcium hydride. In the case of the amide solvents, dimethylformamide and *N*-methylpyrrolidone, stirring overnight under argon at 40–50°C over calcium hydride preceded vacuum distillation. The solvents were then stored over calcium hydride in flasks equipped with serum caps which allowed for transfer by syringe.

Bulk Reactions. MDI and DGEBA (0.006 mol each) were melted in a vial at 50–60°C with 0.5% (by weight) of catalyst. After stirring for 5–10 min to homogenize the mixture, samples consisting of several drops of the melt were transferred to 2-in.-square Teflon sheets. These were covered with a second set of sheets to create a sandwich structure which was weighed down between 2-lb metal plates. The whole assembly was then placed in the curing oven. Cure samples consisting of a single sandwich assembly were periodically taken from the oven, and the polymer was removed from the Teflon sheet for analysis by FT-IR.

Solution Reactions. The most successful procedure utilized dry NMP as solvent and 0.1% (by weight of combined monomers) EMI catalyst. In a typical procedure, DGEBA (2.72 g, 0.008 mol) was combined in a three-neck flask with EMI and 10 mL NMP. MDI (2.00 g, 0.008 mol) was dissolved in an addition funnel using 10 mL NMP. All liquid transfers were done by syringe and an argon atmosphere was maintained throughout the experiment. The temperature of the DGEBA/EMI stirred solution was raised to 180–185°C using an oil bath, and the MDI solution was slowly added over the course of 1 h. The mixture was allowed to remain at 180–185°C for an additional 4 h, and then cooled. The viscous, amber mixture was precipitated into 300 mL of methanol. Occasionally a colloidal suspension had to be broken by the addition of several mL of methanol saturated with ammonium chloride. The filtered solution was redissolved in DMF and reprecipitated in excess methanol, as before. At least four precipitations were performed, and the polymer was dried overnight in vacuum at 60°C. The yield of polymer after the final purification step was, typically, 75%.

Infrared spectra were obtained using a Nicolet MX-1 FT-IR instrument which displayed a spectrum based on 27 scans. Absorption values at desired wave numbers (isocyanate at 2270 cm⁻¹, oxazolidone carbonyl at 1754 cm⁻¹, isocyanurate carbonyl at 1710 cm⁻¹, and epoxide at 915 cm⁻¹) were normalized by dividing by the absorption of the bisphenol-A methyl C—H stretching frequency at 2970 cm⁻¹. This value is termed "absorption ratio" in Figure 1.

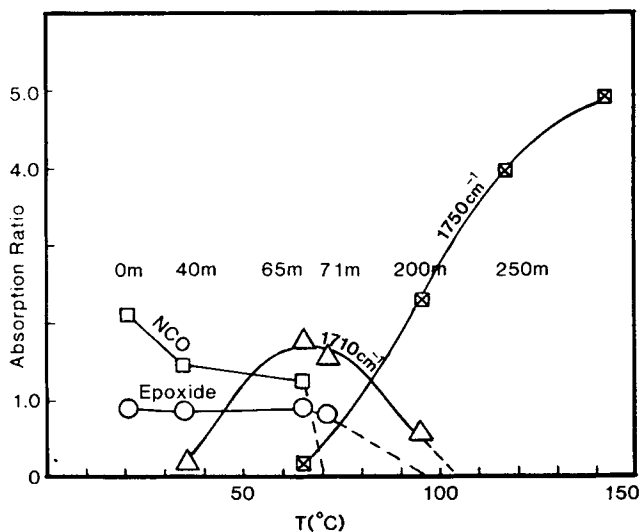
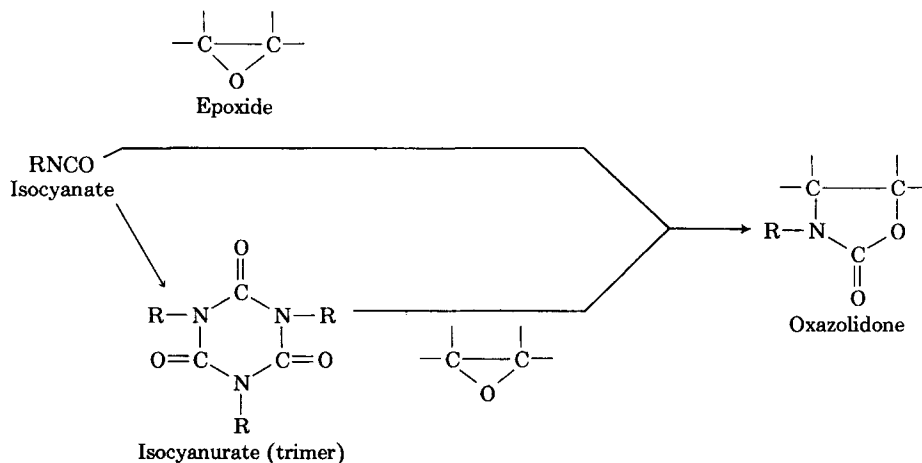


Fig. 1. Infrared absorptions of functional groups during bulk reaction between phenyl isocyanate and DGEBA: phenyl isocyanate, 12×10^{-3} mol; DGEBA, 6×10^{-3} mol; EMI catalyst, 6×10^{-4} mol; nitrogen atmosphere. Times in minutes displayed.

Differential scanning calorimetry runs were performed on a Perkin-Elmer System-2 instrument using a $10^\circ\text{C}/\text{min}$ scanning rate.

RESULTS AND DISCUSSION

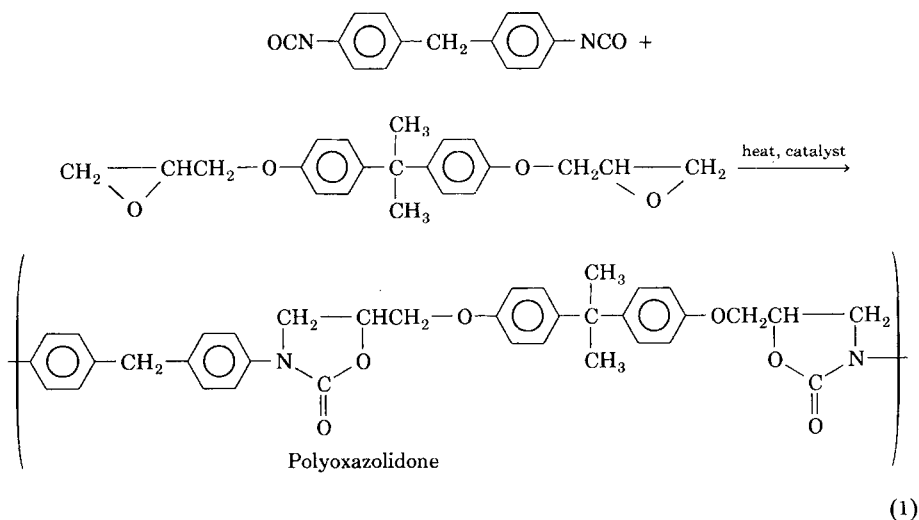
When isocyanates are heated with epoxides in the presence of catalysts, a number of transformations may take place, as shown in Scheme I^{2,3} below:



Scheme I

This scheme has been recognized by a number of earlier investigators, and it is generally accepted that isocyanate trimerization to form isocyanurate is

favored at temperatures below 120°C while oxazolidone formation becomes more significant at higher temperatures. Additional reactions are possible if the isocyanate and epoxide contain contaminants such as amines or hydroxylic compounds, as is the usual case with commercial monomers. Much of the published work has been done with unpurified starting materials. Trimerization of the isocyanate will result in crosslinking and branching, while reaction with hydroxyl or amino groups introduces urethane and urea structures. The thrust of the research described herein is aimed at determining which catalysts and conditions are able to direct the reaction in favor of linear polyoxazolidone [eq. (1)] while utilizing highly purified starting materials.



As a model reaction, DGEBA was heated in bulk with phenyl isocyanate (2 mol eq) using 10% EMI as catalyst. The temperature was gradually increased from ambient up to 150°C over a 300-min period. Samples were removed periodically for infrared analysis. The plots in Figure 1 of infrared absorption ratios indicate that from 50 to 70°C isocyanate disappears rapidly as it is converted to isocyanurate. At 70°C oxazolidone begins to appear and continues to increase thereafter. As is to be expected for a reaction intermediate, the isocyanurate reaches a maximum at about 70°C and then decreases. The epoxide group weakly absorbs in the infrared spectrum, and its presence is not easily monitored below 50% consumption. However, it too is seen to gradually disappear.

In the bulk polymerization studies, MDI and DGEBA were heated with a variety of catalysts which were evaluated. Reactions were conducted at 150°C, and, in some cases, higher temperatures were used. The disappearance of isocyanate and epoxide and appearance of oxazolidone and trimer were monitored by FT-IR. The carbonyl region of the IR spectrum of one study which utilized EMI as catalyst is depicted in Figure 2. The trimer carbonyl at 1710 cm^{-1} is evident almost immediately [Fig. 2(A)]. As heating continues, the oxazolidone carbonyl at 1754 cm^{-1} increases in intensity until it becomes equal to or surpasses the intensity of the trimer carbonyl [Fig. 2(B) and 2(C)]. Changing the IR absorptions to the absorption ratio for the groups of interest

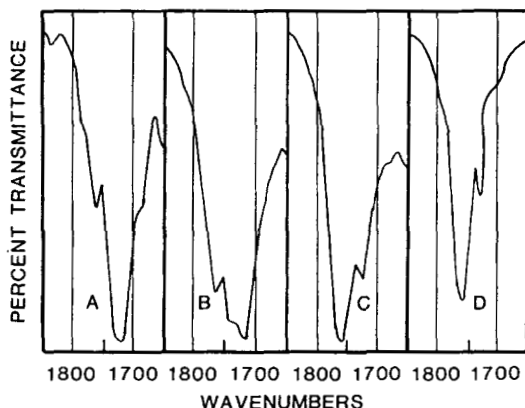


Fig. 2. Carbonyl infrared absorption at various heating times for bulk reaction between MDI and DGEBA: 1 : 1 mole ratio of monomers, EMI catalyst, 0.5% on monomers: (A) 150°C, 0.5 h; (B) 150°C, 1.0 h; (C) 150°C, 5.5 h; (D) DSC sample heated to 280°C.

resulted in a time-conversion plot for a 150°C cure shown in Figure 3. As in the model system which utilized phenyl isocyanate, the free isocyanate groups of MDI disappeared quickly and trimer rapidly formed. The oxazolidone formation increased gradually with time until it attained a level comparable to the isocyanurate. This was accompanied by an approximate 60% decrease in epoxide. Heating for longer periods of time or increasing the reaction temperature to 185°C resulted in no further changes in the relative absorptions due to trimer and oxazolidone. It is quite evident that trimerization creates crosslinks which severely immobilize the system and prevent further reaction.

A similar conversion plot is shown in Figure 4 for a study using tetramethylammonium iodide as catalyst. This type of catalyst was reported by Sandler et al.² as being capable of producing polyoxazalidones; however, in

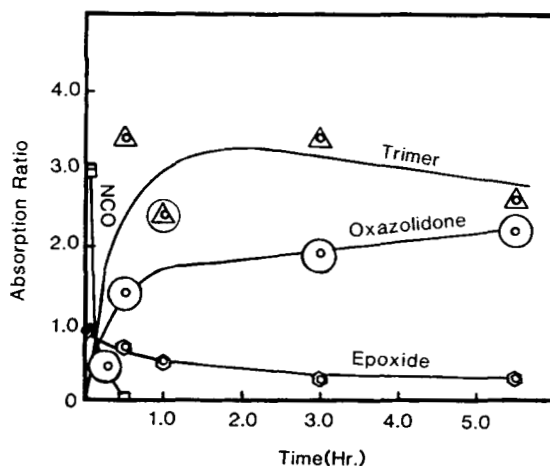


Fig. 3. Infrared absorptions of functional groups during bulk reaction between MDI and DGEBA: 1 : 1 mole ratio of monomers, EMI catalyst, 0.5% on monomers.

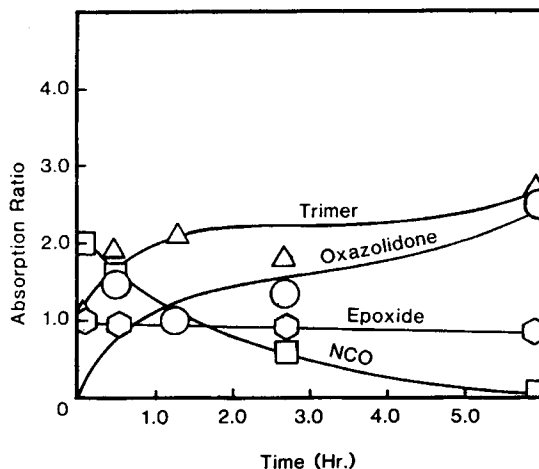


Fig. 4. Infrared absorptions of functional groups during bulk reaction between MDI and DGEBA: 1:1 mole ratio of monomers, $(\text{CH}_3)_4\text{NI}$ catalyst, 0.5% on monomers.

our hands it proved to be less effective than EMI. In this study, the isocyanate disappeared much more slowly and its IR absorption was still visible after 6 h. Even formation of trimer was not as rapid as with EMI catalysis.

A survey of a number of potential catalysts was conducted and the qualitative results of these studies are summarized in Table I. The observations based on FT-IR analysis indicate that, in bulk, trimerization is a very much favored reaction over oxazolidone formation with all of the catalysts examined. In some cases, observation was difficult or even misleading due to the catalyst either being insoluble or very reactive and, consequently, surrounding

TABLE I
Diisocyanate-DGEBA Cure Studies (150°C)^a

Exp	Diisocyanate	Catalyst	NCO disap.	Trimer appear.	Oxazol. appear.	Epoxide disap.
66	MDI	EMI	Rapid	Rapid	Incomplete	Incomplete
68	MDI	DBTDL	Partial	Slow	No	No
75	MDI	DBU	Rapid	Rapid	Incomplete	Incomplete
80	MDI	LiOH	V. slow	Slow	No	No
82	MDI	$\Phi_2\text{Zn}$	V. slow	Slow	No	No
87	MDI	<i>n</i> -BuOLi	Partial	Slow	No	No
89	MDI	PhAn	Partial	V. slow	No	No
92	MDI	Et_4NI	Moderate	Rapid	Incomplete	Incomplete
94	H-MDI	EMI	Slight	V. slight (20 h)	No	No
97	MDI	ZnCl_2	Moderate	Rapid	Incomplete	Incomplete

^aExperiments conducted as melt films between Teflon sheets. Catalyst content: 0.1%. Legend: EMI = ethylmethylimidazole, DBTL = dibutyltindilaurate, DBU = diazabicycloundecene, PhAn = phthalic anhydride, MDI = methylene-bis(4-isocyanatophenyl), H-MDI = ring hydrogenated MDI.

itself with insoluble gel during the initial mixing. This was true for zinc chloride, DBU, and lithium butoxide. Of the catalysts so far examined, EMI appears to have the most desirable catalytic and solubility properties.

Since imidazoles have been reported¹² to catalyze the homopolymerization of epoxides, a control experiment was performed in which DGEBA alone was heated at 150°C with EMI. At the end of a 6-h heating period, FT-IR indicated that at least 90% epoxide remained unreacted.

DSC analysis of the bulk reaction using EMI catalyst is shown in Figure 5. Several exothermic regions are evident; however, two regions seem prominent. This has also been observed by Uribe and Hodd.¹³ The first region lies between 112 and 147°C, and the second has a maximum at 170°C. A minimum between the two regions occurs at about 160°C. A similar two-exotherm behavior was observed by us for the model system consisting of phenyl isocyanate and DGEBA. By stopping the DSC scan at the minimum, it was possible to examine by FT-IR the structure of the polymeric material formed up to this point. The infrared spectrum of this partially cured sample showed the absence of isocyanate (2270 cm^{-1}) while epoxide is still visible (915 cm^{-1}). A very strong carbonyl absorption was seen at 1710 cm^{-1} as in Figure 2(A), indicative of isocyanurate, while only a shoulder is visible in the vicinity of 1750 cm^{-1} for oxazolidone. The infrared spectrum of the final cured material (final temperature: 280°C) shows carbonyl absorptions similar to Figure 2(D). There is a reversed ratio in carbonyl intensities with a strong oxazolidone absorption seen at 1756 cm^{-1} and a weaker shoulder at 1710 cm^{-1} . There is an accompanying significant reduction in epoxide absorption. Thus, while oxa-

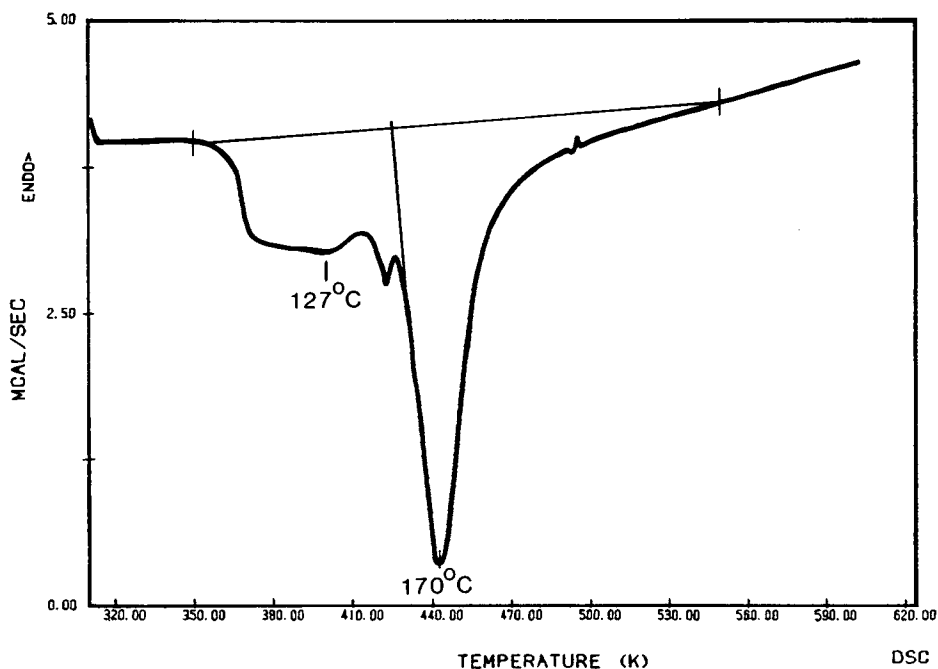


Fig. 5. Differential scanning calorimetry trace for bulk reaction between MDI and DGEBA catalyzed by 0.5% EMI. Heating rate $10^\circ\text{C}/\text{min}$.

zolidone formation is favored at higher temperatures, it is difficult to totally eliminate isocyanurate crosslinking in a bulk curing process.

Two model reactions were performed which bear upon the reactivity of the trimeric isocyanurate. The trimer of phenyl isocyanate was prepared and heated at 120°C with DGEBA in the presence of EMI catalyst. The trimer gradually disappeared over a 10-h period. When the trimer was similarly heated with a dihydroxy ether prepared from DGEBA (reaction of DGEBA with the sodium salt of *p*-*t*-butylphenol), no reaction took place. If the trimer was in equilibrium with the free isocyanate, it would be expected to rapidly convert to urethane by the hydroxyl groups. Thus the trimer appears to be irreversibly formed from isocyanate.

Solution reactions between MDI and DGEBA with EMI catalyst were attempted in a variety of solvents having a range in boiling point and

TABLE II
DGEBA-MDI Solution Reactions^a

Exptl	Percent EMI catalyst on monomers	Solvent	Reaction temp (°C)	Results
1-77	0.33	DMSO	155-155	Reaction mixture gels when 80% MDI added; IR shows both trimer and oxazolidone
1-99	0.33	2-EEE	187	Tan suspension forms at 50% MDI added; IR shows strong oxazolidone carbonyl and less trimer carbonyl
2-37	0.1	NMP	180-185	Reaction homogeneous to end; polymer ppts in methanol; IR shows strong oxazolidone carbonyl, no trimer
2-9	0.1	DPE	235-245	Reaction homogeneous to end; mixture does not ppt in methanol but does in PET ether; IR shows doublet at 2135 cm ⁻¹ and 2110 cm ⁻¹ (carbodiimide) carbonyl at 1707 cm ⁻¹

^a Reactions performed with stirring under nitrogen. Reaction scale: 0.01 mol monomers as 10% solution in solvent. MDI solution added dropwise to DGEBA/EMI solution. DMSO = dimethylsulfoxide, 2-EEE = 2-ethoxyethylether, NMP = N-methylpyrrolidone, DPE = diphenyl ether.

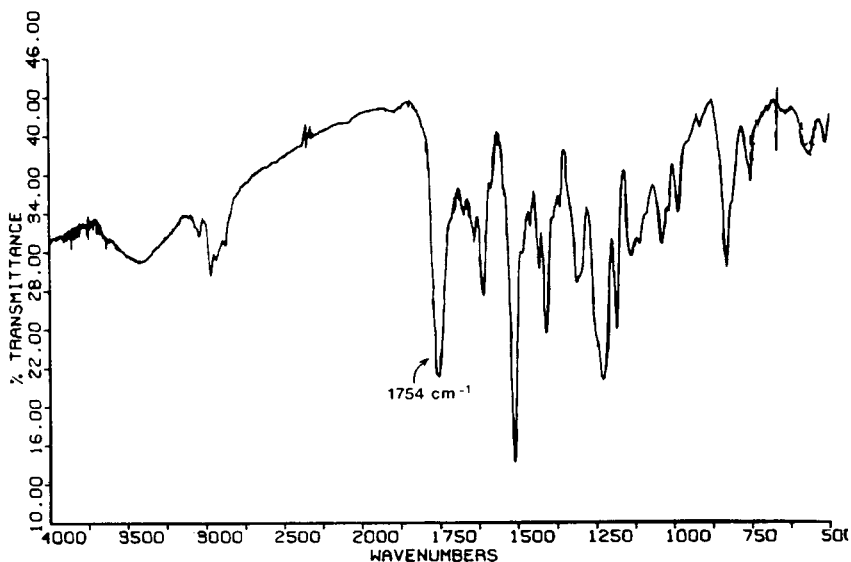


Fig. 6. Infrared spectrum of polyoxazolidone prepared by solution reaction in NMP between MDI and DGEBA using 0.1% EMI catalyst.

polarity. The results of these studies are summarized in Table II. The ideal solvent appears to be one with a boiling point not less than 170°C and a fairly high solubility parameter. Lower temperature reactions, even in a polar solvent such as DMSO, result in precipitation of the reaction mixture even before all of the MDI solution has been added. It is interesting that reaction at well over 200°C in diphenyl ether does not augment the tendency toward oxazolidone formation, but rather carbodiimide structures are formed along with trimer. The most satisfactory solvent so far investigated is NMP, using the procedure described in the experimental section.

The FT-IR of the polymer isolated from an NMP solution polymerization is shown in Figure 6. This material shows a single, strong carbonyl absorption at 1754 cm^{-1} with virtually no indication of the presence of trimer structure.

The dry polymer is tan in color and gives pale amber, gel-free solutions in NMP, DMF, and DMSO. Intrinsic viscosities in DMF at 26°C range from 0.25 to 0.31 dL/g. Glass temperature was found by DSC to be 160°C. Samples of the polyoxazolidone could be compression molded at 210°C and 10,000 psi to give dark amber, transparent films.

It is important that reactants and solvent be as dry as possible. Inadequate drying of the NMP results in premature decomposition of the MDI (bubbling and yellowing of the MDI-NMP solution) and a much darker and lower molecular weight polymer.

Further work is in progress toward improving the polymerization methods and examining the mechanical and thermal properties of linear polyoxazolidones.

References

1. G. P. Speranza and W. J. Peppel, *J. Org. Chem.*, **23**, 1922 (1958).
2. S. R. Sandler, F. Berg, and G. Kitazawa, *J. Appl. Polym. Sci.*, **9**, 1984 (1965).

3. M. Kitayama, Y. Iseda, F. Odaka, S. Anzai, and K. Irako, *Rubber Chem. Technol.*, **53**(1), 1 (1980).
4. R. R. Dileone, *J. Polym. Sci., A-1*, **8**, 609 (1970).
5. P. Kordomenos, J. E. Kresta, and K. C. Frisch, *Am. Chem. Soc., Org. Coat. Plast. Chem.*, **38**, 450 (1978).
6. K. Ashida and K. C. Frisch, *J. Cell. Plast.*, **8**, 194 (1972).
7. Y. Iwakura, S. Izawa, and F. Hayano, *J. Polym. Sci.*, **4**, 751 (1966).
8. Y. Iwakura, A. Nabeya, F. Hayano, and K. Kurita, *J. Polym. Sci.*, **5**, 1865 (1967).
9. S. R. Sandler and W. Karo, in *Polymer Synthesis*, Academic, New York, 1980, Vol. III, Chap. 4.
10. N. Kinjo, S. Numata, T. Koyama, and T. Narahara, *J. Appl. Polym. Sci.*, **28**, 1729 (1983).
11. M. Chung, S. Wong, and D. Klemperner, *Am. Chem. Soc., Org. Coat., Appl. Polym. Sci. Proc.*, **49**, 325 (1983).
12. F. Riccardi, W. A. Romanchick, and M. M. Joullié, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 1475 (1983).
13. M. Uribe and K. A. Hodd, *Am. Chem. Soc., Polym. Prepr.* **25**(2), 43 (1984).

Received June 10, 1988

Accepted June 25, 1988