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Synthesis and Polymerization Studies of Cyano Epoxides

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ABSTRACT

The polar epoxides β-cyanoethyl glycidyl ether, cyanomethyl glycidyl ether, β-chloro-β-cyanoethyl glycidyl ether, and 3,4-epoxy valeronitrile were prepared, characterized, and their polymerization reactions studied. Novel cyanoethylation of glycidol produced the β-cyanoethyl glycidyl ether in a quantitative yield. Reported is the first practicable synthesis of epicyanohydrin, which failed to polymerize. Homo-, co-, and terpolymerizations of the polar α-epoxy nitriles with various alkylene oxides were achieved by employing a complex catalyst obtained from an aluminum alkyl, acetyl acetone, and water. The polymers produced a series of vulcanizable elastomers which displayed an excellent balance of solvent resistance and low temperature flexibility, as well as good ozone resistance. The presence of a third monomer such as allyl glycidyl ether was required to facilitate rubber vulcanization. However, it was possible to vulcanize homo- and copolymers of β-chloro-β-cyanoethyl glycidyl ether through the pendant chlorine atom. Catalyst efficiency in all cases was poor due to the complexing of the aluminum catalyst by the nitrile function.

INTRODUCTION

The advantage of elastomers possessing a polyalkylene ether backbone are excellent low-temperature properties, excellent ozone resistance, and good heat stability. A further extension of the utility of the polyalkylene ethers evolved with the introduction of homo- and copolymers of epichlorohydrin. These polyalkylene ethers combined a polar functional group with the alkylene oxide backbone, resulting in solvent resistance [1]. The co- and terpolymerization of α-epoxy nitriles with various alkylene oxides produces elastomers which are superior to the well-known nitrile rubber (copolymers of butadiene and acrylonitrile) and possess solvent resistance and low-temperature properties similar to, or in most cases superior to, the commercial polymers based on epichlorohydrin [2]. The main objective of this paper is to report on the novel preparation of several of the α-epoxy nitrile monomers and to discuss the properties of the elastomers which they produced.

EXPERIMENTAL

Monomer Preparation

β-Cyanoethyl Glycidyl Ether (CEGE)-Anion Exchange Resin Method

Regenerate the resin (IRA-400) by washing it on a Buchner funnel with 5% sodium hydroxide (5 or 6 times the volume of resin); rinse the resin with distilled water until the washings are neutral and dry in the air.

In a 500-ml three-necked flask equipped with a reflux condenser, stirrer, thermometer, and a dropping funnel were placed 100 g (1.35 moles) of glycidol (freshly distilled) and 2.2 g of IRA-400 resin. The flask and its contents were heated slowly to 50°C and then the acrylonitrile (100 g, 1.9 moles) was added over a period of 1 hr. Cooling, as well as the rate of addition of the acrylonitrile, was employed to control the reaction. Afte final addition, a sample was removed and submitted to vapor-phase chroma tographic analysis which indicated complete conversion of the glycidol. The resin was removed via filtration and the excess acrylonitrile removed under reduced pressure. The product was distilled to produce 165 g (97% yield), bp 98-101°C (3 Torrs), n_D^{20} 1.4423.

Benzyltrimethyl Ammonium Hydroxide (Triton B) Method

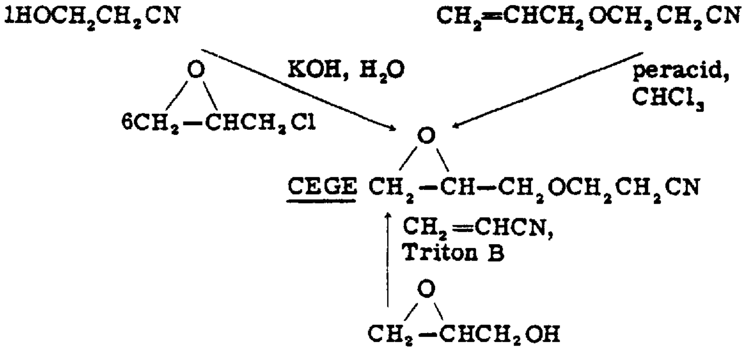
Into a 1-liter three-necked flask, fitted with a stirrer, thermometer, and dropping funnel, were placed 100 g (1.35 moles) of glycidol and 300 g (5.66 moles) of acrylonitrile. The mixture was stirred rapidly and heated to 40°C, then 10 drops of 40% (in methanol) Triton B was added. An exotherm developed in 5 min and cooling was applied. The temperature rose to 80°C and was cooled to 40°C with an ice bath. Analysis via vapor-phase chromatography indicated that all the glycidol had been converted to CEGE

A few drops of acetic acid were added to remove the benzyltrimethyl ammonium hydroxide, followed by two 50-ml portions of water. The acrylonitrile layer was separated and dried over anhydrous magnesium sulfate. Distillation at 100-150 Torrs removed the excess acrylonitrile. The remaining dark oil was distilled at 2-3 Torrs to yield 135 g (79%) of pure CEGE.

CEGE via Epichlorohydrin (ECH) Route

In a 2-liter, three-necked flask fitted with a Trubore stirred and Teflon paddle, nitrogen inlet tube, dropping funnel, and thermometer, were placed 558 g (6 moles) of epichlorohydrin and 65 g of (85% pure) potassium hydroxide dissolved in 280 ml of cold water. With very rapid stirring, 71 g (1 mole) of 3-hydroxypropionitrile was added. An exotherm was noted and cooling was employed to maintain the reaction mixture at 15-30° C throughout the course of the addition. The reaction mixture was stirred at room temperature overnight. The organic layer was removed and the aqueous layer saturated with potassium carbonate and extracted with two 25-ml portions of epichlorohydrin which was added to the original ECH layer and dried over anhydrous magnesium sulfate. The excess ECH was removed via vacuum distillation. The remaining residue was distilled at 5 Torrs to produce two major fractions; unreacted 3-hydroxypropionitrile (bp 85-90° C) and the desired CEGE (bp 110-114° C) in a 70% conversion based on recovered starting materials.

The two preparations described here (Chart 1) are superior to the published ones in which epoxidation of allyloxypropionitrile was employed [2, 3]. The IR spectrum of CEGE was characterized by prominent bands for the epoxide group at 1270 cm^{-1} (epoxide C-O stretching) and a strong absorption for the nitrile at 2200 cm^{-1} (Fig. 1).



(1)

CHART 1. Preparation of β-cyanoethyl glycidyl ether.

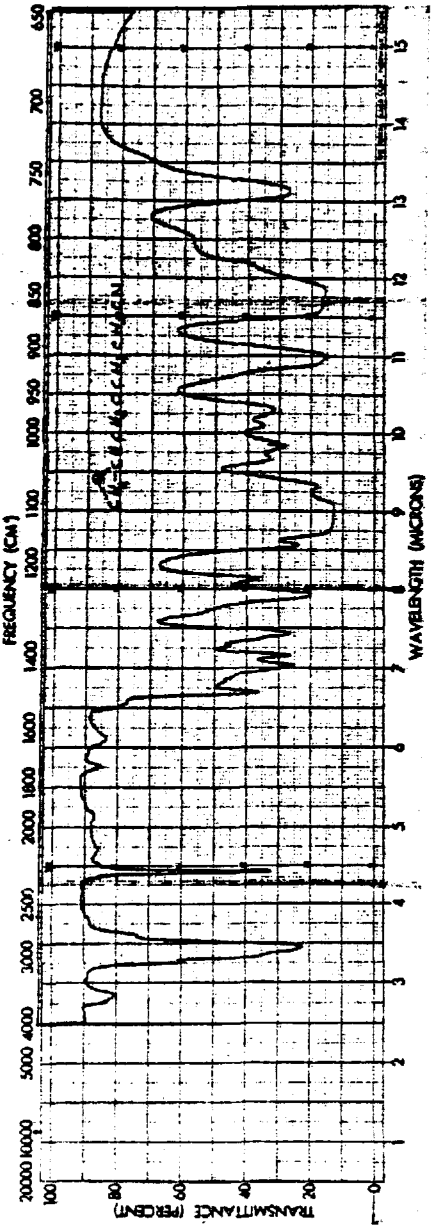
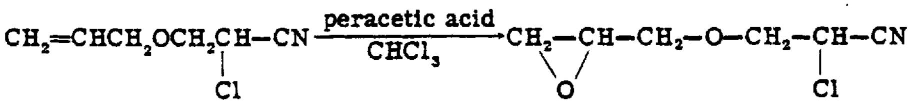


FIG. 1. IR spectrum of β-cyanoethyl glycidyl ether.

β-Chloro-β-cyanoethyl Glycidyl Ether (Cl-CEGE)

An attempt to prepare the monomer directly from α-chloroacrylonitrile and glycidol failed. The synthesis was realized by the epoxidation of 2-chloro-3-allyloxypropionitrile.



$$CH_2{=}CHCH_2OCH_2\underset{\displaystyle Cl}{\underset{|}{C}}H{-}CN \xrightarrow[CHCl_3]{\text{peracetic acid}} \underset{\diagdown O \diagup}{CH_2{-}CH}{-}CH_2{-}O{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}H{-}CN \qquad (2)$$

Cl-CEGE

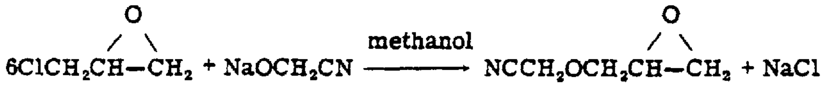
In a 1-liter, three-necked flask, fitted with a dropping funnel, a Trubore stirrer, and a nitrogen inlet tube, were placed 87.5 g (1 mole) of α-chloroacrylonitrile (Marbon Chemical Co.) and 4 moles of allyl alcohol. The contents were stirred and heated to 55°C, then 1 mole of allyl alcohol which had been treated with 0.05 g-atom of sodium was added slowly. A dark color was imparted to the reaction mixture and a mild exotherm was noted. After complete addition (1 hr) the flask and its contents were allowed to stir at RT overnight. Solid carbon dioxide was added and then the dark solution vacuum distilled to remove the excess allyl alcohol. The product, bp 52-53° (3 Torrs), n_D^{20} 1.4513, was 2-chloro-3-allyloxypropionitrile in a 71% yield [4].

Into a 1-liter, three-necked flask was placed 50 g (0.34 mole) of α-chloro-β-alloxypropionitrile and 10 ml of chloroform. The solution was stirred and cooled with an ice bath to 5°C, then a chilled mixture of 98 g of 40% peracetic acid, 2.5 g of sodium carbonate, and 50 ml of chloroform was added slowly. The reaction mixture was allowed to stir at RT for 18 hr, then a large quantity of solid sodium carbonate was added. The chloroform layer was separated, washed, and dried. Removal of the chloroform, followed by vacuum distillation, produced two major fractions. The first was unreacted starting material; the higher boiling fraction, bp 97-98° (3 Torrs), n_D^{20} 1.4612, was the desired epoxide obtained in a 79% yield.

The IR spectrum displayed a prominent band at 1255 cm^{-1} (epoxide C—O stretching) and a weak CN absorption at 2220 cm^{-1}. Prominent C—Cl stretching bands were present in the 700-760 cm^{-1} region (Fig. 2).

Cyanomethyl Glycidyl Ether (CMGE)

Generation of the sodium or potassium salt of glycolonitrile in an excess of epichlorohydrin produced the monomer in a 50% yield.



$$6ClCH_2\overset{\diagup O \diagdown}{CH{-}CH_2} + NaOCH_2CN \xrightarrow{\text{methanol}} NCCH_2OCH_2\overset{\diagup O \diagdown}{CH{-}CH_2} + NaCl \qquad (3)$$

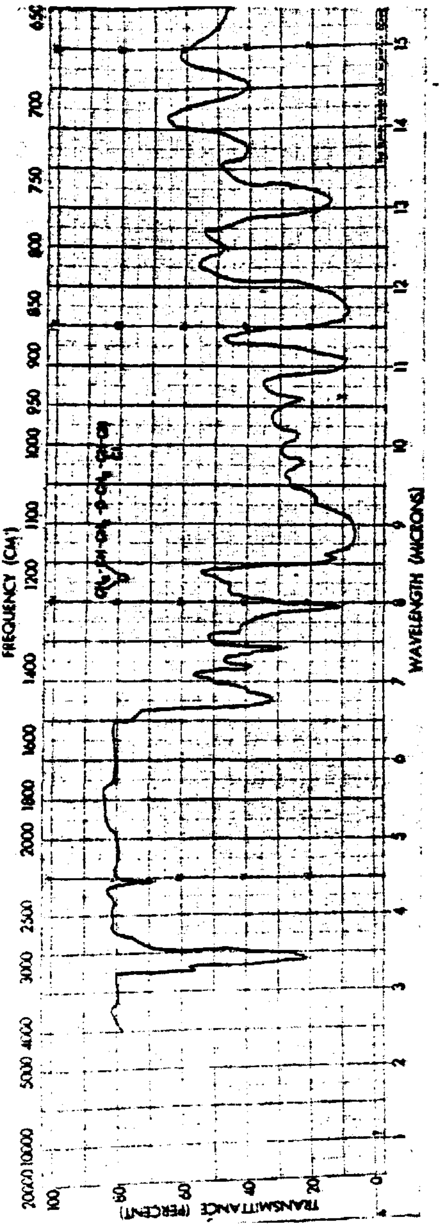


FIG. 2. IR spectrum of β-chloro-β-cyanoethyl glycidyl ether.

Powdered sodium cyanide (49 g, 1 mole) was added slowly to 90 ml of a 37% formalin solution diluted with 100 ml of methanol. The cooled solution was allowed to stir for 1 hr after the complete addition.

$$NaCN + CH_2O\ (H_2O) \xrightarrow{\text{methanol}} NaOCH_2CN$$

The glycolonitrile solution was added slowly, with rapid stirring, to 6 moles of epichlorohydrin (ECH) at 8-15°C. The temperature was raised slowly to 30° and allowed to run for 2.5 hr during which time a salt precipitated. The reaction mixture was treated with 500 ml of cold water and the organic layer extracted twice with ethyl ether. The ether layer was washed three times with cold water (neutral to litmus) and dried over anhydrous magnesium sulfate. The ether and excess epichlorohydrin were removed under reduced pressure (100-150 Torrs) and the remaining light yellow oil distilled to produce one fraction, bp, 68-70°C (3 Torrs); n_D^{26} 1.4338, yield 51 g (46%).

CMGE via Epoxidation of Allyloxyacetonitrile

In a 500-ml three-necked flask, fitted with a Trubore stirrer, thermometer, and dropping funnel, were placed 48 g (0.5 mole) of allyloxyacetonitrile [5] and 150 ml of chloroform. To this stirred and cooled solution was added 150 g of 40% peracetic acid dissolved in 100 ml of chloroform which had been treated with 4 g of sodium carbonate. The peracid solution was added slowly to the allyloxyacetonitrile and the reaction mixture was stirred at room temperature overnight. The excess peracid was removed by addition of sodium carbonate, followed by aqueous washing. The layers were separated and the organic layer dried over anhydrous magnesium sulfate. After removal of the drying agent the solvent was removed via a rotary evaporator. The remaining oil was distilled at 3 Torrs to produce one fraction, bp 68-73°C, n_D^{24} 1.4335, in a 48% yield. The product, bp 67-68°C (3 Torrs), n_D^{20} 1.4362, displayed strong C—O stretching at 1250 cm^{-1} but failed to display the nitrile absorption (Fig. 3). This phenomenon has been observed in other systems in which the nitrile function is directly attached to a carbon bearing an oxygen atom [6].

3,4-Epoxyvaleronitrile

The epoxidation of 4-cyanobutene-1 with peracid produced 3,4-epoxyvaleronitrile in a 40% yield. The product, bp 68-70°C (4 Torrs), n_D^{20} 1.4324, displayed C—O stretch at 1260 cm^{-1} and a nitrile absorption at 2220 cm^{-1} as indicated by the IR spectrum.

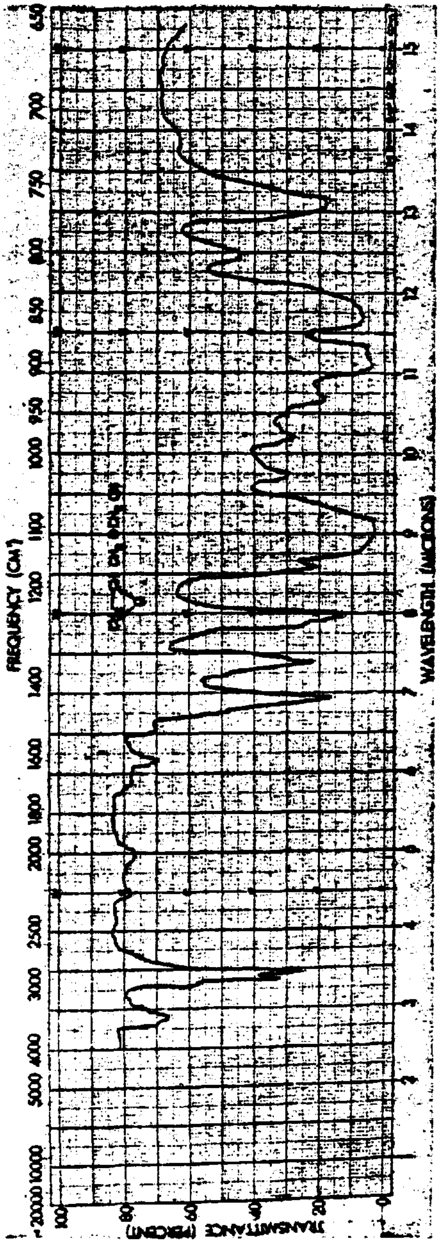


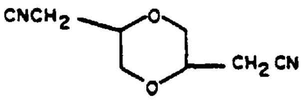
FIG. 3. IR spectrum of cyanomethyl glycidyl ether.

3-(Glycidoxy-methoxy)-propionitrile

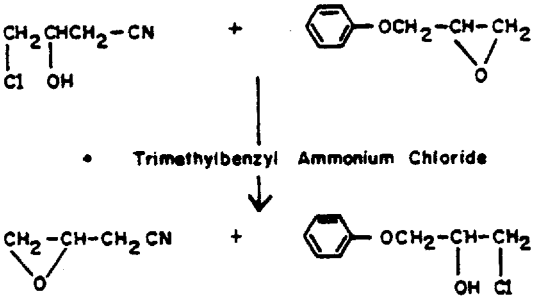
The epoxidation of 3-(allyloxymethoxy)-propionitrile produced the monomer in a 56% yield. The liquid, bp 100-105°C (1 Torr), n_D^{20} 1.4451, was characterized by elemental analysis, epoxide titration, and its IR spectrum.

3,4-Epoxybutyronitrile (Epicyanohydrin) (EPICH)

Hartenstein and Pazschke reported the synthesis of epicyanohydrin, $\overline{O-CH_2CH}CH_2CN$, by condensing potassium cyanide and epichlorohydrin [7, 8]. Wei and Butler reported that this condensation product was actually an unpolymerizable dimer [9]:



McClure conducted a very special mild, dehydrohalogenation of 4-chloro-3-hydroxybutyronitrile with a mole of silver oxide to produce the monomeric epoxide in a 20% yield [10]. A transetherification reaction involving the 4-chloro-3-hydroxybutyronitrile and phenyl glycidyl ether in the presence of an ammonium chloride catalyst produced the novel monomer.



It was difficult to remove pure epicyanohydrin from the reaction mixture because it readily polymerized upon heating. The direct epoxidation of allyl cyanide was realized by the use of molybdenum hexacarbonyl and tertiary butyl hydroperoxide. The liquid, bp 58°C (3 Torrs) was not too stable and darkened upon standing at room temperature.

The IR spectrum contains bands at 1150 and 1220 cm^{-1} (C—O stretching) and 2215 cm^{-1} for the nitrile group (Fig. 4). The epoxide titration indicated that the material was 98% pure as

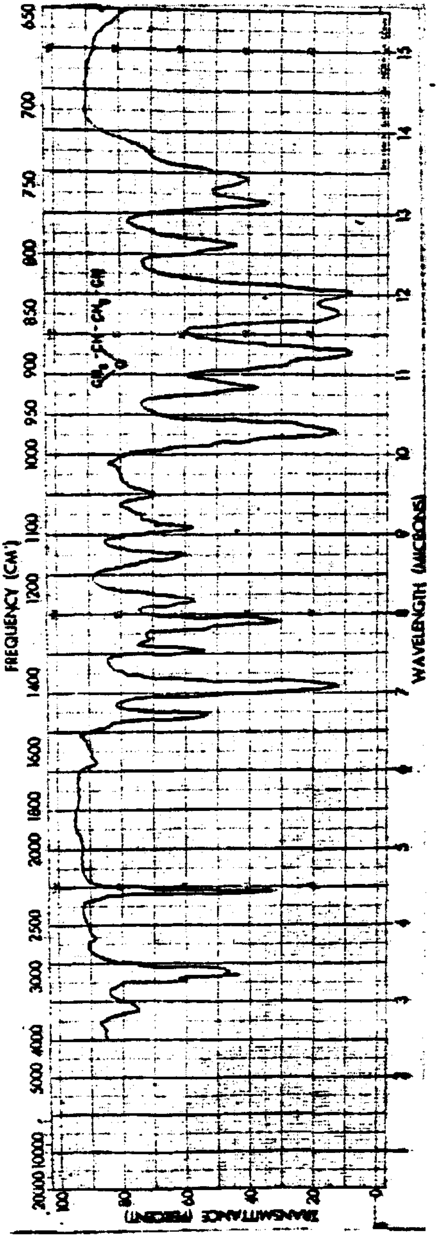


FIG. 4. IR spectrum of epicyanohydrin.

confirmed by GPC analysis [11]. The 60 MHz NMR spectrum displayed a typical ABX pattern for the ring methylene and methine protons (Fig. 5).

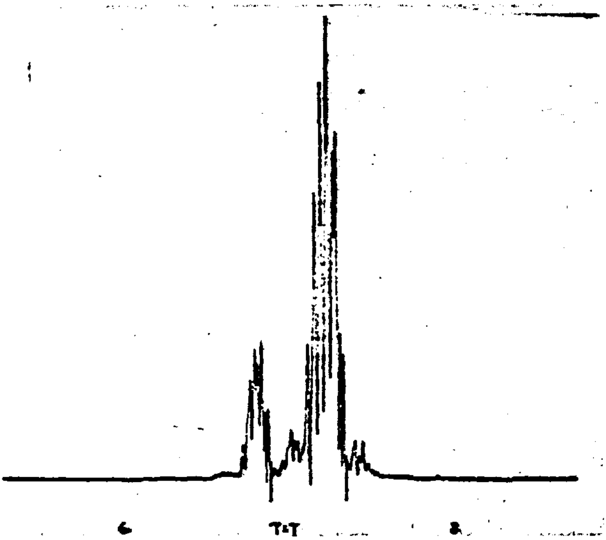


FIG. 5. NMR spectrum of epicyanohydrin.

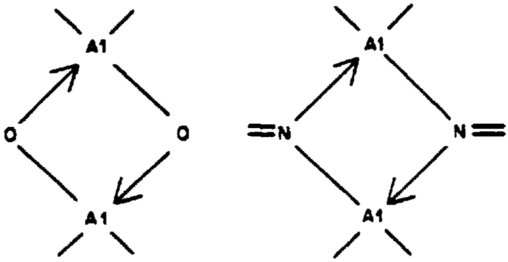
POLYMERIZATION STUDIES

Polymerizations were conducted in 8 oz bottles, quart green bottles, 4.0 liter resin kettles, and 10 gal reactors. The bottles were placed in a chain-driven rotating water bath at constant temperature. Solvents and commercial monomers were freshly distilled under nitrogen and over calcium hydride. Bottles were loaded in a dry nitrogen stream, first the solvent, then the monomers, and finally the catalyst. With the use of toluene in place of n-hexane, a thick cement was always obtained. At higher levels of nitrile incorporation, n-hexane failed to prevent precipitation of the elastomer. The toluene cements were worked up in two general methods. The cement was either poured into boiling water containing emulsified antioxidant (ditertiary butyl p-cresol) or poured into a nonsolvent such as ethyl ether or petroleum ether. However, in all cases large quantities of catalyst residue remained with the rubber (1-7%). Careful washing of the rubber cements with dilute hydrochloric acid and fresh cold water lowered the residue to 0.3-0.7%. However, these acid washed elastomers degraded markedly upon hot air drying.

Catalyst Preparation and Level

The triisobutyl aluminum (TIBAL), acetyl acetone, water system developed by Vandenberg was used in all successful polymerizations [12]. For example, the catalyst solution employed was prepared by treating a chilled 400 ml solution of 20% by weight of TIBAL in hexane (or toluene) with 100 ml of anhydrous ethyl ether followed by a slow addition of 3.72 g of water and finally 21.6 g of acetyl acetone. The reaction was conducted under nitrogen and the catalyst solution allowed to age at room temperature for various periods of time.

α-Epoxy nitrile polymerizations require large quantities of catalyst as compared to the polymerizations of other alkylene oxides such as epichlorohydrin or propylene oxide. It has been shown that the nitrile function can complex effectively with available ligands of the aluminum atoms [13]. Thus β-cyanopropionaldehyde, having a polar nitrile group, exhibits polymerization different from that of common aliphatic or chlorinated aldehydes. It was found that the nitrile group, as well as the aldehyde group, participates in a reaction with triethyl aluminum:



Vulcanization

Incorporation of 5 mole % of allyl glycidyl ether (AGE) was required to produce a sulfur curable vulcanizate. Use of a metal oxide cure system was possible in elastomer systems containing pendant chlorine functions such as are found in the copolymers of CEGE and CMGE with epichlorohydrin or the polymers containing Cl-CEGE. The polymers were mixed with fillers in a Brabender and the vulcanization ingredients added on a two-roll mill. The stocks were heated in a mold under pressure. The sample pads were tested with a Scott Tester for tensile properties. The solvent swell tests were a standard ASTM Fuel B at RT. The low temperature properties were obtained by ASTM Gehman and Brittle Point methods and by DSC.

RESULTS AND DISCUSSION

It has been shown that a wide variety of catalyst systems are capable of polymerizing alkylene oxides to high molecular weight elastomers [14, 15]. Thus systems based on $FeCl_3$. propylene oxide; $ZnEt_2.H_2O$, and AlR_3 .acetylacetone. H_2O were employed to prepare novel elastomers. The α-epoxy nitriles were successfully polymerized with only the aluminum alkyl system. In our earlier attempts a series of glycidonitriles were synthesized but they failed to polymerize. This same effect was noted by Wei and Butler [9]. However, we were able to prepare the novel monomer epicyanohydrin which failed to polymerize, indicating that the electron withdrawing effect of the nitrile function, either directly attached to the epoxide (glycidonitriles) or one atom removed, destroyed the ability of the epoxide to coordinate with the catalyst system. For convenience, the following abbreviations are used: PO = propylene oxide, EO = ethylene oxide, ECH = epichlorohydrin, AGE = allyl glycidyl ether, CEGE = β-cyanoethyl glycidyl ether, Cl-CEGE = β-chloro-β-cyanoethyl glycidyl ether, CMGE = cyanomethyl glycidyl ether, EPICN = epicyanohydrin.

Homopolymerizations

All of the α-epoxy nitriles except epicyanohydrin were capable of homopolymerization in the presence of the alkyl aluminum catalyst. Table 1 lists the reaction conditions and the conversions.

The conversions were dependant on the amount of catalyst, increasing with increased catalyst level. The homopolymers were tough, snappy elastomers which were not too soluble in a wide variety of organic solvents. During polymerization they remained soluble in the toluene medium; however, after precipitation and drying they were difficult to redissolve. The elastomers did not appear to be gelled, for they formed clear films and processed readily.

The glass transition temperatures (T_g's) of the homopolymers decreased as the length of the pendant chain increased. The effect of the ether linkage in the pendant chain also lowered the T_g.

TABLE 1. Homopolymerizations of α-Epoxy Nitrile Monomers[a]

Monomer structure $\overset{O}{\diagup\ \diagdown}$ CH_2-CH-R	Monomer (mole)	Solvent (ml)	TIBAL catalyst[b] (mole)	Yield (%)	T_g (°C)
$-CH_2CN$	0.10	Benzene (200)	0.05	-	-
$-CH_2CH_2CN$	0.41	Hexane (250)	0.08	10	-13
$-CH_2OCH_2\underset{\substack{\vert \\ Cl}}{CH}CN$	0.62	Hexane (500)	0.22	88	-19
$-CH_2OCH_2CN$	0.43	Toluene (500)	0.20	98	-18
$-CH_2OCH_2CH_2CN$	0.39	Hexane (250)	0.08	74	-28
$-CH_2OCH_2OCH_2CH_2CN$	0.31	Benzene (250)	0.20	60	-32

[a] Polymerization conditions: 50°C for 18–20 hr.

[b] TIBAL system = triisobutyl aluminum/H_2O/acetylacetone (1/0.5/0.5). Aged 24 hr at room temperature. 150 ml = 0.1 mole of Al.

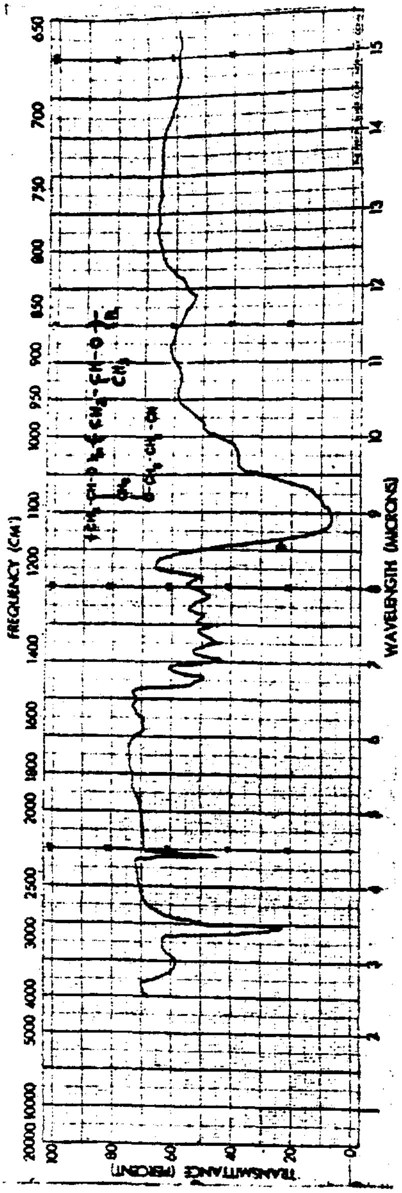


FIG. 6. IR spectrum of a CEGE/PO copolymer.

α-Epoxy Nitrile Copolymerizations

In all examples the α-epoxy nitriles copolymerized better than they homopolymerized. All of the products were rubbery, solvent-resistant elastomers. To insure maximum conversion of the nitrile monomer, high levels of catalyst were employed. The mole % conversions ranged from a low of 35.5 to a high of 93.5. These conversions were based on Kjeldahl nitrogen analysis.

Figure 6 depicts the IR spectrum of a typical CEGE/PO copolymer.

Copolymerization of CEGE or CMGE with ECH produced a series of highly solvent resistance elastomers which were readily vulcanized through the pendant chloromethyl group. The polymerization conditions and conversion data are found in Table 2.

α-Epoxy Nitrile Terpolymerizations

The polar α-epoxy nitriles terpolymerized readily with PO, EO, and AGE as shown in Tables 3 and 4. With increased CEGE in the monomer mixture the overall conversions decreased but the CEGE conversions remained almost constant as shown in Fig. 7. The top curve (⊙) indicates the decrease in the overall conversion to polymer. The straight line (×'s) demonstrates that the mole % of CEGE converted remained almost constant even though the mole % of CEGE was increased in the original monomer feed. This effect may be caused by the large quantities of catalyst required to initiate polymerization. The allyl glycidyl ether (AGE) was charged at 5 mole % and assumed to be completely incorporated for the calculations.

VULCANIZATE PROPERTIES

Physical Properties (Tables 5, 6, and 7)

Satisfactory physical properties were obtained from all of the copolymers and terpolymers of CMGE and CEGE with other alkylene oxides. Tensile values were in the 1700-2400 psi range, with 300% modulus values from 1000-1800 psi. Poor physical properties were obtained from Cl-CEGE homo- or copolymers cured with a metal oxide system.

Oil Resistance

Examination of Fig. 8 demonstrates that excellent resistance to hydrocarbon solvents such as toluene/isooctane is displayed by these

TABLE 2. Copolymers of ECH/α-Epoxy Nitriles[a]

ECH (moles)	CEGE (moles)	Toluene (ml)	TIBAL catalyst[b] (moles)	% Yield/g	N (wt%)	Wt% CEGE incorp.	Mole % CEGE incorp.	CEGE conversion (mole %)
0.328	0.126	350	0.10	74/34	4.08	40	32.5	88.0
0.272	0.197	350	0.18	40/20	5.15	48	38.9	35.5
5.45	3.94	19,000	1.9	60/600	6.20	56	47.7	67.1
1.31	0.630	1,500	0.40	40/80	6.68	63	55.0	62.5
	CMGE					CMGE	CMGE	CMGE
0.272	0.221	250	0.02	98/49	6.00	48	42.9	93.5

[a] Polymerization conditions: 50°C for 18-22 hr.

[b] TIBAL system = triisobutyl aluminum/H_2O/acetylacetone (1/0.5/0.5). Aged 24 hr at room temperature. 150 ml = 0.1 mole of Al.

TABLE 3. α-Epoxy Nitrile/PO/AGE[a] Terpolymerizations

PO (moles)	Epoxy nitrile (moles)	Toluene (ml)	TIBAL catalyst[b] (mole)	% Yield/g	N (wt%)	Wt% incorp. epoxy nitrile	Mole % epoxy nitrile incorp.	Epoxy nitrile conversion (mole %)
0.572	CMGE-0.150	250	0.10	92/53	3.58	29.1	22.8	86.1
0.294	CMGE-0.284	250	0.10	75/39	7.50	61.0	44.4	62.2
0.725	CEGE-0.039	250	0.10	98/49	0.99	9.0	5.31	83.2
2.21	CEGE-0.473	1200	0.40	88/176	3.33	30.0	16.6	82.0
0.238	CEGE-0.300	300	0.10	82/40	6.68	60.0	40.8	74.2
0.594	Cl-CEGE-0.093	250	0.10	78/41	2.91	34.1	15.7	88.4

[a] 5 mole % AGE charged, assumed 100% conversion for calculations. Polymerization conditions: 50°C for 18–20 hr.

[b] TIBAL system = triisobutyl aluminum/H_2O/acetylacetone (1/0.5/0.5). Aged 24 hr at room temperature. 150 ml = 0.1 mole of Al.

TABEL 4. α-Epoxy Nitrile/EO/AGE[a] Terpolymerizations

EO (moles)	Epoxy nitrile (mole)	Toluene (ml)	TIBAL catalyst[b] (mole)	% Yield/g	N (wt%)	Wt% incorp. epoxy nitrile	Mole % epoxy nitrile incorp.	Epoxy nitrile conversion (mole %)
1.00	CEGE-0.153	350	0.12	84/54	3.19	29.1	11.0	66.2
0.39	CEGE-0.244	350	0.10	97/49	6.54	59.3	37.5	87.6
1.11	CMGE-0.194	250	0.10	85/64	3.14	26.4	8.92	76.3

[a] 5 mole % AGE charged. Polymerization conditions: 50°C for 18-22 hr.

[b] TIBAL system = triisobutyl aluminum/H_2O/acetylacetone (1/0.5/0.5). Aged 24 hr at room temperature. 150 ml = 0.1 mole of Al.

TABLE 5. Vulcanizate Properties of Epoxy Nitrile Elastomers[a]

Raw elastomer		Vulcanizate[b]				
	N (wt%)	Tensile (psi)	Elongation (%)	300% Modulus (psi)	Swell in ASTM[c] Fuel B (70/30 iso-octane/toluene)	ASTM Brittle Point[d] (°F)
CMGE	3.58	2090	380	1820	49	-44
CMGE	7.50	2550	260	-	7	-17
CEGE	0.99	2100	450	1650	111	-68
CEGE	3.32	2010	500	1580	48	-54
CEGE	6.68	1550	530	1000	14	-36
Cl-CEGE	2.91	2180	220	-	53	-25

[a] Epoxy nitrile-PO-AGE.

[b] Formulation: Elastomer, 100 parts; HAF carbon black, 50 phr; stearic acid, 3.0 phr; zinc oxide, 5 phr; sulfur, 2.0 phr; TUEX, 1 phr; Tellurac, 0.5 phr; cured at 302°F for 30 min.

[c] Room temperature 24 hr, % by volume.

[d] ASTM D-746.

TABLE 6. Vulcanizate Properties of Epoxy Nitrile Elastomers[a]

Raw elastomer		Vulcanizate[b]				
	N (wt%)	Tensile (psi)	Elongation (%)	300% Modulus (psi)	Swell in ASTM[c] Fuel B(70/30 iso-octane/toluene	ASTM brittle point (°F)
CMGE	3.14	2750	440	2300	13	-30
CEGE	3.19	2880	470	2260	6	-34
CEGE	6.54	1760	210	-	4	-18

[a] Epoxy nitrile-EO-AGE.

[b] Formulation: Elastomer, 100 parts; HAF carbon black, 50 phr; stearic acid, 3.0 phr; zinc oxide, 5 phr; sulfur, 2.0 phr; TUEX, 1 phr; Tellurac, 0.5 phr; cured at 302° F for 30 min.

[c] Room temperature 24 hr, % by volume.

TABLE 7. Vulcanizate Properties of Epoxy Nitrile-ECH Copolymer Elastomers

Raw elastomer		Vulcanizate[a]				
	N (wt%)	Tensile (psi)	Elongation (%)	200% Modulus (psi)	Swell in ASTM[c] Fuel B (70/30 isooctane/toluene	ASTM brittle point (°F)
CMGE	6.00	3180	200	3170	2	0
CEGE	4.08	850	790	440	11	-1
CEGE	6.25	1600	290	1200	2	+2

[a] Formulation: Elastomer, 100 parts; FEF carbon black, 50 phr; red lead, 5 phr; zinc stearate, 1.0 phr; nickel dibutyldithiocarbamate, 1.0 phr; NA-22, 2.5 pph, cured at 320° F for 45 min.

[b] Room temperature 24 hr, % by volume.

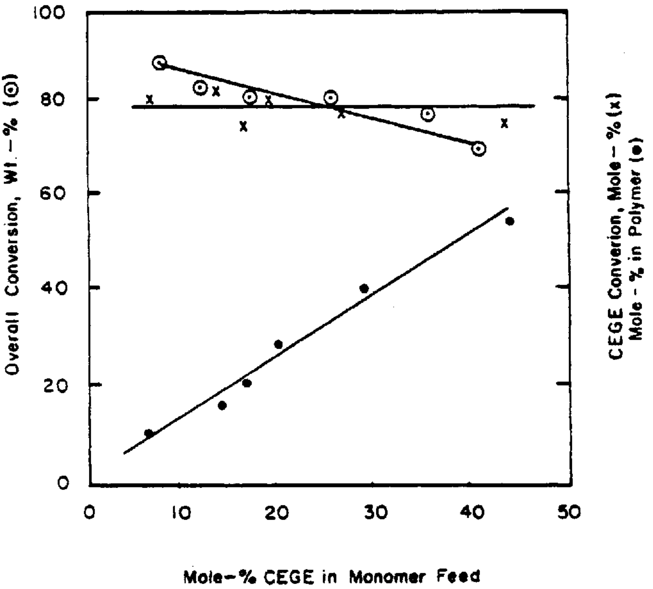


FIG. 7. Conversion of PO/AGE/CEGE terpolymer vs level of CEGE in monomer feed.

novel elastomers. The oil resistance is related to the amount of incorporated epoxy nitrile monomer. The plot of mole % incorporated monomer vs solvent resistance indicates that a linear relationship does not exist. However, it does indicate that at low levels of incorporation the effect on oil resistance is quite pronounced. At high incorporation levels a vulcanizable elastomer with less than 5% swell in Fuel B was obtained.

Ozone Resistance

A saturated backbone elastomer such as polyepichlorohydrin, polypropylene oxide, and ethylene-propylene-terpolymer displays excellent resistance to ozone. The polymers described in this paper are no exception. They can withstand 100 pphm of ozone at 120°F for 100 hr without any antioxidant or antiozonant.

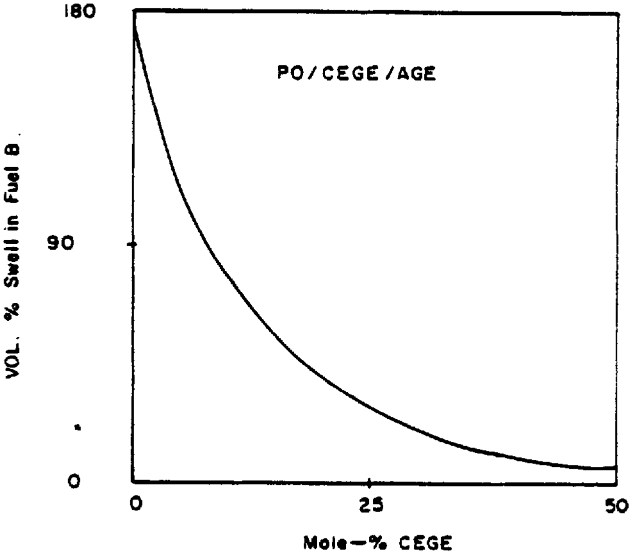


FIG. 8. Effect of CEGE incorporation vs swell in Fuel B.

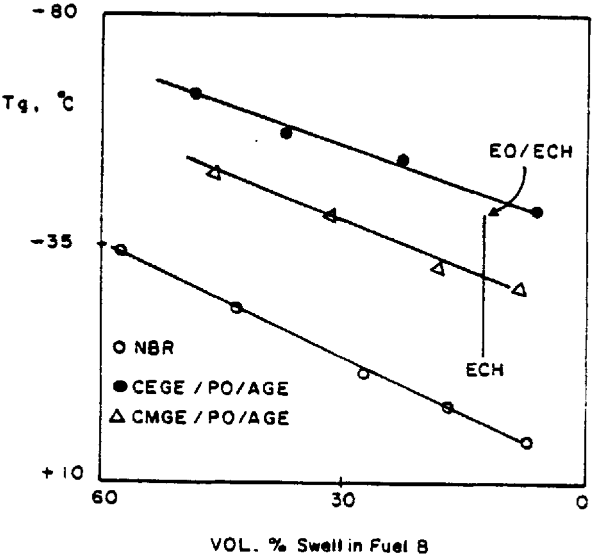


FIG. 9. Comparison of NBR, ECH, and α-epoxynitrile elastomers.

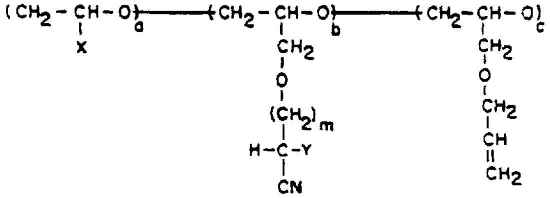


FIG. 10. Schematic polymer structure. x = H for EO, CH_3 for PO, and CH_2Cl for ECH (c = 0 for ECH polymers). m = 0 and Y = H for a cyanomethyl; m = 1 and Y = H for β-cyanoethyl polymers, m = 1 and Y = Cl for β-chloro-β-cyanoethyl polymers. a and b vary; c is constant at 5 mole %.

Low Temperature

The glass transition (T_g) of a polymer chain is markedly affected by the introduction of ether linkages. Therefore a copolymer of propylene oxide/allyl glycidyl ether displays excellent low temperature properties (T_g = -64° C). As the mole % of epoxy nitrile increases in the polymer, the value of the glass transition rises; this is a well-documented phenomenon in the field of NBR elastomers. However, a good balance of low temperature properties vs solvent resistance is established at a 16.6 mole % incorporation of CEGE (Fig. 9).

COMPARISON OF NITRILE (NBR), EPICHLOROHYDRIN (ECH), AND EPOXY NITRILE ELASTOMERS

Also to be seen in Fig. 9 is the data obtained for a comparison between two commercially available solvent resistant elastomers NBR and ECH and the α-epoxy nitrile elastomers. The nitrile rubber (copolymer of butadiene and acrylonitrile) displayed a maximum oil resistance of +10% but at this level the low temperature properties were poor. The epichlorohydrin elastomers, particularly the copolymer of EO/ECH, exhibited good low temperature properties (T_g = -40° C) and good resistance to solvent (Fuel B +21%). However, the CEGE/PO/AGE elastomers duplicate the best ECH/EO results and are capable, by the use of higher nitrile incorporation, of displaying superior solvent resistance and a comparable low temperature flexibility.

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