

Synthesis and Characterization of Ethoxyethyl α -Cyanoacrylate and Reaction Intermediates

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ABSTRACT: Ethoxyethyl α -cyanoacrylate was synthesized by first making oligo(ethoxyethyl α -cyanoacrylate) through a condensation reaction of ethoxyethyl cyanoacetate with paraformaldehyde, followed by a depolymerization of the oligomer at an elevated temperature in an acidic atmosphere with a high vacuum. The ethoxyethyl cyanoacetate was in turn synthesized from an esterification of ethoxyethanol and cyanoacetic acid. The molecular structure of the target monomer and the corresponding intermediates were corroborated by IR and ¹H-NMR. Solvents having a lower polarity led to the formation of oligomers having higher molecular weights. The molecular weight distribution of the oligomer revealed that the reaction of ethoxyethyl

cyanoacetate with formaldehyde followed a mechanism comprising monomer activations, anionic reactions, and chain scissions. DSC thermograms demonstrated the cured ethoxyethyl α -cyanoacrylate was nearly amorphous, containing little or low crystallinity. Mechanical testing data indicated that the cured ethoxyethyl α -cyanoacrylate was a hard adhesive with higher toughness than the conventional ethyl α -cyanoacrylate. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1758–1773, 2003

Key words: adhesive; ethoxyethyl α -cyanoacrylate; formaldehyde; oligomer; ethoxyethyl cyanoacetate

INTRODUCTION

α -Cyanoacrylates are an important class of adhesives that are widely used by industry and homeowners in various applications.^{1–5} They polymerize (cure) very quickly at room temperature without the need of any curing agent and form a strong bond between two adherends. Among all α -cyanoacrylates, the most common ones are alkyl α -cyanoacrylates such as methyl, ethyl, butyl, and isobutyl α -cyanoacrylates.¹ Methyl and ethyl α -cyanoacrylate adhesives, with or without promoters, have been shown as effective adhesives for nonpolar or polar surfaces.² Isobutyl α -cyanoacrylate was superior in hard tissue applications.³ Butyl α -cyanoacrylate has excellent binding strength for skin closure.⁴ Alkyl α -cyanoacrylates have rapid curing characteristics and good tensile strength and are applicable to a broad range of adherends. However, the cured alkyl α -cyanoacrylate is hard and brittle and lacks toughness and hence has insufficient resistance to impact or flexure. This deficiency has thus limited the use of alkyl α -cyanoacrylates for bonding electronic and automobile parts. To improve

the toughness, it is conceivable and of interest to study the synthesis and characterization of alkyloxyalkyl α -cyanoacrylate that contains a flexible ether linkage.

Our target is the ethoxyethyl α -cyanoacrylate of which the cured form is a polymer comprising long side chains with a flexible ether linkage. Analogous to alkyl α -cyanoacrylate, the high reactivity of ethoxyethyl α -cyanoacrylates precludes a direct synthesis of this monomer. To make this monomer, an oligo(ethoxyethyl α -cyanoacrylate) has to be synthesized first by reacting ethoxyethyl cyanoacetate with paraformaldehyde via a Knoevenagel reaction, which is then followed by depolymerization at an elevated temperature in an acidic atmosphere with a high vacuum. The ethoxyethyl cyanoacetate, in turn, can be synthesized from ethoxyethanol and cyanoacetic acid using typical esterification methods.

This article describes our work for the syntheses of ethoxyethyl cyanoacetate and oligo(ethoxyethyl α -cyanoacrylate) and the subsequent depolymerization forming ethoxyethyl α -cyanoacrylate. Both intermediates and target monomer are characterized. In addition, the mechanical properties of the cured ethoxyethyl α -cyanoacrylate are measured.

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EXPERIMENTAL

Materials

The cyanoacetic acid and ethoxyethanol used in this work were purchased from Tokyo Chemical Industry.

Paraformaldehyde (91–99% pure), hydroquinone, phosphorus pentoxide, mercaptan, and nitrocellulose were provided by Cartell Chemical Co. Piperidine and pyridine were purchased from Lancaster. Sulfuric acid and *p*-toluenesulfonic acid were obtained from ACROS. Benzene and toluene were purchased from TE-DIA (98% pure).

Synthesis of ethoxyethyl cyanoacetate

The esterification reaction was performed in a four-necked glass flask equipped with a stirrer, a thermometer, and a Dean–Stark reflux trap. A solution comprising 42 g of cyanoacetic acid and various specified amounts of water was first charged into the reactor under a nitrogen environment and cooled to 9°C. Next the catalyst, antioxidant, and 34 g of the cosolvent were added. After charging 46 g of ethoxyethanol, the temperature was elevated according to a programmed profile: to 45°C in 1 h, to 65°C in 3 h, to 130°C in 1 h, and maintaining at 130°C for 10 h. The conversion was 78% and the hot mixture contained 84% ethoxyethyl cyanoacetate. The condensate collected in the reflux trap separated into 21 g of cosolvent phase and 19 g of water phase. More of the condensate (7 g) could be collected at an increased nitrogen purge rate for an additional 1 h. The hot mixture was put into a 250-mL beaker and agitated for 8 h before it was filtered. The filtered product had a purity of 95% measured by gas chromatography (GC) using a calibration standard acquired from Tateyama Kasei Co. This mixture was again vacuum dried at 50 mbar in a rotary evaporator for 8 h to raise the purity to 98%.

Synthesis of oligo(ethoxyethyl α -cyanoacrylate)

Thirty grams of paraformaldehyde and 60 mL of the solvent were put into a four-necked glass flask in the presence of 0.5 g of piperidine catalyst, and the mixture was heated to the target temperature of 85°C. Then 165 g of ethoxyethyl cyanoacetate was gradually charged over 40 min. The mixture was allowed to react under reflux at the specified temperature, while removing water formed by the reaction. The reaction was stopped when 18 mL of water had been collected in the trap. An amount of 2 mL of samples each were taken at fixed time intervals for analyses.

Acetic acid (4–5 mL) was added into the mixture to neutralize the piperidine catalyst, and the solution was agitated at 80°C for 30 min. This acid-neutralized solution was then put under a 720-torr vacuum at 80°C with a constant 60-rpm agitating speed for solvent removal.

Depolymerization of oligo(ethoxyethyl α -cyanoacrylate)

Into a four-necked flask equipped with a reflux condenser were added 2.36 g of hydroquinone, 3.35 g of

phosphorus pentoxide, 23.6 g of dioctyl phthalate (DOP), and 4 mL of sulfur dioxide aqueous solution together with 170 g of oligo(ethoxyethyl cyanoacrylate) collected in the above step. The mixture was preheated to 70°C before applying a vacuum and a programmed temperature increase. Oligo(ethoxyethyl cyanoacrylate) started depolymerizing at 165°C under a 740-torr vacuum, and crude ethoxyethyl α -cyanoacrylate monomer was collected in the bottle under the condenser in a form of a clear liquid with a light yellow color.

The crude ethoxyethyl α -cyanoacrylate was then put under nitrogen and a small amount of *p*-toluenesulfonic acid, 2 g of phosphorus pentoxide, and 2 g of hydroquinone were added. The mixture was redistilled under a 740-torr vacuum. The redistillation procedure was repeated 3 times, and a refined ethoxyethyl α -cyanoacrylate was collected. The final adhesive composition was prepared by adding 0.5 wt % metaphosphoric acid, 0.2 wt % phosphorus pentoxide, 0.1 wt % sulfur dioxide, 0.1 wt % mercaptan, 0.1 wt % hydroquinone, and 0.2 wt % nitrocellulose to this refined ethoxyethyl α -cyanoacrylate.

Analysis of synthesized polymers

The molecular weight and molecular weight distribution of the synthesized oligomers were determined by gel permeation chromatography (GPC) with a Shimadzu LC-10AT apparatus equipped with Shimadzu RID-10A differential refractive index detectors. The GPC instrument was typically operated using Tosoh G3000HXL columns at a nominal flow rate of 1 mL/min with a sample concentration of 0.1% in THF solvent. Because the GPC was calibrated using polystyrene standards (Polymer Laboratories), the determined molecular weight was actually a polystyrene-equivalent molecular weight. The chemical structures of the polymers were determined by a Shimadzu FTIR8000 Fourier transform spectrophotometer (KBr, 2 cm⁻¹ resolution) and ¹H-NMR spectra using a Bruker AMX400 100.61-MHz spectrometer at 25°C in CDCl₃ at a 5% polymer concentration. The thermal stability was determined using a thermogravimetric analyzer (TGA 2050, TA Instruments). The temperature was ramped from room temperature to 400°C at a rate of 10°C/min. The glass-transition and melting temperatures were determined by a differential scanning calorimeter (MDSC 2910, TA instruments).

RESULTS AND DISCUSSION

Preparing ethoxyethyl cyanoacetate by esterification reaction

Three catalysts were tried for the esterification reaction of cyanoacetic acid with ethoxyethanol, namely,

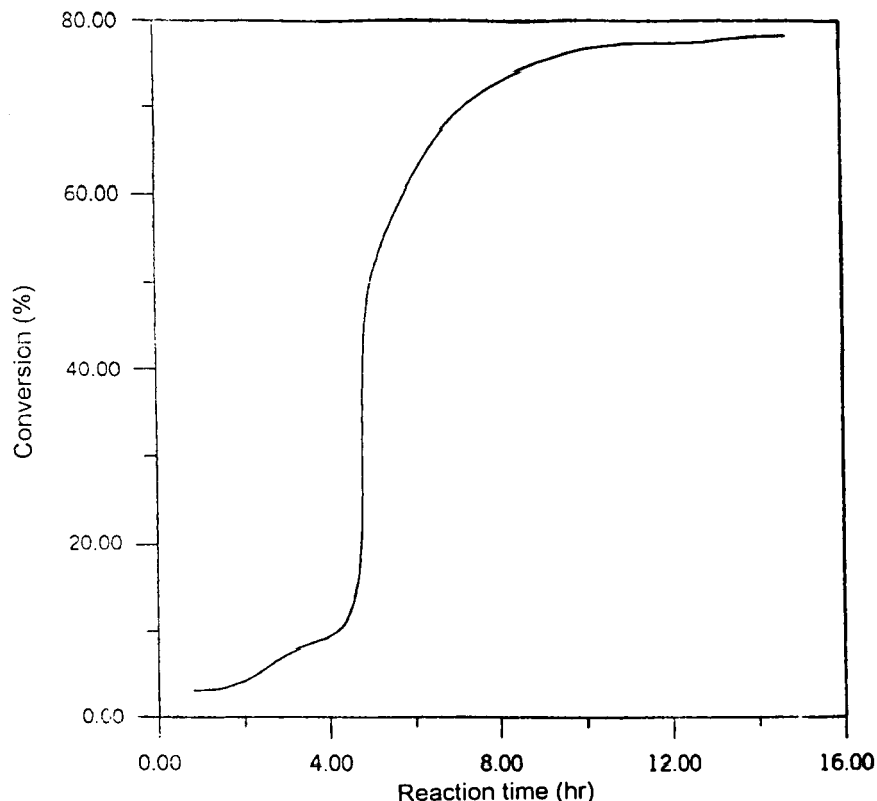


Figure 1 The conversion of the esterification reaction of ethoxyethanol and cyanoacetic acid.

sulfuric acid, *p*-toluenesulfonic acid, and Amberlyst 15 (a cation-exchange polymeric resin). Although the conversions of the esterification were nearly equal, the sulfuric acid system often contained a significant amount of white precipitates that were not observed in the other two systems. Because of the ease of separation between the reaction product and the catalyst residue, Amberlyst 15 was considered as the best catalyst in our work. The reaction rate can be viewed in Figure 1. The conversion, which was calculated based on the amount of water by-product collected during the reaction, approached 78–79% asymptotically in 12 h.

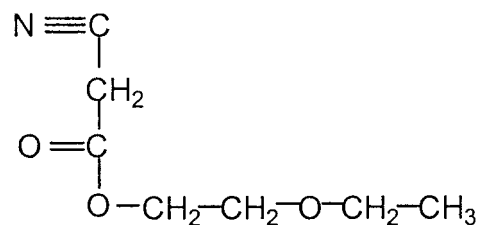
Cyanoacetic acid solutions with concentrations ranging from 70 to 89 wt % led to approximately the same conversions. Thus, the concentration of the cyanoacetic acid solution was not a critical variable. Addition of a cosolvent was important in forming an azeotrope of water and assisting its distillation. Benzene was a better cosolvent than either toluene or the benzene–toluene mixture because of the lower azeotropic temperature with water. Furthermore, toluene formed an additional azeotrope with ethoxyethanol and tended to carry ethoxyethanol out of the system.

The addition of a minimum of 0.16 wt % of the antioxidant BHT during the esterification reaction effectively prevented the product from changing color.

Although BHT did not affect the esterification reaction, it was inseparable from the product and was detected by GC. Although esterification required a high reaction temperature, the boiling of solvents and ethoxyethanol generally posed an upper limit for the temperature. We found that a maximum conversion was achieved when the esterification reaction was conducted at 130°C.

The GC/mass spectrometry chromatogram of the reaction product is shown in Figure 2. Besides the major component ethoxyethyl cyanoacetate, the product contains traces of cyanoacetamide, ethoxyethanol, acetonitrile, and BHT. The species with molecular weights of 131 and 204 are not identified yet.

The IR spectrum shown in Figure 3 corroborated the molecular structure of the product:



The $\text{C} \equiv \text{N}$ stretch occurred at 2261 cm^{-1} , the $\text{C} = \text{O}$ stretch occurred at 1750 cm^{-1} , the $\text{C} - \text{C}(=\text{O}) - \text{O}$

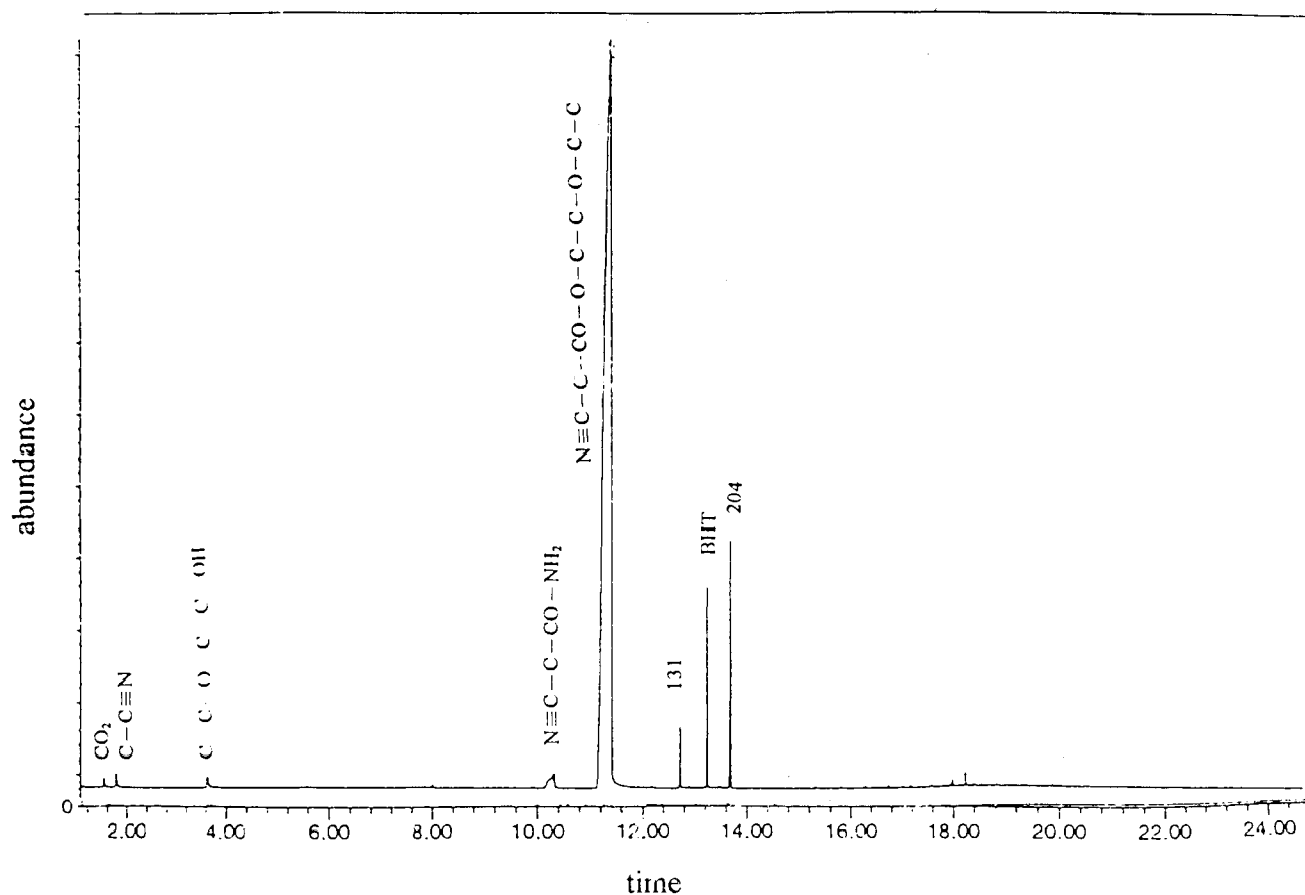


Figure 2 The GC/mass spectrometry spectrum of ethoxyethyl cyanoacetate.

stretch occurred at 1192 cm^{-1} , and the $\text{O}-\text{C}-\text{C}$ stretch occurred at 1034 cm^{-1} . The $\text{C}-\text{O}-\text{C}$ ether stretch appeared at 1121 cm^{-1} , and the $\text{C}-\text{H}$ stretch occurred in the range of $3000-2840\text{ cm}^{-1}$. The peak at 2971 cm^{-1} represented the asymmetric stretch of the

methyl group, and the peaks at 2931 and 2875 cm^{-1} were due to the asymmetrical and symmetrical stretches, respectively, of the methylene group. The ethoxyethanol residue showed an $\text{O}-\text{H}$ stretch at 3483 cm^{-1} .

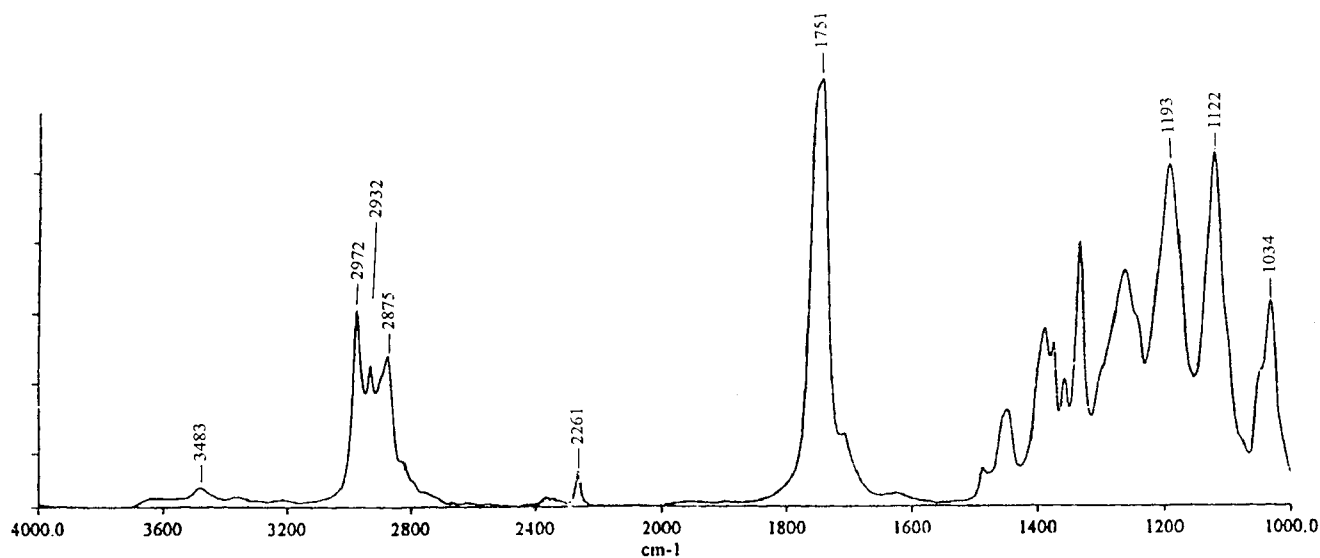


Figure 3 The Fourier transform IR spectrum of ethoxyethyl cyanoacetate.

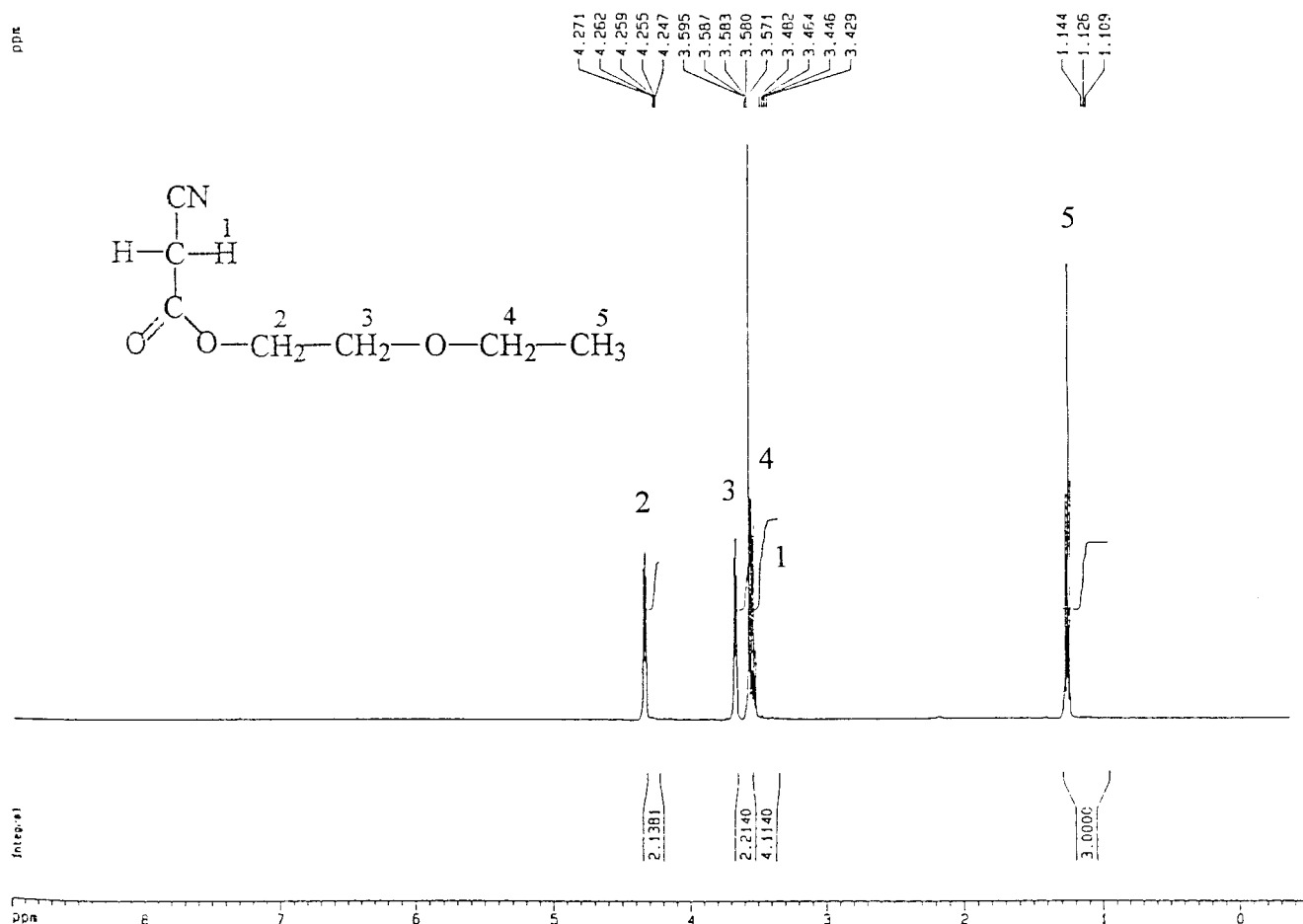


Figure 4 The $^1\text{H-NMR}$ spectrum of ethoxyethyl cyanoacetate.

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra are shown in Figures 4 and 5, respectively. Of particular interest was the methylene proton adjacent to the cyanide group. This proton had a chemical shift at 3.42–3.49 ppm in the $^1\text{H-NMR}$ spectrum and disappears after the ethoxyethyl cyanoacetate reacts with formaldehyde.

Condensation reaction of ethoxyethyl cyanoacetate with paraformaldehyde

The completion of the condensation reaction was determined by measuring either the molecular weight of oligo(ethoxyethyl α -cyanoacrylate) using GPC or the weight of the collected water by-product. Because the piperidine catalyst forms an azeotrope with water at 95°C , the condensation reaction was controlled at temperatures ranging from 65 to 95°C . Benzene and toluene mixed at various ratios were used as the reaction solvent system. At a reaction temperature of 90°C , the amount of collected water is shown in Figure 6 for each solvent system as a function of time. The amount of water increased with an increase in the benzene content in the solvent system. This could be attributed

to the nonpolarity of benzene and the lower boiling temperature of the benzene/water azeotrope. Similar effects are also shown in Figure 7 for the molecular weight changes as a function of time. Solvents having a higher benzene content led to the formation of oligomers with higher molecular weights. To fortify the conclusion that the polarity of the solvent causes the formation of the low molecular weight polymers, strong polar solvents such as *n*-butyl acetate and xylene were tested as the reaction medium. In both solvent systems, the formed oligomers had low molecular weights with a narrow distribution.

It is worthy to note that, although the amount of water collected increased with time, the molecular weight did not increase accordingly. The molecular weight actually decreased slightly and the biggest decrease occurred in a 100% toluene system. The fact that the molecular weight stopped increasing seemed to indicate the completion of the condensation reaction. Nevertheless, the GPC chromatograms in Figures 8–10 show that the molecular weight distribution kept changing and the average molecular weight decreased because of the continuous formation of low molecular

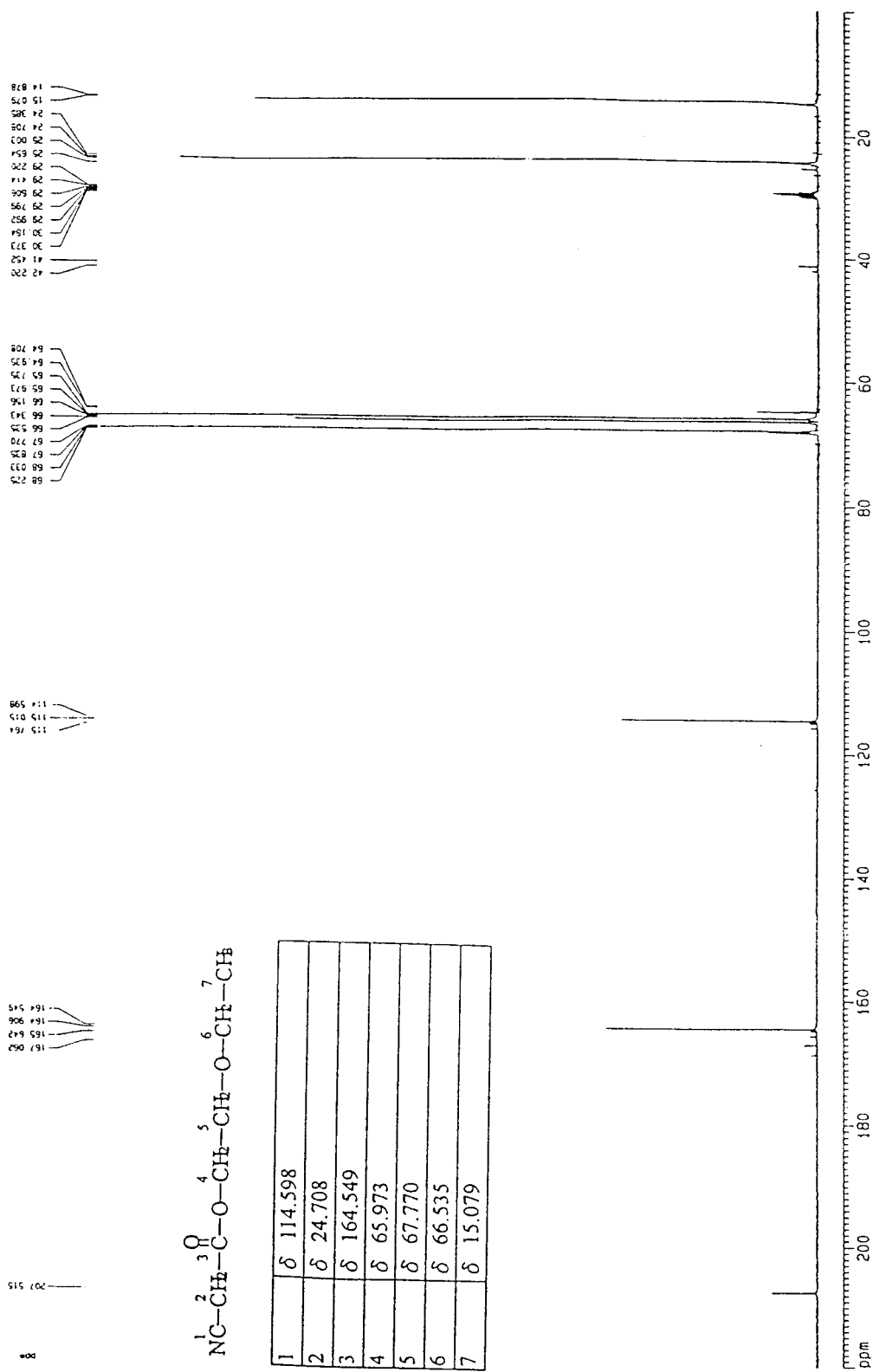


Figure 5 The ¹³C-NMR spectrum of ethoxyethyl cyanoacetate.

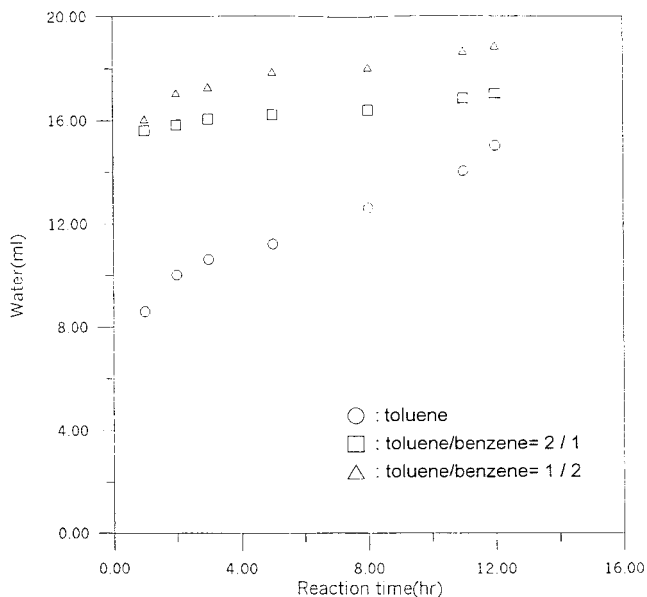


Figure 6 The amount of water collected during the formation of oligo(ethoxyethyl α -cyanoacrylate) at 90°C.

weight species (possible reasons are given in the reaction mechanism section). On the other hand, the formation of low molecular weight species could be minimized by lowering the reaction temperature. At a reaction temperature of 75°C (which is 15°C lower than previous cases), the molecular weight distribution of the formed oligomers are shown in Figure 11 as a function of time.

Characterization of oligo(ethoxyethyl α -cyanoacrylate)

The DSC thermogram in Figure 12 is of the oligo(ethoxyethyl α -cyanoacrylate) formed in the afore-

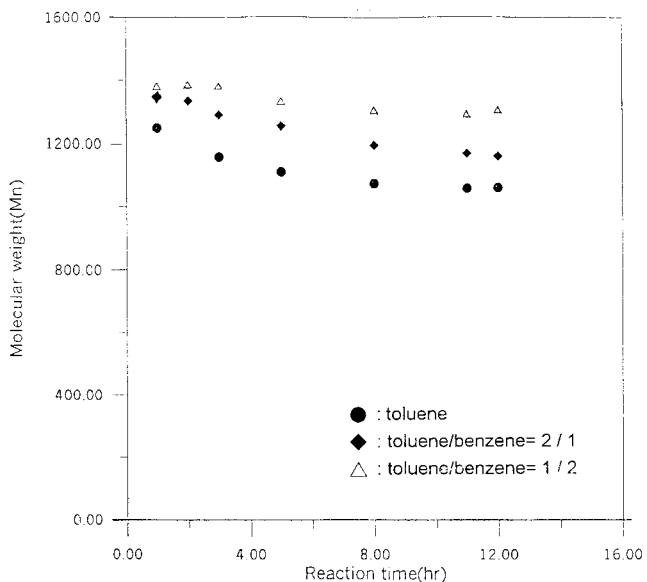


Figure 7 The changes in the molecular weight of oligo(ethoxyethyl α -cyanoacrylate) formed at 90°C.

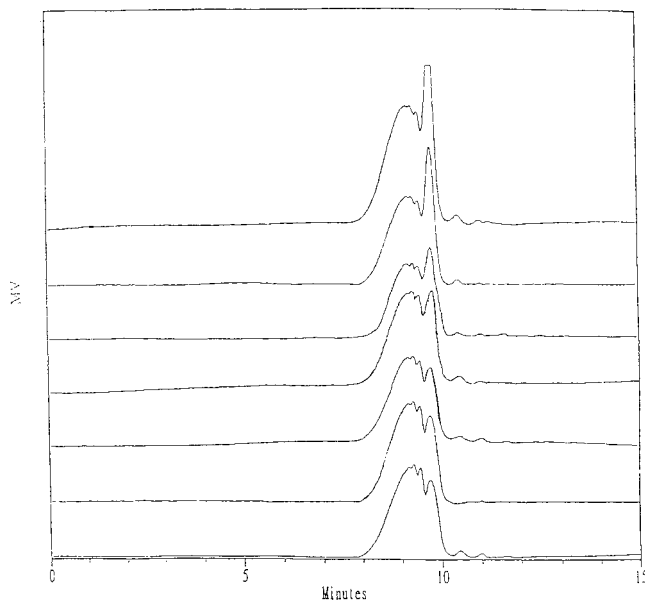


Figure 8 The molecular weight distribution of oligo(ethoxyethyl α -cyanoacrylate) formed in toluene at 90°C in (bottom to top) 1, 2, 3, 5, 8, 11, and 12 h.

mentioned condensation reaction, and it clearly shows a glass-transition temperature at -14.9°C . The absence of a melting temperature indicated that oligo(ethoxyethyl α -cyanoacrylate) was a noncrystalline, amorphous material. The elemental analysis results as tabulated in Table I further corroborated its composition. The data were in satisfactory agreement with the theoretical numbers.

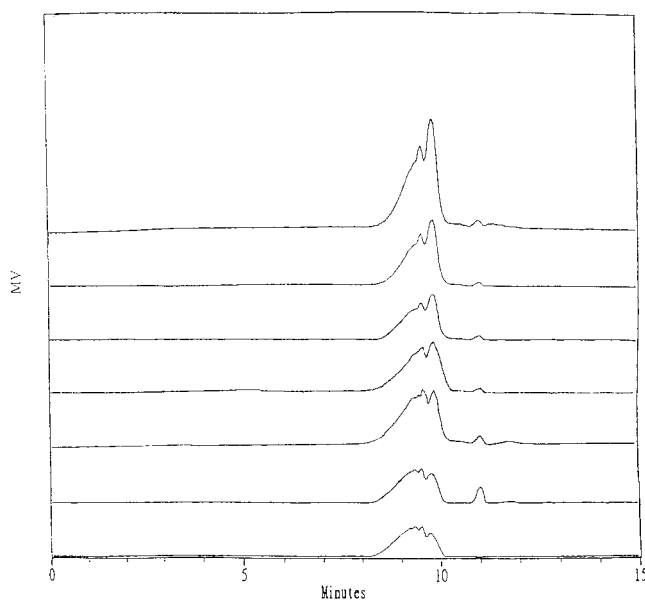


Figure 9 The molecular weight distribution of oligo(ethoxyethyl α -cyanoacrylate) formed in 1:0.5 toluene/benzene mixed solvent at 90°C in (bottom to top) 1, 2, 3, 5, 8, 11, and 12 h.

The $^1\text{H-NMR}$ spectrum of oligo(ethoxyethyl α -cyanoacrylate) is shown in Figure 13. The methylene protons adjacent to the cyanide group (located at 3.42–3.49 ppm originally) disappear and new peaks appear at 2.06–2.80 ppm, indicating the reaction of ethoxyethyl cyanoacetate with paraformaldehyde.

Although the oligo(ethoxyethyl α -cyanoacrylate) exhibited a distribution of the molecular weight, the noticeable growth of the low molecular weight species (Figs. 8–10) strongly suggested that the low molecular weight species might behave differently. Therefore, a TGA analysis was conducted on our oligo(ethoxyethyl α -cyanoacrylate) sample under nitrogen from 30 to 400°C. As shown in Figure 14, two distinct thermal degradation temperatures existed, 194 and 253°C. The former stemmed from the depolymerization of high molecular weight oligo(ethoxyethyl α -cyanoacrylate), which accounted for an 80.5% weight loss; and the latter was due to the depolymerization of low molecular weight species, which accounted for an 11.6% weight loss. However, in the absence of further experimental information, this statement remains speculative.

Reaction mechanism of condensation reaction

Paraformaldehyde dissolves in a nonpolar solvent and exists in the form of a formaldehyde monomer.⁶ The rate of dissociation of paraformaldehyde has been shown previously to have an insignificant effect on the

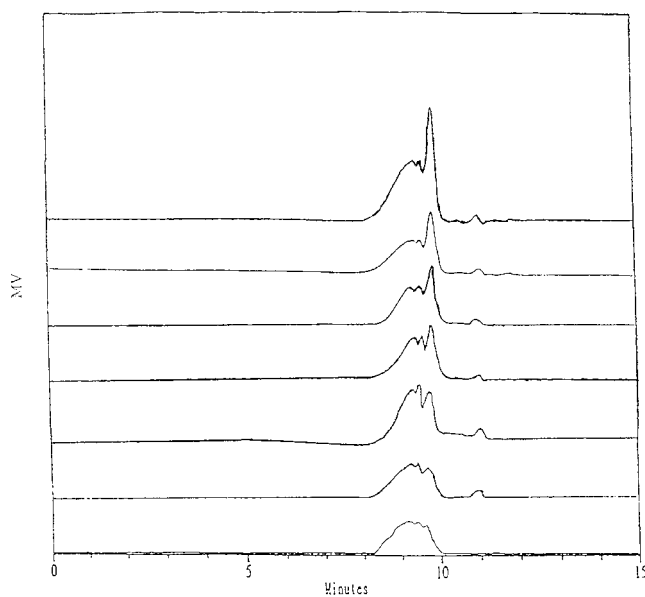


Figure 10 The molecular weight distribution of oligo(ethoxyethyl α -cyanoacrylate) formed in 1:2 toluene/benzene mixed solvent at 90°C in (bottom to top) 1, 2, 3, 5, 8, 11, and 12 h.

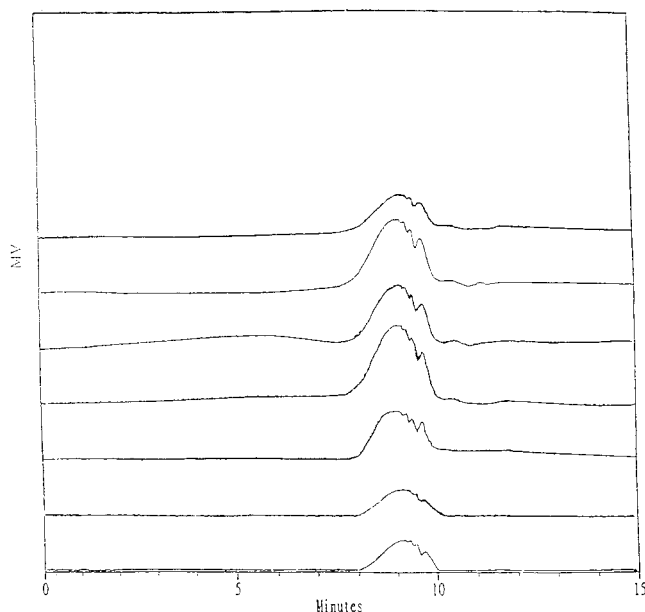
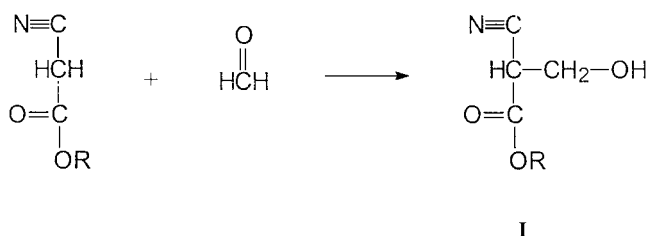
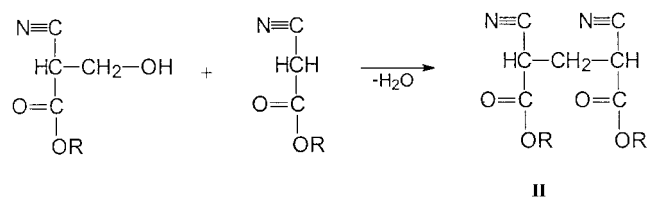


Figure 11 The molecular weight distribution of oligo(ethoxyethyl α -cyanoacrylate) formed in benzene at 75°C in (bottom to top) 1, 2, 3, 5, 8, 11, and 12 h.

condensation reaction of cyanoacetate with formaldehyde.⁷ Several mechanisms have been proposed in the past for this Knoevenagel reaction. According to the first one, the formation of oligo(ethoxyethyl α -cyanoacrylate) could be described as a stepwise condensation reaction catalyzed by an alkaline catalyst.^{8,9} The cyanoacetate underwent a nucleophilic reaction with formaldehyde and formed compound I.



The succeeding reaction of I with cyanoacetate formed compound II with the release of a water molecule.



The intermediate II again reacted with formaldehyde and formed compound III.

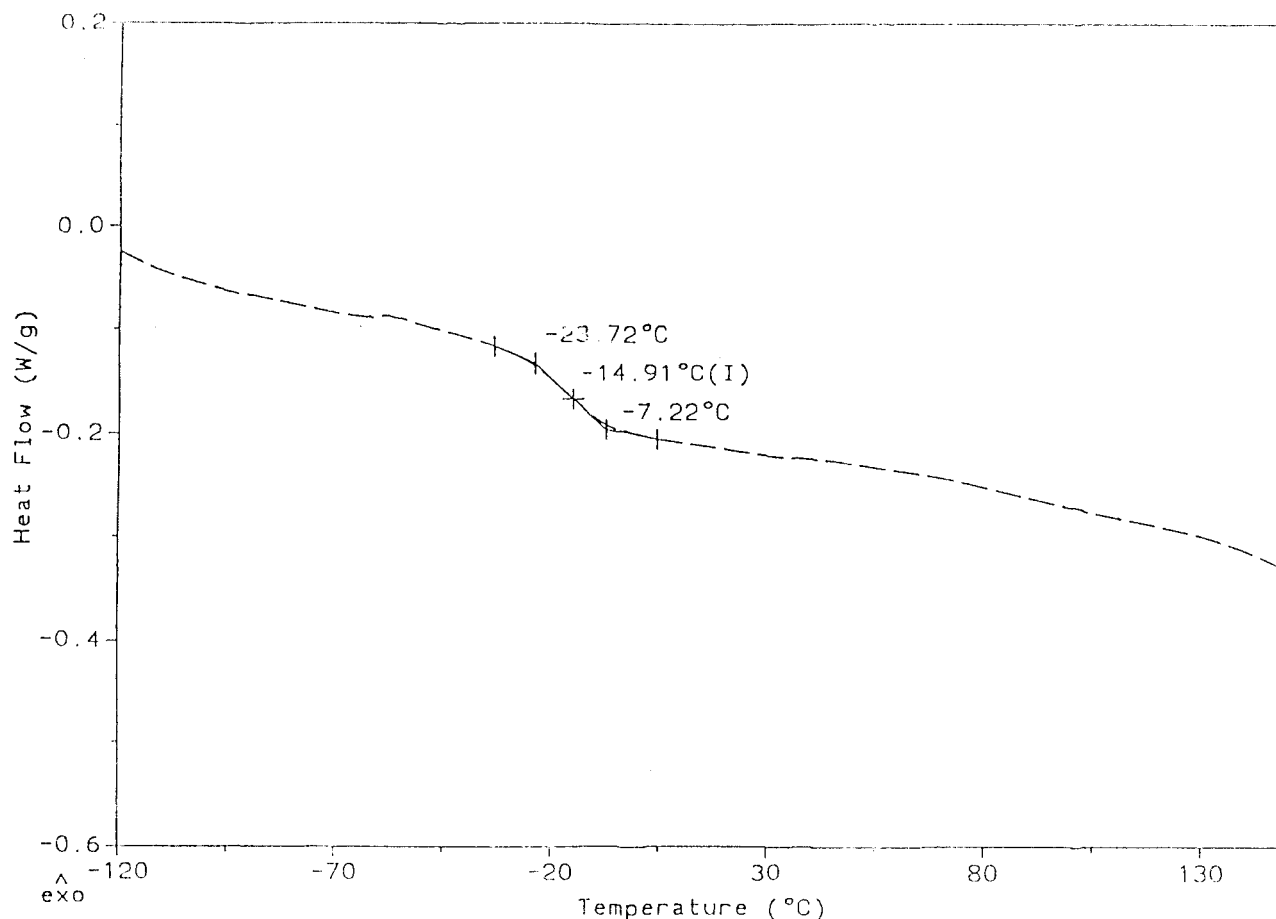
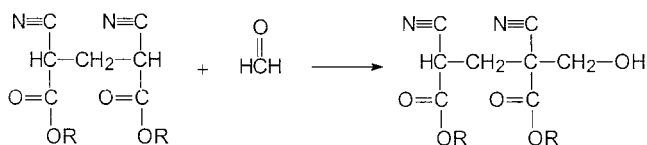
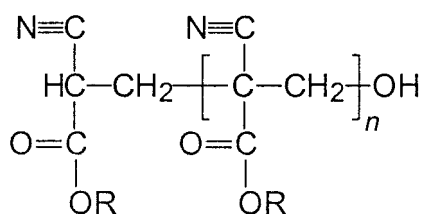


Figure 12 A DSC thermogram of oligo(ethoxyethyl α -cyanoacrylate).



III

Then the cycle was repeated and the final polymer was formed:



This stepwise condensation mechanism showed that the water by-product was continuously released concomitant with the build-up of the molecular weight. However, in our reaction between ethoxyethyl cyanoacetate and formaldehyde, the molecular weight reached the maximum very rapidly and did not in-

crease much further, even though water was still being continuously released. This observation was thus contradictory to the stepwise condensation mechanism in which the molecular weight increased rapidly only when the conversion approached 100%.

Another mechanism involved the formation of a α,β -unsaturated carbonyl and a Michael addition reaction.¹⁰ Because cyanoacetate tended to form a stable anion in the presence of an alkaline catalyst,

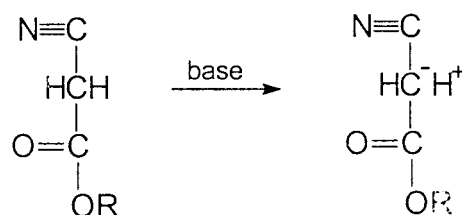


TABLE I
Elemental Analysis of Oligo(ethoxyethyl α -cyanoacrylate)

Formula		Elemental Analysis (%)			
		C	H	N	O
$\text{C}_8\text{H}_{11}\text{N}_1\text{O}_3$	Theoretical	56.24	6.71	8.32	—
	Measured	56.20	6.75	8.32	—

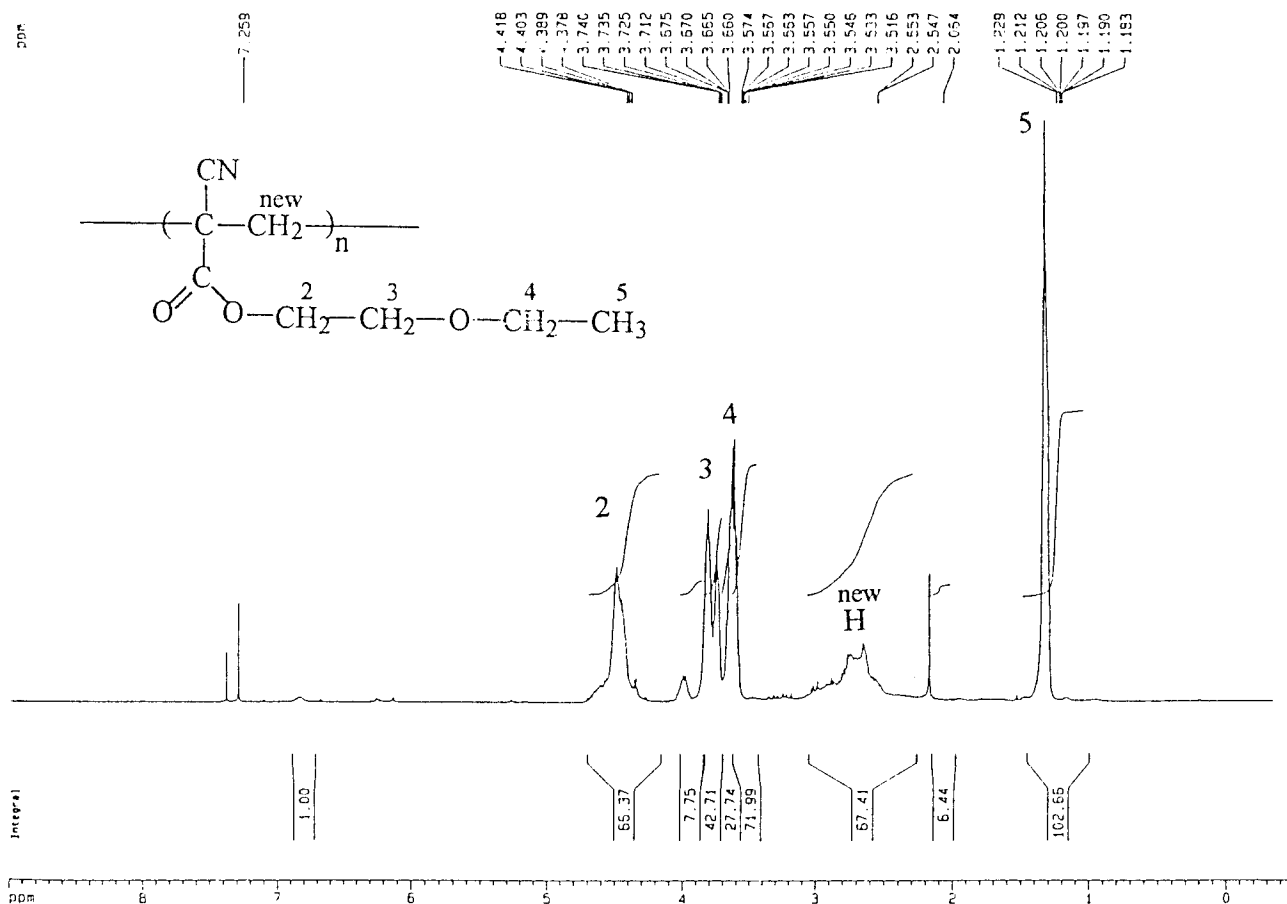


Figure 13 The ¹H-NMR spectrum of oligo(ethoxyethyl α-cyanoacrylate).

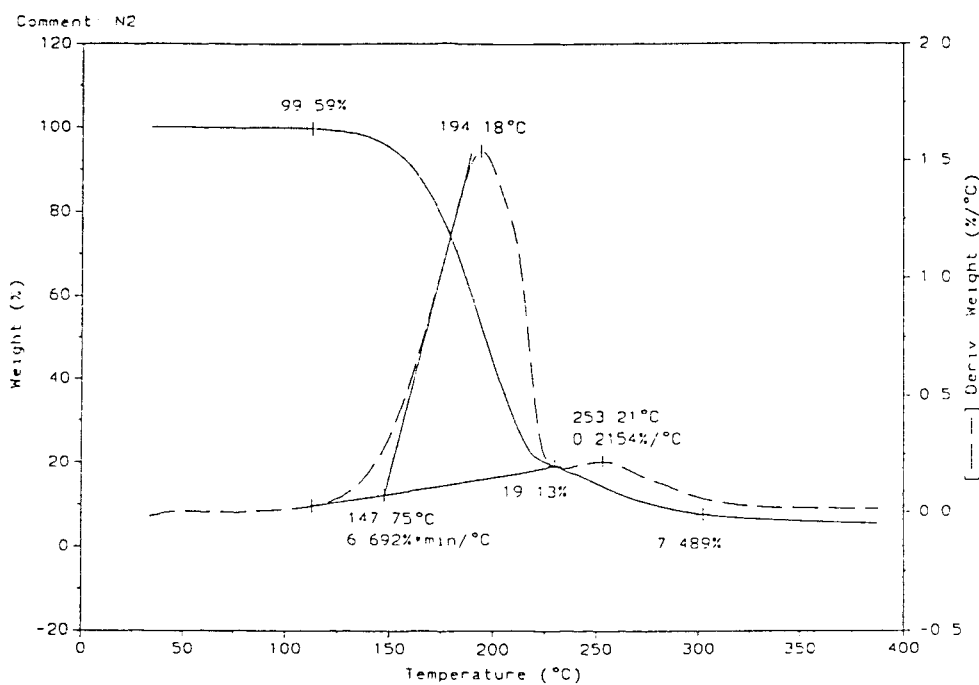
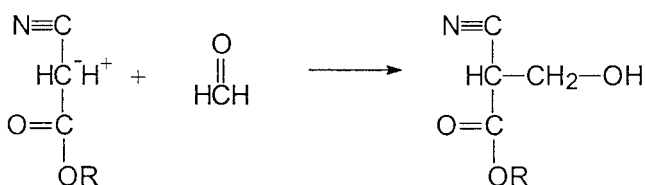
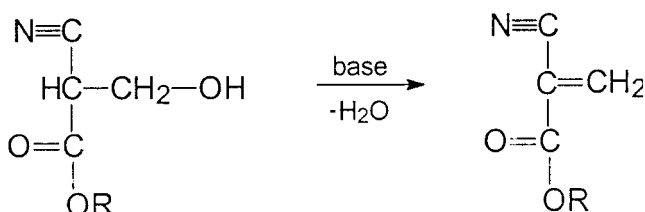


Figure 14 The TGA weight curve of oligo(ethoxyethyl α-cyanoacrylate).

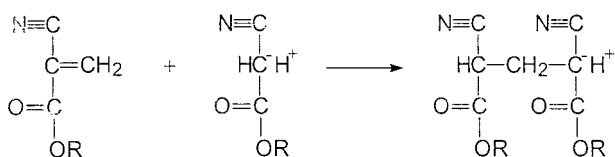
It has been proposed that this anion proceeded with a nucleophilic reaction with formaldehyde.



The following reaction catalyzed by the alkali led to the formation of a α,β -unsaturated carbonyl with the release of a water molecule:

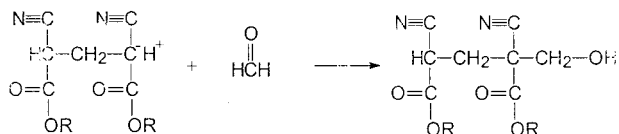


The α,β -unsaturated carbonyl then underwent a Michael addition reaction with the stabilized cyanoacetate anion, forming **IV**.



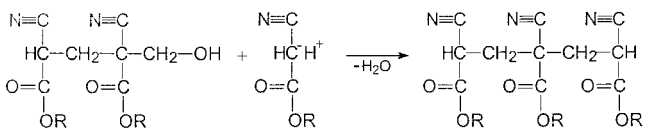
IV

The intermediate **IV** again reacted with formaldehyde and formed **V**.



V

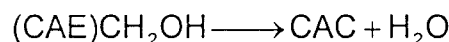
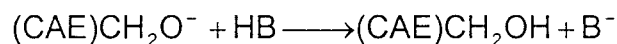
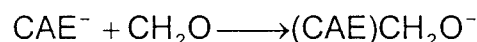
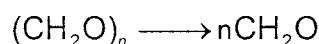
The intermediate **V** then reacted repeatedly with the stabilized cyanoacetate anion and formed the final polymer:



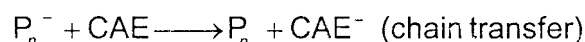
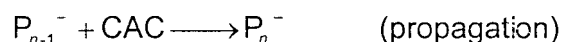
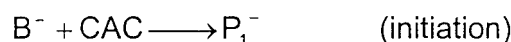
This mechanism also showed continuously released water concomitant with the continuous build-up of the molecular weight, which again did not agree with our experimental observations. Furthermore, the lack

of methyl hydrogen on the tertiary carbon in **V** made the last reaction less likely (than the formation of a α,β -unsaturated carbonyl followed by the Michael addition reaction) because the reaction was severely limited by the steric hindrance. Therefore, the molecular weight could hardly increase beyond the dimeric or trimeric state.

The observation that the molecular weight built up very quickly made the anionic mechanism plausible.^{7,11} For the reaction of cyanoacetate (CAE) with formaldehyde in the presence of an alkaline catalyst (B^-), the α -cyanoacrylate monomer (CAC) was considered to be formed first with the release of water by-product.

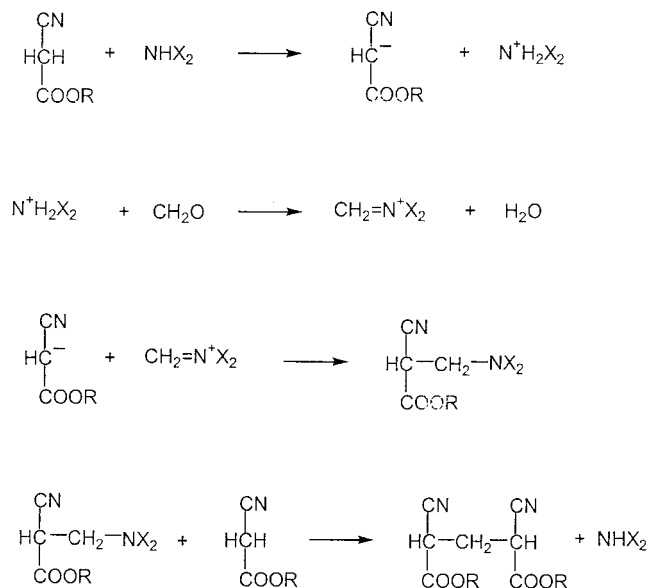


The α -cyanoacrylate monomer proceeded next with an anionic polymerization as follows:



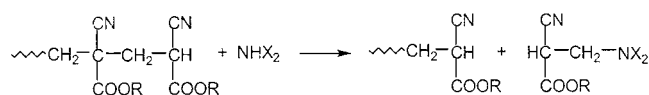
where the molecular weight was limited by the chain transfer to the cyanoacetate. However, in our case this mechanism could not explain why the low molecular weight species were continuously formed, even when the maximum molecular weight of the polymer was attained.

Our observation that the by-product water was continuously released, the molecular weight reached a maximum very quickly, and it was followed by the formation of low molecular weight species suggested that the mechanism proposed by Chorbadjiev and Novakov¹² was more appropriate. According to this mechanism, the piperidine catalyst (secondary amine) was first protonated and then reacted with formaldehyde to form an intermediate $\text{CH}_2=\text{N}^+\text{X}_2$. This intermediate reacted next with the activated cyanoacetate anion and yielded imine compounds (Manish bases), CAC-NX_2 . The imine compounds then reacted with cyanoacetate to form a dimeric compound:



Again, this dimeric compound underwent a deprotonation with NHX_2 and thus the entire process was repeated.

Simultaneously, the basic catalyst caused chain scission as follows:



The formation of a Manish base required a low reaction temperature and the removal of water, and this was consistent with our observations that an optimal reaction between ethoxyethyl cyanoacetate and form-

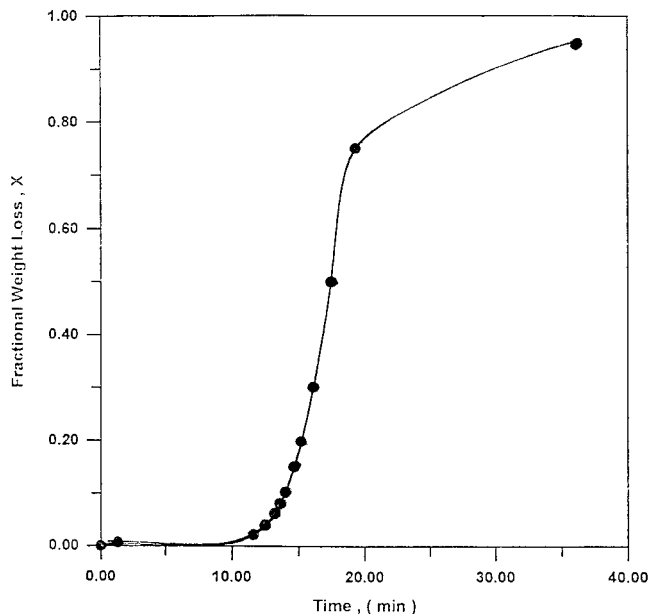


Figure 15 The rate of depolymerization of oligo(ethoxyethyl α -cyanoacrylate).

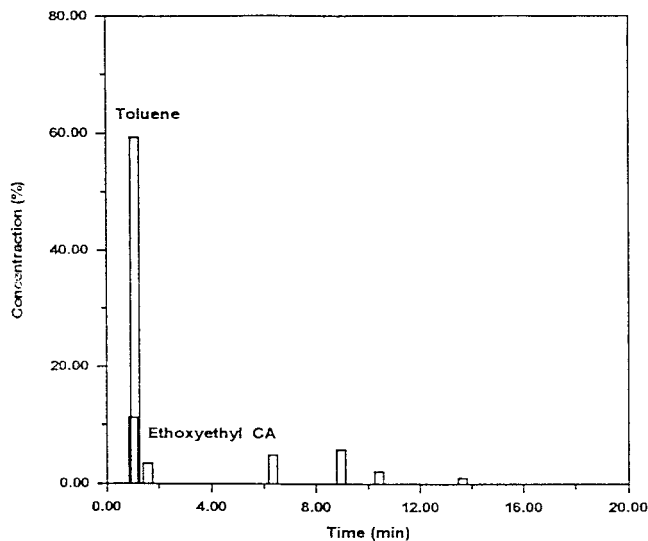


Figure 16 A GC chromatogram of depolymerized oligo(ethoxyethyl α -cyanoacrylate).

aldehyde necessitated such conditions. The formaldehyde kept reacting with the basic catalyst, and the by-product water was released continuously. The observation that the molecular weight did not increase with the water formation could be ascribed to the chain scission reaction leading to an increased amount of low molecular weight species. The chain scission reaction predominated over the oligomerization later in the reaction when formaldehyde was diminished and the excess catalyst reacted primarily with oligomeric chains. Furthermore, because of the longer carbon chain, the ethoxyethyl group was likely to impart a lower oligomerization rate for ethoxyethyl cyanoacetate than the ethyl group for the ethyl cyanoacetate.

Depolymerization of poly(ethoxyethylcyanoacrylate)

The rate of depolymerization of oligo(ethoxyethyl α -cyanoacrylate) was determined from the previous TGA curve by plotting the weight loss as a function of time. As depicted in Figure 15, the maximum depolymerization rate occurred within a temperature range of 150–200°C. Clearly, oligo(ethoxyethyl α -cyanoacrylate) depolymerized into the ethoxyethyl α -cyanoacrylate monomer and evaporated out of the system, causing the weight loss.

The crude ethoxyethyl α -cyanoacrylate monomer collected in the experiments was analyzed by GC. The sample was diluted into a 30% solution by toluene to prevent the column from being blocked. As observed in Figure 16, the purity of the monomer was estimated as 10.4% (other species were the residual reactants and intermediates). In addition, it was worthy to note that no ethoxyethanol existed in the GC chromatogram (which would otherwise exhibit a peak at 12.2 min),

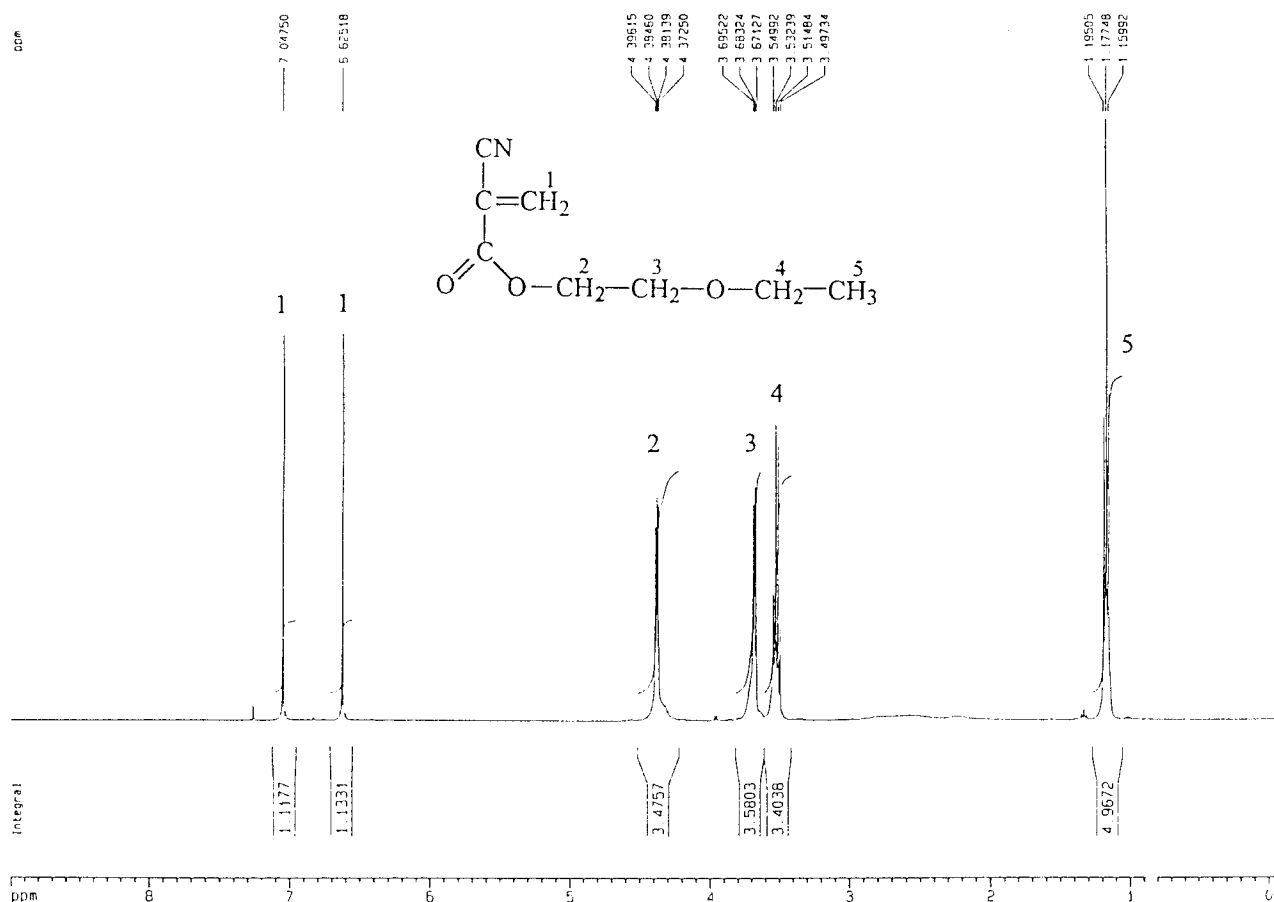
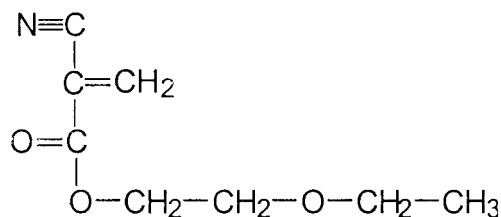


Figure 17 The ¹H-NMR spectrum of ethoxyethyl α-cyanoacrylate.

indicating the C—OR bond in the carboxylate group remained intact.

The ¹H-NMR spectrum of ethoxyethyl α-cyanoacrylate monomer is shown in Figure 17. Compared to the spectrum of oligo(ethoxyethyl α-cyanoacrylate) in Figure 13, the methylene protons on the backbone of oligo(ethoxyethyl α-cyanoacrylate) molecule disappeared and two additional peaks at 6.63 and 7.05 ppm for the protons of =CH₂ appeared. This observation clearly substantiated the depolymerization of oligo(ethoxyethyl α-cyanoacrylate) into the ethoxyethyl α-cyanoacrylate monomer.

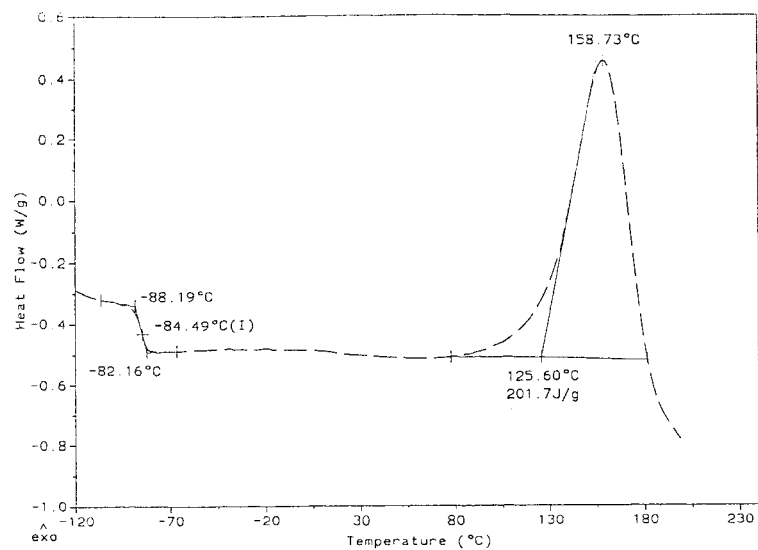


Characteristics of cured ethoxyethyl α-cyanoacrylate

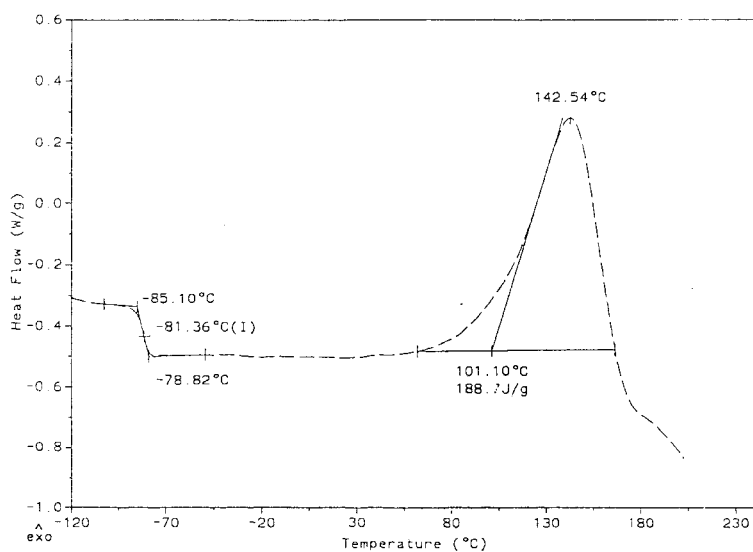
The cured ethoxyethyl α-cyanoacrylate exhibited strong adhesion properties typical of cyanoacrylate

adhesives. Its TGA thermogram is analogous to Figure 14 and suggests 120°C as the upper limit for maintaining the desired adhesive properties. DSC thermal scans were taken from -120 to 230°C for ethoxyethyl α-cyanoacrylate samples that were cured for 0 min, 30 min, 8 h, 16 h, or 24 h. The resulting thermograms are shown in Figure 18. The curing reaction was an exothermic reaction with the exotherm diminishing with time, and the complete curing occurred in 24 h. The glass-transition temperature increased with an increase in the extent of curing, and a completely cured ethoxyethyl α-cyanoacrylate had a glass-transition temperature of 53°C. Apart from this temperature, the cured ethoxyethyl α-cyanoacrylate did not have any detectable melting transition as exhibited in Figure 18(e). Thus, the cured ethoxyethyl α-cyanoacrylate can be considered as nearly an amorphous material containing little or low crystallinity.

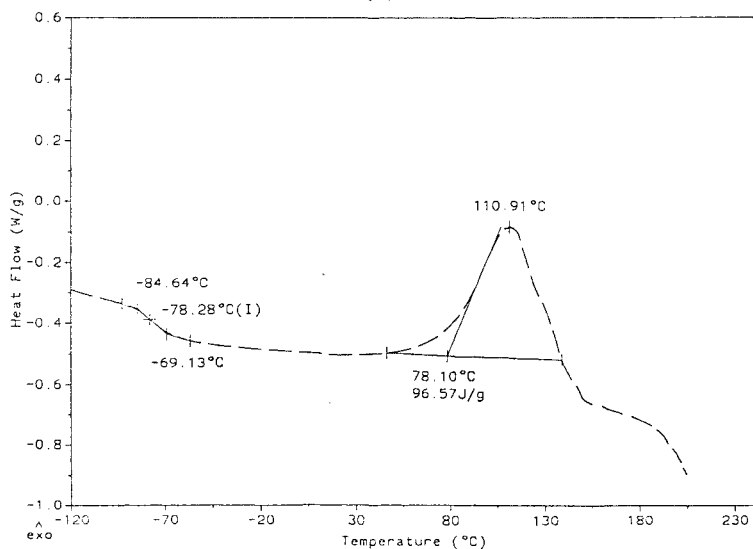
The mechanical properties of the cured ethoxyethyl α-cyanoacrylate were measured using a steel plate as the substrate. The steel plate was sanded to increase the surface roughness using AA-240 sand paper prior to the measurements. Either pure ethoxyethyl α-cyanoacrylate or ethoxyethyl α-cyanoacrylate thickened by blending poly(methylacrylate) into it was applied



(a)

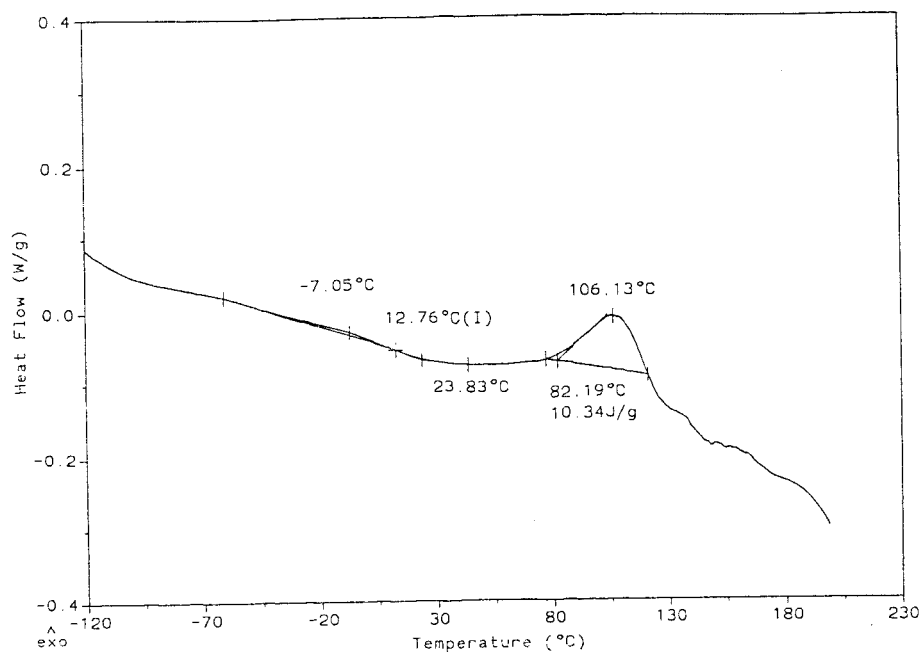


(b)

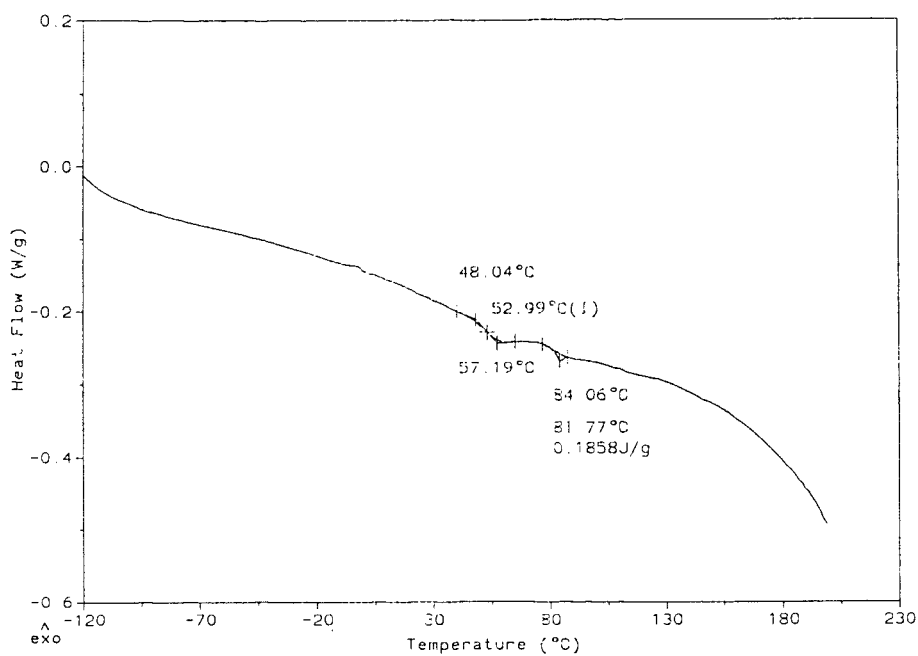


(c)

Figure 18 DSC spectra of cured ethoxyethyl α -cyanoacrylate at different curing times of (a) 0 h, (b) 30 min, (c) 8 h, (d) 16 h, and (e) 24 h.



(d)



(e)

Figure 18 (Continued from the previous page)

to the substrates, and the tensile and shear properties were both measured. The results are tabulated in Table II. After being cured at room temperature for 24 h, the Young's modulus was approximate 1105–1606 N/mm², and the shear modulus was 898–1024 N/mm². The thickening of the sample significantly

improved the mechanical strength. Also noteworthy was that the maximum strength and break strength were almost equal, indicating the absence of or an extremely short yielding process. The break strain (ultimate elongation) was 2.9–3.0% for tensile testing and 3.0–3.1% for shear testing. Compared to the conven-

TABLE II
Mechanical Testing of Cured Ethoxyethyl
 α -Cyanoacrylate

	Max. Strength (N/mm ²)	Max. Strain (%)	Break Strength (N/mm ²)	Break Strain (%)	Modulus* (N/mm ²)
V_{PN}	32.1	2.9	32.1	2.9	1105.7
V_{TN}	48.7	3.0	48.7	3.0	1606.3
V_{PS}	27.8	3.0	27.8	3.0	898.6
V_{TS}	32.9	3.1	32.9	3.1	1023.5

The modulus is the calculated value based on a linear approximation of the strength-strain curve. V_{PN} , ethoxyethyl α -cyanoacrylate, tensile testing; V_{TN} , thickened ethoxyethyl α -cyanoacrylate, tensile testing; V_{PS} , ethoxyethyl α -cyanoacrylate, shear testing; V_{TS} , thickened ethoxyethyl α -cyanoacrylate, shear testing.

tional ethyl α -cyanoacrylate (<2% break strain), the cured ethoxyethyl α -cyanoacrylate was a hard material with improved toughness.

CONCLUSIONS

The high reactivity of ethoxyethyl α -cyanoacrylates precludes a direct synthesis of this monomer. Therefore, an oligo(ethoxyethyl α -cyanoacrylate) was synthesized first by reacting ethoxyethyl cyanoacetate with paraformaldehyde, followed by depolymerization at an elevated temperature in an acidic atmosphere with a high vacuum. The ethoxyethyl cyanoacetate was then synthesized from ethoxyethanol and cyanoacetic acid. Solvents, such as benzene, with a lower polarity led to the formation of oligomers with

higher molecular weights. The molecular weight distribution of the oligomer revealed that the reaction of ethoxyethyl cyanoacetate with formaldehyde followed a mechanism comprising monomer activations, anionic reactions, and chain scissions. A DSC thermogram showed the cured ethoxyethyl α -cyanoacrylate was nearly an amorphous material containing little or low crystallinity. Mechanical testing results indicated that the cured ethoxyethyl α -cyanoacrylate was a hard adhesive with higher toughness than the conventional ethyl α -cyanoacrylate.

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