

A NEW CLASS OF POLYETHERS— POLY(1,4-DICHLORO-2,3-EPOXYBUTANE)S— SYNTHESIS, MECHANISM AND PROPERTY ASPECTS†

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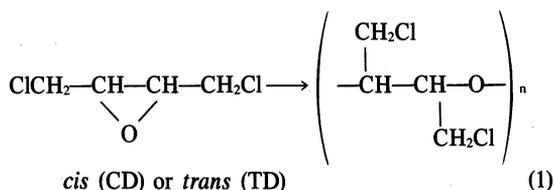
Abstract—The cationic ring opening polymerization and copolymerization of the *cis* and *trans* isomers of 1,4-dichloro-2,3-epoxybutane (CD and TD) with an $i\text{Bu}_3\text{Al} - 0.7 \text{H}_2\text{O}$ catalyst at -78°C has led to an interesting new class of polyethers containing 50% chlorine. The crystalline, racemic diisotactic polymer, obtained from CD in quantitative yield, has the most interesting combination of properties. It has a high melting point (235°C), a high glass transition (95°C), crystallizes readily from the melt, is unusually stable to heat and light, can be melt-processed up to 270°C , is flame resistant, has good barrier properties for air and water, and has good electrical properties. Its main deficiency is poor impact strength which can be overcome by orientation and other methods. This polymer is derived from low-cost raw materials, i.e. Cl_2 , butadiene, and O_2 . The interesting combination of properties of the CD polymer combined with its potential moderate cost should lead to such uses as flame resistant plastics, fibers, films and coatings. The CD polymer crystallizes with a helical chain conformation which appears to persist in the melt and in solutions and which appears to influence the crystallization and glass transition behavior of CD polymer and copolymers.

The cationic polymerization of CD to highly stereoregular diisotactic polymer has unusual mechanistic aspects. A possible polymerization mechanism is proposed.

INTRODUCTION

General

This paper describes the preparation and properties of a new family of polymers from the ring opening polymerization of the *cis* and *trans* isomers of 1,4-dichloro-2,3-epoxybutane (eqn 1)



These polymers were first described by the author in a U.S. patent.¹ Subsequently a detailed presentation of this new family of polymers was given at a Symposium in honor of Professor Carl S. Marvel's eightieth birthday.²

These new polymers may be thought of as poly(ethylene oxide) with a chloromethyl group on each carbon or, alternatively, polyepichlorohydrin with an added CH_2Cl group on the unsubstituted CH_2 carbon. The added chloromethyl group has an unexpected, large influence on both the synthesis and the properties of these polyethers.

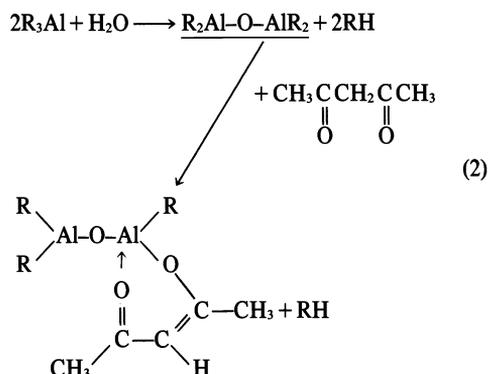
The preparation of these polymers has some unusual stereochemical and mechanistic aspects. In addition, the polymers have an interesting combination of properties of possible value in the plastic, film and fiber areas; most important is their flame resistance due to their 50% chlorine content and their high thermal stability compared with other commercial chlorine-containing polymers such as poly(vinyl chloride). Also, these polymers are based on inherently low cost raw materials—chlorine, butadiene, and oxygen. This combination of circumstances will, I believe, lead to their ultimate commercial development.

Early polyepoxide studies

Low molecular weight polymers of epoxides are readily prepared with ordinary acid and base catalysts and have

been known for many years. However, it has only been in the last 15–20 yr that it has been possible to make high polymers of a wide variety of epoxides. This recent progress has resulted from the discovery of new catalyst systems. My own participation in this area came about initially from the discovery of some unique and widely effective organometallic catalysts.^{3,4} Some of these new catalyst systems are the reaction products of aluminum, zinc, and magnesium organometallics with water (Table 1). The ratio of components used generally gives a very effective catalyst. However, the ratio of these ingredients can be varied over a wide range, and the best composition will depend on the conditions, the epoxide, and the type of products desired; but, in general, the preformed catalyst retains organometal bonds.

Although all of these new organometallic catalysts are quite effective, they do vary a great deal in their behavior and nature. In our work we have found the alkylaluminum-based catalysts to be especially useful. The two types of alkylaluminum catalysts shown (Table 1) vary considerably in their performance. Both of these alkylaluminum-water catalysts are stable and soluble in organic media. These properties are to be contrasted with those of the organozinc and organomagnesium catalysts which usually are not storage stable and usually are heterogeneous. The fundamental reactions involved and basic structures formed in making these alkylaluminum catalysts are indicated in eqn (2).



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Table 1. Organometallic catalyst systems

$R_3Al-0.5 H_2O$
$R_3Al-0.5 H_2O-0.5$ acetylacetone
$R_2Zn-1.0 H_2O$
$R_2Mg-1.0 H_2O$

With the alkylaluminum- H_2O catalyst, water reacts at both of its active hydrogens to form a bis(dialkylaluminum) oxide species and liberates a hydrocarbon. Then, in the formation of the acetylacetone-modified catalyst, to be called the chelate catalyst, acetylacetone reacts further with the underlined organoaluminum intermediate to liberate another mole of hydrocarbon and form what we believe to be the chelated type of species shown. The general nature of the initial alkylaluminum-water reaction has been determined by measuring the residual organoaluminum groups in the final catalysts and also by using tritiated water and showing that the final catalysts did not retain radioactivity. The exact nature of the catalytic species is unknown, because it is difficult to determine during a polymerization. However, it is probably built of the fundamental structural units by their association with themselves, by their coordination with epoxide or other donor solvents, and by the reaction of the organoaluminum groups with the epoxide. The presence of the metal-oxygen-metal grouping in the catalyst is particularly noteworthy. The zinc and magnesium catalysts also contain these groupings, as our work as well as the work of Furukawa⁵ and others has shown. We early recognized the importance of having two or more organometal groups joined together by another atom such as oxygen to obtain a good epoxide polymerization catalyst.

These new catalysts enabled us to synthesize many new high molecular weight polyepoxides, both homopolymers and copolymers (Table 2).^{3,4} A few of the more interesting monosubstituted epoxides that were polymerized to both amorphous and crystalline homopolymers are illustrated. Some interesting amorphous copolymers are also shown. The epichlorohydrin amorphous homopolymer and its amorphous copolymer with ethylene oxide are especially

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interesting as oil-resistant rubbers.^{6,7} These rubbers are being made in multi-million-pound quantities by Hercules Incorporated under the registered trademark, HERCLOR and by the B. F. Goodrich Chemical Co. under the trademark HYDRIN.† The properties and advantages of these rubbers make an interesting story.^{8,9} Briefly, the copolymer is especially unusual—having a unique combination of properties. It has the oil resistance of the nitrile rubbers combined with good rubber properties and environmental resistance of neoprene.

The amorphous copolymers of propylene oxide with small amounts of an unsaturated epoxide, such as allyl glycidyl ether, are sulfur vulcanizable rubbers with excellent low temperature properties, excellent dynamic properties similar to natural rubber, good ozone resistance, and good heat aging resistance. This polyether elastomer is available commercially from Hercules Incorporated under the registered trademark PAREL and has been found to be especially useful as a specialty elastomer in applications such as automotive engine mounts. The development and properties of this interesting elastomer has been described recently.^{10,11}

Butadiene monoxide is interesting because it can be polymerized to both an amorphous rubber and a low melting crystalline polymer without affecting its vinyl group. Styrene oxide has given both amorphous and crystalline, isotactic high polymers which have physical properties and behavior very much like amorphous and crystalline, isotactic polystyrene (Table 2).

2,3-Epoxybutane studies

My studies of the polymerization of symmetrical disubstituted epoxides as exemplified by the *cis*- and *trans*-2,3-epoxybutanes proved to be particularly instructive (Table 3),⁴ and, of course, are especially pertinent to this paper.

Catalyst behavior (Table 3). The alkylaluminum-water catalyst polymerized both isomers essentially instantaneously at dry ice temperature. This rapid polymerization is to be contrasted with the fairly slow polymerization of propylene oxide with this catalyst, even at room temperature. With this catalyst, the *cis*-oxide gives only an amorphous high

Table 2. High polymers from monosubstituted epoxides

	Amorphous	Crystalline (m.p., °C)
$\begin{array}{c} -CH_2-CH-O- \\ \\ CH_2Cl \end{array}$		120
$\begin{array}{c} -CH_2-CH-O-CH_2-CH_2-O- \\ \\ CH_2Cl \end{array}$	Solvent-resistant rubbers	—
$\begin{array}{c} -CH_2-CH-O-CH_2-CH-O- \\ \qquad \qquad \\ CH_3 \qquad \qquad CH_2 \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad O-CH_2-CH=CH_2 \end{array}$	S-Vulcanizable rubber	—
$\begin{array}{c} -CH_2-CH-O- \\ \\ CH=CH_2 \\ -CH_2-CH-O- \\ \\ C_6H_5 \end{array}$	Rubber	74
	Like polystyrene	149

Table 3. High polymers from *cis* and *trans*-2,3 epoxybutane

	Catalyst	Temp. (°C)	Polymerization rate	Polymer
<i>cis</i>	R ₃ Al-H ₂ O	-78	Instantaneous	Amorphous rubber
<i>trans</i>	R ₃ Al-H ₂ O	-78	Instantaneous	Crystalline polymer m.p., 100°C
<i>cis</i>	R ₃ Al-H ₂ O-Acetylacetone	65	Slow	Crystalline polymer m.p., 162°C
<i>trans</i>	R ₃ Al-H ₂ O-Acetylacetone	65	Very little	

molecular weight rubber; the *trans*-oxide gives only a crystalline high molecular weight plastic with a melting point of 100°C. On the other hand, the alkyaluminum-water-acetylacetone catalyst polymerizes the *cis*-oxide slowly at 65°C, and, under these conditions, the product is largely a crystalline polymer with a melting point of 162°C. This crystalline polymer from the *cis*-oxide is totally different from the crystalline polymer obtained from the *trans*-oxide with the alkyaluminum-water catalyst, having a completely different X-ray pattern, different solubility properties, and a higher melting point. This chelate-modified catalyst, however, caused very little polymerization of the *trans*-oxide at 65°C. In general, these results indicate that the polymerization site in the acetylacetone-modified catalyst is much more hindered than that of the unmodified catalyst, since the modified catalyst facilitates the formation of crystalline polymer from the less hindered *cis*-oxide and does not polymerize the more hindered *trans*-oxide very well. Based on this work, we classified the chelate catalyst, the alkyaluminum-H₂O-acetylacetone catalyst, as a coordination catalyst.

The chelate catalyst also polymerizes oxetanes such as trimethylene oxide by a coordination route. This result was first reported by the author in the patent literature¹² and further details were presented in 1974.¹⁰ In copolymerizations of trimethylene oxide with epoxides with the chelate catalyst, evidence was given that this catalyst contains sites varying in copolymerization ability and, thus, presumably varying in steric hindrance.¹⁰

The unmodified alkyaluminum-H₂O catalyst, on the other hand, is apparently behaving as a cationic catalyst with the *cis*- and *trans*-oxide, based on the very facile, low temperature polymerization observed. With epoxides which do not readily polymerize with cationic catalysts but do polymerize readily with coordination catalysts, this catalyst can also behave as a coordination catalyst.

However, with the 2,3-epoxybutanes and the 1,4-dichloro-2,3-epoxybutanes, this catalyst appears to behave solely in a cationic manner.

Mechanism aspects. Our ability to polymerize the 2,3-epoxybutanes with different catalysts to different products offered us a unique opportunity to learn more about the mechanism of epoxide polymerization. Since both the main chain carbon atoms in the monomer unit of the polymer are asymmetric, the stereochemistry of the monomer unit would tell us whether the ring-opening carbon atom retained or inverted configuration during polymerization. Of course, the crystalline polymers initially appeared most attractive since we would expect these to have regular steric sequences.

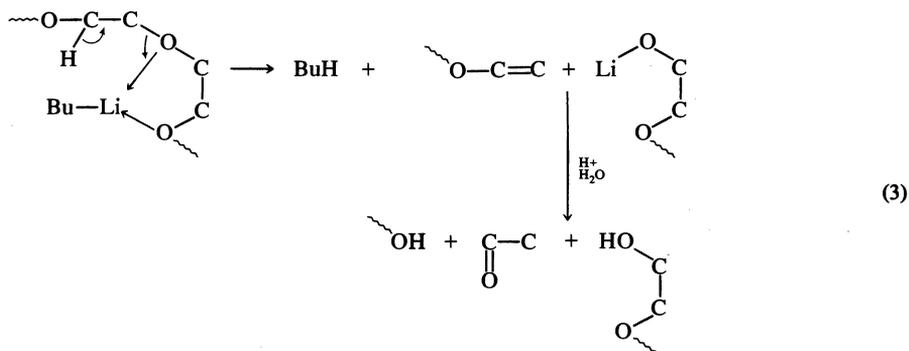
Table 4 shows the possible stereochemical configuration of dimer units from these crystalline polymers and indicates the polymerization mechanisms by which each could be produced. Fortunately, there are only four regular stereochemical structures possible, two diisotactic and two disyndiotactic. The 2,3-epoxybutane polymers are ideal for studying stereochemistry since all the carbon atoms in the chain are chemically equivalent, thereby restricting the number of isomers to the four indicated. Of the four possible stereo sequences, only one, the racemic diisotactic sequence, can exist in an optically active form. The other three structures are all meso. Any particular structure could theoretically be obtained from either the *cis*- or *trans*-oxide by using an appropriate mechanism. There are two features associated with each oxide that influence the final steric structure of the crystalline polymer. First: each isomer, *cis* or *trans*, can polymerize with either inversion or retention of configuration of the ring-opening carbon atom. Secondly: the *cis*-oxide is a meso-isomer and can polymerize either head-to-tail or head-to-head. On the other hand, the *trans*-oxide is a racemic mixture and can polymerize by either an isomer selection process or by an

Table 4. Stereochemistry and polymerization mechanism of the 2,3-epoxy butane polymers

Carbon atom configurations	Polymerization mechanism	
	<i>cis</i> -oxide	<i>trans</i> -oxide
Meso-diisotactic	-RS-RS-	Inversion, selection
Racemic diisotactic	-RR-RR- -SS-SS-	Retention, selection
Meso ₁ -disyndiotactic	-RS-SR-	Inversion, alternation
Meso ₂ -disyndiotactic	-RR-SS-	Retention, alternation

isomer alteration process, but there is no possibility of head-to-tail or head-to-head polymerization, since each enantiomorph has an identical head and tail. Whether one has retention or inversion of the configuration of the ring-opening carbon atom is readily determined by examining the stereochemistry of a monomer unit in the polymer chain. On the other hand, whether a head-to-tail or head-to-head polymerization is involved with the *cis*-oxide, or an isomer selection process or alternation process is involved with the *trans*-oxide, can only be determined by examining the stereochemistry of a dimer unit.

The stereochemistry of the *cis*- and *trans*-2,3-epoxybutane polymers was elucidated by devising a facile, unique, general method of cleaving polyethers (eqn 3).^{4,13}



This method involves cleaving the polyethers with a Group IA organometallic, such as butyl lithium, in an organic solvent, such as benzene, at room temperature or at elevated temperature. In this reaction, a β -elimination occurs by attack of the butyl anion of butyl lithium on a hydrogen beta to the ether atom to yield a lithium alkoxide chain end and a double-bond chain end. The lithium alkoxide chain end is, of course, readily converted with acid to the hydroxyl group. Further random reaction will ultimately yield some fraction of the product with hydroxyl groups on each end of the cleaved fragment. In this way we were able to obtain diols containing monomer, dimer, trimer and higher polymer units. From the monomer and dimer diols we unequivocally established the stereochemistry of the *cis*- and *trans*-2,3-epoxybutane polymers (Table 5).⁴

Thus the *cis*-oxide crystalline polymer prepared with

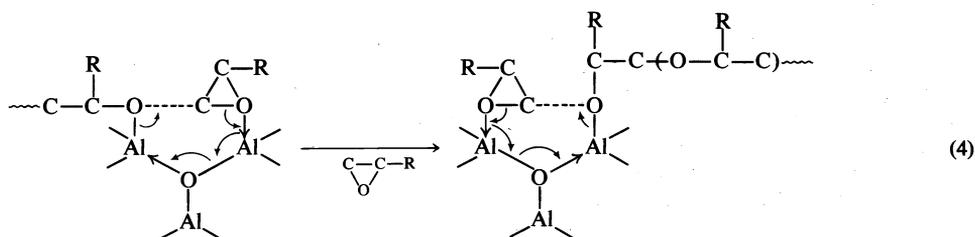
the chelate coordination catalyst was the racemic diisotactic polymer, the *trans*-oxide crystalline polymer prepared with the alkylaluminum-H₂O cationic catalyst was meso-diisotactic, and, surprisingly, the amorphous *cis*-oxide polymer, also prepared with the alkylaluminum-H₂O cationic catalyst, or indeed any cationic catalyst, was largely (about 80%) meso-disyndiotactic.

A number of important mechanistic conclusions come from these results. First, the observed products, whether prepared by a coordination or cationic mechanism, were all formed by inversion of configuration of the ring-opening carbon atom. My subsequent work as well as that of Price¹⁴ indicated that all polymerizations of mono- as well as di-substituted epoxides with all known anionic, cationic, or coordination catalysts occur with complete inversion of configuration of the ring-opening carbon

atom. This result appears to be a very important first principle of epoxide polymerization. Let us consider now, briefly, our proposed mechanism for these stereoregular polymerizations. First, as shown in eqn 4, the coordination polymerization of a monosubstituted epoxide must involve two metal atoms in order to make possible a rearward attack on the epoxide. A similar coordination mechanism also applies for a disubstituted epoxide such as the *cis*-oxide. It is now clear why we obtain active epoxide catalysts by reacting organometallics with difunctional reagents such as H₂O. Two metal atoms are required in the propagation step. Thus, the epoxide coordinates with one aluminum atom prior to its attack by the growing chain on the other aluminum atom. In this mechanism the coordination bonds in the catalyst structure are needed to move the growing polymer chain from one metal to an

Table 5. Stereochemistry of 2,3-epoxybutane polymers

	Polymer	Stereochemistry of dimer unit
<p style="text-align: center;"><i>trans</i></p>	Cationic →	Cryst. RS-RS
	coordination →	Trace, cryst. RS-RS
		} Meso-diisotactic
<p style="text-align: center;"><i>cis</i></p>	Cationic →	Amorph. RR-SS disyndiotactic
	coordination →	Cryst. RR-RR } SS-SS }
		} racemic diisotactic



adjacent one without altering the valence of the metal. The formation of the racemic diisotactic polymer from the *cis* isomer required that this isomer be presented to a particular type of chain end in the same way in each successive propagation step, i.e. in a head-tail propagation, where a chain end with an RR monomer unit attacks only the S carbon of the monomer. There is no chemical difference in whether the R or S carbon is attacked but just purely stereo differences. Thus, the propagation site must have the precise stereochemistry to make this occur. There are, of course, enantiomorphous sites which will grow either all R or all S chains. The steric requirements of these sites must be quite severe, so that it is not unreasonable that the more sterically hindered *trans*-oxide would not polymerize well by this coordination route.

The cationic polymerization of the *cis*- and *trans*-oxides involves a very different mechanism. Usually, we think of carbenium ions in cationic polymerization. However, with the very basic oxygen atom of the epoxide, one would expect the oxonium ion to be the predominant, if not indeed the sole, reactive species (Fig. 1). Thus, the cationic mechanism proposed involves growth of the oxonium ion as shown. This cationic mechanism is similar to that first suggested by Meerwein for the polymerization of tetrahydrofuran with Friedel-Crafts catalysts.¹⁵ This mechanism involves a rearward, nucleophilic attack of an epoxide molecule, B, on either equivalent carbon atom of the epoxide molecule, A, involved in the propagating oxonium ion.

With racemic monomer, A and B must be the same optical isomer to obtain the stereoregular diisotactic polymer. Molecular models of the transition state, based on the likely assumption that the plane of epoxide ring B is perpendicular to the plane of the epoxide ring A, indicate that steric hindrance inherent in the monomer can bring about this selection process. Thus, the stereoregularity of this polymerization appears to be controlled by the monomer rather than by the catalyst structure which often controls the stereoregularity of many other polymerizations, particularly of epoxides, 1-olefins and vinyl ethers. This conclusion is supported by the fact that one can obtain only stereoregular polymer with a wide variety of cationic catalysts, including the Friedel-Crafts type such as BF_3 -etherate. An occasional failure of this

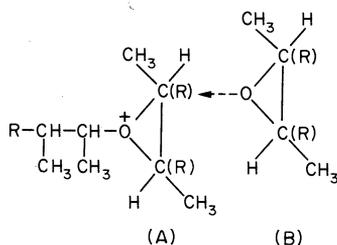


Fig. 1. Mechanism of polymerization of *trans*-2,3-epoxybutane.

isomer selection process would lead to a stereo-block structure with $-\text{RS}-\text{RS}-\text{RS}$ sequences followed by $-\text{SR}-\text{SR}-\text{SR}$ -sequences of carbon atoms. Such a stereo-block structure appears to occur in the crystalline polymer prepared from the racemic monomer since the polymer obtained from a pure enantiomorph has somewhat different solubility properties.¹⁶ Also our examination of dimer and trimer cleavage fractions from the racemic polymer confirms that it is a stereoblock polymer with rather short block lengths.⁴

A proposed propagation mechanism by which the *cis*-oxide gives disyndiotactic polymer is shown in Fig. 2. The mechanism is essentially the same as proposed for the cationic polymerization of the *trans*-oxide with a rearward attack by monomer on a growing oxonium ion, but differing greatly in the stereochemical details. Now, in this case, the carbon atoms in the oxonium ion are sterically different although still chemically equivalent. Since we have only one monomer, the meso *cis*-oxide, the stereochemistry of the chain unit formed is determined solely by whether it attacks the R or S carbon on the oxonium ion. If the S carbon of the oxonium ion, i.e. the carbon with the same configuration as the last unit in the polymer chain, is attacked, as shown, that carbon is inverted and the ring opened to form an RR unit, thus giving the required unit to propagate a disyndiotactic chain. In the process, the oxonium ion is regenerated. In the next propagation step the R carbon is attacked. Thus, as the chain propagates, the R and S carbons of the oxonium ion are alternately attacked.

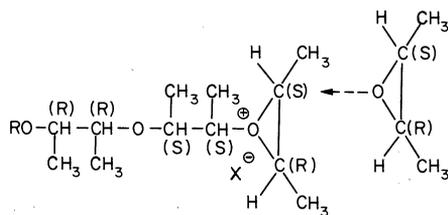


Fig. 2. Propagation mechanism for disyndiotactic poly (*cis*-2,3-epoxybutane).

How is this rather unusual result explained? If you look at the right side of the oxonium ion, particularly if you use models, it is quite clear that there is no steric factor involved at either site of attack that would cause it to attack one or the other carbon preferentially, and certainly nothing that would say it ought to alternate. Therefore, you have to look to the other side of the propagation step, that is, the chain end side. At first sight one might conclude that the counterion, X^- , was playing a role. However, this possibility was excluded since we examined a wide variety of cationic catalysts and found that the stereochemistry of the chain was independent of the nature of the counter-ion. Therefore, we were forced to conclude that the chain end dictates which carbon in

the oxonium ion is attacked, but how? Actually, if you make models of the chain end, as shown in Fig. 3, you find that when you have an *SS* configuration for the last monomer unit in the chain, a particularly favorable conformation for the chain end permits the β -methyl group of the last monomer unit of the chain to be very close to the *S* carbon in the oxonium ion. This leads to a steric facilitation of ring opening at that point. Of course, once you form the *RR* unit, then that will cause steric facilitation of the attack at the *R* carbon of the oxonium ion and thus give the required alternation. This is an example, then, of stereoregularity via chain end control rather than the more usual one of catalyst site control as we noted for the coordination catalyst.

and *trans*-1,4-dichloro-2-butenes are of potential low cost since they are formed by the addition of chlorine to butadiene along with 3,4-dichloro-1-butene as shown in Fig. 4. These dichlorobutenes are commercial intermediates in the synthesis of nylon 6,6¹⁷ and, more recently neoprene.¹⁸ The mixed dichlorobutenes are available commercially from Petro-Tex. The various isomers can be separated by distillation. All three isomers are in equilibrium with one another so that it is theoretically possible to convert the entire dichlorobutene mixture into any one isomer.¹⁸

In our studies we prepared the *cis*- and *trans*-1,4-dichloro-2,3-epoxybutanes by the peracetic acid epoxidation of the respective dichloro-2-butenes (Fig. 4). The

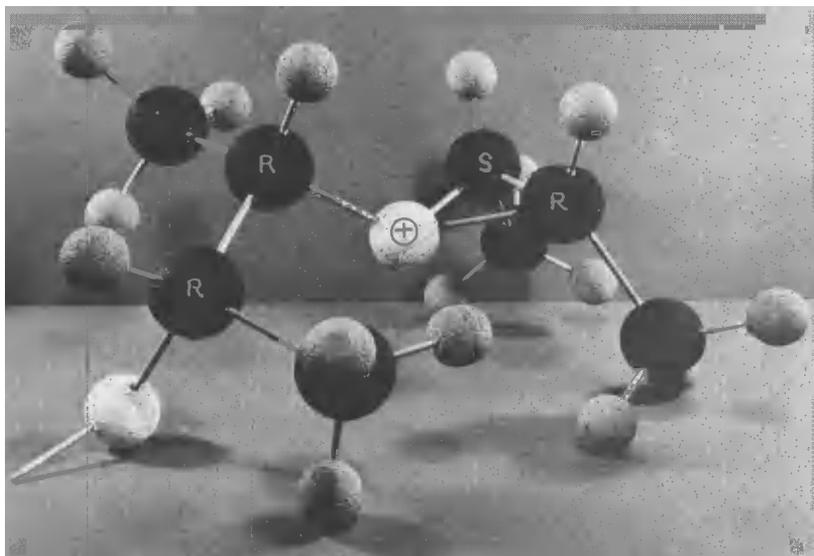


Fig. 3. Preferred conformation of growing oxonium ions in the cationic polymerization of *cis*-2,3-epoxybutane.²⁵

RESULTS AND DISCUSSION

General

Let us consider now our work with the *cis*- and *trans*-1,4-dichloro-2,3-epoxybutanes, i.e. the symmetrical dichloro substituted analogues of the 2,3-epoxybutanes. These monomers were studied in detail not only because of our interesting results with the *cis*- and *trans*-2,3-epoxybutanes, but also because they are chloromethyl substituted derivatives of polyepichlorohydrin, which had interesting enough properties to become a product of commercial importance. Also, the starting olefins, the *cis*-

peracetic acid epoxidation has been described by Phillips and Starcher in a U.S. patent assigned to Carbide.¹⁹ *cis*-Olefin gives *cis*-oxide (CD) and *trans*-olefin, *trans*-oxide (TD). Since peracetic acid can be made by the air oxidation of acetaldehyde, the overall reaction of dichloro-2-butenes to give epoxide and acetic acid is an indirect air oxidation of these olefins to epoxide.

Polymerization studies

Homopolymerization. Based on our prior studies on the 2,3-epoxybutanes, we felt that the *cis* isomer would polymerize with our chelate coordination catalyst to give the most interesting and the highest melting stereoregular polymer, i.e. a racemic diisotactic polymer. However, we soon found that it did not polymerize well with our chelate catalyst. This behavior is best typified by the experiment in Table 6 which shows the copolymerization of CD with ethylene oxide by use of our chelate catalyst. Thus, using a 90-10 CD-EO charge we obtained 3.4% conversion to a copolymer containing only 3.0% CD. Based on ideal copolymerization, EO enters the copolymer about four hundred times more readily than does CD. This result is to be compared with a similar copolymerization of epichlorohydrin in which the EO enters the copolymer about 7 times as readily as does the ECH. Thus, CD is about sixty times less reactive in copolymerization with EO than is ECH. There are two possible explanations for this large

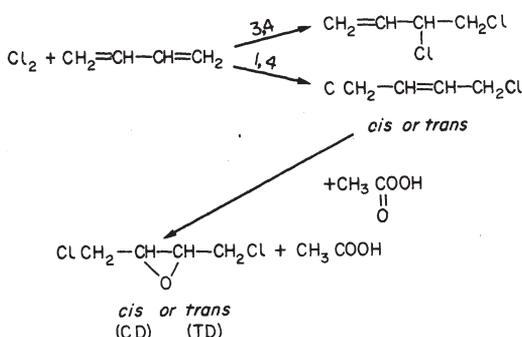


Fig. 4. Preparation of *cis*- and *trans*-1,4-dichloro-2,3-epoxybutanes.

Table 6. Coordination copolymerization of CD with ethylene oxide

Polymerization	
CD, g	9
EO, g	1
Toluene, ml	48
Chelate catalyst, mmol Al 4 hr, 65°C	4
Product	
3.4% conv., η_{inh} 3.5	
2.6% CD (Based on % Cl)	

Based on ideal copolymerization, EO enters copolymer ca. 400× as readily as CD.

difference. First, the much larger CD molecule may not be able to fit into coordination sites which are large enough for EO and mono-substituted epoxides as ECH. As noted earlier, small steric differences in epoxides affect their coordination polymerization. Also, the oxygen atom of CD must be much less basic because of the two electron-withdrawing chloromethyl groups attached to the oxirane ring. Therefore, CD should be less strongly coordinated with a coordination site on a metal than EO and ECH and thus less likely to participate in a coordination copolymerization. Probably, both factors apply.

The cationic polymerization of both CD and TD was then studied in the best system found previously for the *cis*- and *trans*-2,3-epoxybutanes, i.e. CH₂Cl₂ diluent with *i*Bu₃Al-0.7 H₂O catalyst at -78°C (Table 7). Both monomers polymerized quite readily in this system—both giving high conversions and nearly quantitative yields of high molecular weight, CH₂Cl₂-insoluble, crystalline polymer. X-ray clearly showed that two different crystalline polymers, I, and II, with different X-ray patterns, were obtained. The CD polymer was much more interesting since it was higher melting (235°C) compared with the TD polymer (145°C), was of higher molecular weight, and was less soluble, being insoluble in all common solvents at room temperature, whereas the TD polymer was soluble in THF at room temperature. Both crystalline polymers were soluble in dimethyl formamide at 50°C and these conditions were used for measuring inherent viscosity (heating to a higher temperature to dissolve, if required). The CD polymer is about 35%

crystalline, based on heat of fusion (ΔH_F) data (Table 7) and the estimation that 100% crystalline CD polymer has a ΔH_F of 31 cal/g, based on Ke's extrapolation method.²¹

Both CD and TD also polymerized with an ordinary Lewis acid type cationic catalyst, BF₃, to similar but much lower molecular weight polymers. Also the polymers from CD with BF₃ catalyst were clearly less stereoregular, based on the decreased melting points, the increased amount of CH₂Cl₂-soluble polymer, and the lower heats of fusion.

Since CD gives the most interesting and the highest molecular weight polymer, and polymerizes more readily than TD, the effect of the important variables in CD polymerization was studied. Some of the requirements of this polymerization result from the fact that CD is a crystalline solid at lower temperatures (melting point—11°C) and is insoluble in aliphatic hydrocarbons such as *n*-heptane. In our experience, CD does not polymerize when it is completely in the solid state. Thus, one must use a diluent which not only has a low freezing point, but also one which is fairly good solvent for CD, e.g. CH₂Cl₂ and CH₃CHCl₂. Mixtures of these good solvents with nonsolvents such as aliphatic hydrocarbons can be used.

Monomer concentration is critical in CD polymerization and must, in general, be at least 5%, or preferably higher, e.g. in the 10–20% range. Higher monomer concentrations generally give higher rates, conversions, and catalyst efficiencies but can also lead to monomer crystallization from solution, depending on the temperature and solvent. Very low monomer concentrations, 2% or less, give very poor polymerization.

Ether is a potent inhibitor and/or retarder of CD polymerization. Ether is no doubt too strong a base compared with CD, so that it complexes with the Lewis acid sites in the catalyst and prevents them from functioning. This result is also in accord with the ineffectiveness of BF₃-etherate as a catalyst.

Polymerization temperature is a very important variable in CD polymerization (Table 8). As with many cationic polymerizations, molecular weight is inversely proportional to temperature. However, more important, polymer stereoregularity is dependent on temperature and decreases rapidly with increasing temperature. The polymer made at -20°C is so low in crystallinity that it does not crystallize from the melt and is completely soluble in CH₂Cl₂ instead of being completely insoluble as is usual for the highly crystalline polymer; incidentally a lower temperature than -78°C does not increase M.P.s

Table 7. Polymerization of CD and TD with cationic catalysts at -78°C

Monomer	Hr	CH ₂ Cl ₂ , 10% (W/V) monomer		X-ray Cryst	m.p. °C	ΔH_F † (cal/g)	% Conv
		CH ₂ Cl ₂ -insol.	CH ₂ Cl ₂ -sol.				
iBu ₃ Al-0.7 H ₂ O catalyst (4 mmol Al/10 g monomer)							
CD	3	88	1.8	I	235	10.8	2
TD	21	66	0.58	II	145	8.9	3
BF ₃ (2 mmol/10 g monomer)							
CD	20	50	0.22	I	229	8.1	32§
TD	20	49	0.12	II	149	12.5	6

† η_{inh} at 0.1%, dimethyl formamide, 50°C.

‡ ΔH_F = heat of fusion from DSC. The estimated ΔH_F of 100% crystalline CD polymer is 31.0 cal/g, based on Ke's extrapolation method.²¹

§ η_{inh} = 0.05, Form I by X-ray, m.p. = 192°C, ΔH_F = 2.4 cal/g.

Table 8. Effect of temperature on CD polymerization

°C	(CH ₂ CHCl ₂ , <i>i</i> -Bu ₃ Al-0.7 H ₂ O catalyst)			
	η_{inh}	$M_w \times 10^{-4}$	m.p.	% Crystallinity
-78	1.4	56	235	30
-50	0.6	13.5	210	15
-20	0.23	2.7	180	9
0	0.17	1.6	—	0

†Based on $[\eta] = 5.44 \times 10^{-4} M^{0.594}$ from Forsman and Poddar.²³

or stereoregularity. Actually, we believe that the polymer made at -78°C is highly stereoregular, based on the results of the LiAlH₄ reduction to be discussed later.

TD polymerizes in much the same way as CD but, in general, less readily. Rates, molecular weights, and catalyst efficiencies are lower at equal monomer concentration. TD melts at 20°C, i.e. 31°C higher than CD, and is less soluble than CD at -78°C, so that the highest usable monomer concentration of TD is lower than CD under the same conditions. Similar diluent requirements and a similar dependence of molecular weight on temperature are also experienced with TD. However, stereoregularity of the polymer is independent of temperature from -78 to -30°C as we previously observed for *trans*-2,3-epoxybutane. Higher temperatures do affect the stereoregularity of the *trans* polymer.

Copolymerization. The copolymerization of CD with TD is surprisingly good, being very close to ideal (Table 9) in solution copolymerizations in CH₂Cl₂ over a wide range of temperatures (-78 to -20°C) and monomer composition. This result was very unexpected in view of the greater rate of polymerization of CD compared to TD. Also, our prior studies on the copolymerization of the *CIS* and *trans*-2,3-epoxybutanes indicated that the *cis* isomer entered the copolymer at twice the rate of the *trans* isomer.

In order to introduce a factor which may play a role in this anomalous behavior, we will digress somewhat and tell you about some aspects of the solid state and solution properties of the crystalline CD and TD homopolymers. Dr. R. J. Samuels of our laboratory and Dr. G. Wildman, formerly of our laboratory, have determined by X-ray structure analysis that TD homopolymer crystallizes with a planar *trans* zig-zag chain conformation, similar to that observed with most crystalline polyethers.²² However, CD homopolymer crystallizes with a helical chain conformation containing four monomer units per turn of the helix. Also solution studies on these polymers by Dr. W. Forsman and Dr. S. Poddar of the University of Pennsylvania suggest that the helical conformation of the *cis* homopolymer chain can persist in solution under some

Table 9. Copolymerization of CD with TD compared to *cis*- and *trans*-2,3-epoxybutanes

Monomer charge % <i>cis</i>	(iBu ₃ Al-0.7 H ₂ O Catalyst, -78°C)		r_{cis}
	Diluent		
CD and TD			
20	CH ₂ Cl ₂		1.3†
55	CH ₂ Cl ₂		1.1†
80	CH ₂ Cl ₂		1.0†
2,3-Epoxybutanes‡			
50	<i>n</i> -Heptane		2.0

†Similar data at temperatures up to -20°C.

‡iBu₃Al-0.5 H₂O catalyst.⁴

conditions—particularly at low temperatures.²³ Thus, the tendency of sequences of *cis* isomer in the polymer chain to assume a helical conformation may, in some undefined manner, such as blocking the chain end, impede the addition of *cis* isomer to the growing oxonium ion and thereby give the more favorable copolymerization observed. Such a factor could also play a role in the stereochemistry of the polymer formed; an alternative mode of chain end control to be compared with the more specific one which will be suggested later.

Another possibility is that a diluent such as CH₂Cl₂ may solvate the CD and TD monomers via hydrogen bonding between the somewhat acidic hydrogens on the CH₂Cl₂ and the somewhat basic oxirane oxygen. Such a complex should be stronger in the case of the less hindered *cis* isomer and thus impede the *cis* copolymerization. However, the apparent faster homopolymerization of CD compared with TD is evidence against this hypothesis. Also, recent preliminary work on the copolymerization of the 2,3-epoxybutanes in CH₂Cl₂ confirms the much more favorable copolymerization behavior of the *cis* isomer found in *n*-heptane. Further work is needed to elucidate the excellent copolymerization behavior of CD and TD.

Stereochemistry of polymers

The stereochemistry of the crystalline CD and TD homopolymers was determined by reducing the polymers with LiAlH₄ to the corresponding 2,3-epoxybutane polymers (Table 10). This general method was previously used by Steller²⁴ to reduce polyepichlorohydrin to poly(propylene oxide) and thereby obtain reliable information on the stereochemistry and the head-to-tail nature of polyepichlorohydrin. The reduced CD polymer was obtained in two highly crystalline fractions, melting at 132°C, and 138°C, which had the same X-ray pattern as the racemic diisotactic 2,3-epoxybutane polymer. The reduced TD polymer melted at 74°C and had the same X-ray pattern as our meso-diisotactic 2,3-epoxybutane polymer. The reduced CD and TD polymers had inherent viscosities of 1.8 and 1.1 respectively, indicating that little or no degradation occurred during the reduction.

Thus, the stereochemistry of the TD polymer is as expected, but the CD polymer stereochemistry is exactly opposite; the meso-disyndiotactic polymer was expected since it was obtained under these polymerization conditions with *cis*-2,3-epoxybutane. Also the good melt crystallizability of the reduced CD polymers indicates the CD polymer is highly stereoregular since our prior preparation of racemic diisotactic poly(*cis*-2,3-epoxybutane) often crystallized poorly from the melt.⁴

Mechanism of polymerization

The unusual, racemic diisotactic stereochemistry of the CD crystalline polymer requires a modification of the propagation mechanism proposed for the cationic polymerization of *cis*-2,3-epoxybutane (Fig. 2). CD monomer must attack the carbon in the oxonium ion with an opposite configuration to that of the chain end; for example, in Fig. 2, the *R* carbon must be attacked to form an *SS* unit which has the same configuration as the chain end. Then the propagation is continued by attack on the *R* carbon of each newly formed oxonium ion. Of course, you will have both *R* and *S* chains growing. How do we explain this? Actually, this same phenomenon was previously reported in our studies of the polymerization of *cis*-2-butene episulfide.²⁵ With a cationic catalyst this *cis*-episulfide gave the same result as we obtained with CD, i.e. formation of the racemic

Table 10. Stereochemistry of crystalline polymers from CD and TD†

	Reduced CD polymer	Reduced TD polymer
$\begin{array}{c} \text{CH}_2\text{Cl} \quad \text{CH}_2\text{Cl} \\ \quad \\ -\text{O}-\text{CH}-\text{CH}-\text{O}-\text{CH}-\text{CH}- \\ \quad \\ \text{CH}_2\text{Cl} \quad \text{CH}_2\text{Cl} \end{array} \xrightarrow{\text{LiAlH}_4} \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ -\text{O}-\text{CH}-\text{CH}-\text{O}-\text{CH}-\text{CH}- \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$		
% yield	48 48‡	92
η_{inh} (0.1, CHCl_3 , 25°C)	1.8	1.1
% CD (or TD) left‡	2.8 3.8	6.5
m.p., °C	132§ 138¶	74
ΔH_f , cal./g	11.4 19.2	7.9
X-ray pattern	Racemic-diisotactic	Meso-diisotactic
Stereochemistry	-RR-RR- -SS-SS-	-RS-RS-

†Using the general method of Steller,²⁴ 1.00 g polymer (η_{inh} : CD, 0.76 and TD, 0.58) mixed under nitrogen with 25 ml of dry tetrahydrofuran (THF) and 35.5 ml of 1M LiAlH_4 in THF (2.6 moles LiAlH_4 per Cl). Agitated 8 hr at 50°C and then 70 hr at 65°C. Isolated product by slowly adding 70 ml of THF containing 5% H_2O , filtering, washing twice with THF and then drying the combined THF extracts.

‡A second fraction was obtained in (a) by treating the THF-insol with 200 mol of 3% (aq) HCl for 3 days, collecting the insol, washing neutral with H_2O and drying.

§Based on % Cl analysis.

¶Crystallized readily from melt.

diisotactic polymer. Our previous explanation for this finding (Fig. 5) postulated that the sulfur atom in the last chain unit coordinates with the counterion and brings the chain away from the carbon of the oxonium ion of the same configuration as the chain end, thus eliminating the steric facilitation. Presumably this causes a steric interaction with the carbon of opposite configuration in the oxonium ion, and thus a steric facilitation at that site would cause ring opening there. We might ask why oxygen doesn't do the same thing and even better? Oxygen normally coordinates better with aluminum than does sulfur. However, in this case the oxygen is in a polymer chain and is flanked by a methyl-substituted carbon on each side and also the carbon-oxygen bond distance is shorter than carbon-sulfur. Therefore, we have concluded that sulfur would operate better in this mechanism than oxygen. Sulfur also forms bonds at greater distance, which is another favorable factor for sulfur.

Actually, on further reflection, coordination of the last sulfur atom in the chain with the negative counterion may not be the most favorable possibility to explain our *cis* episulfide results. Instead, I now suggest that the last sulfur atom in the chain would more reasonably coordinate with the positive sulfonium ion as shown in Fig. 5. This suggestion does involve a four membered ring but this does not appear to be an unreasonable possibility because of the large size of the sulfur atom and the availability of *d* orbitals for bonding in sulfur. Also, coordination of the electronegative sulfur with a positive

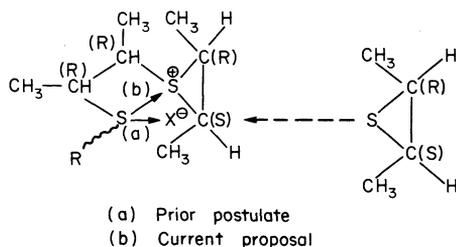


Fig. 5. Mechanism of cationic polymerization of *cis*-episulfide to diisotactic polymer.

ion is more reasonable than coordination with a negative ion which is probably already coordinatively saturated. The counterion effect previously observed can still be incorporated in this mechanism by postulating a variation in the tightness and closeness of binding of the negative counterion, X^- , to the positive sulfonium ion, depending on the nature of the X^- . Oxygen would probably be even less likely to work via this mechanism because of the small size of the oxygen atom and its lack of *d* orbitals.

In accord with the *cis*-episulfide proposal (Fig. 5b), I now propose that the cationic polymerization of CD monomer involves a similar type of mechanism except, in this case, the chlorine on the β chloromethyl groups interacts with the positive oxonium ion in a five-membered ring (Fig. 6). This postulate is reasonable since the electronegative chlorine is known to associate with electrophilic centers.²⁶

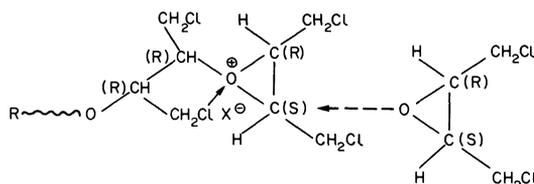


Fig. 6. Mechanism of cationic polymerization of *cis*-1,4-dichloro-2,3-eposubutane to diisotactic polymer.

Polymer properties

Thermal stability. The thermal stability of CD- and TD-based polymers is of considerable interest as well as of possible practical importance. The commercial chlorine-containing polymers such as poly(vinyl chloride) and poly(vinylidene chloride) are very deficient in heat resistance so that it is difficult to melt-fabricate them. The TGA curve for CD homopolymer (Fig. 7) is typical of this entire family of CD and TD homopolymers and copolymers. It shows that appreciable decomposition does not occur until 300°C. This TGA curve is very similar to what one would obtain with other related polyethers such as polyepichlorohydrin, poly(propylene oxide), and the

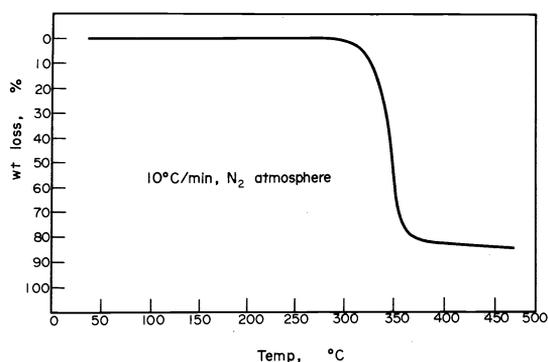


Fig. 7. TGA data on CD homopolymer.

2,3-epoxybutane polymers. The appreciable (18%), stable residue at 400°C is unusual. Typically, the non-halogen polyethers leave little or no residue, whereas polyepichlorohydrin leaves much less (*ca.* 10%). The stable residue has not been studied, but presumably results from crosslinking and/or aromatization reactions after HCl liberation leads to double bonds.

As a result of the good heat stability, these polymers can be melt-processed at temperatures up to 270°C without any problems. Thus, the thermal stability is about 100°C higher than that of poly(vinyl chloride) or poly(vinylidene chloride). This result also means that the high melting CD homopolymer can be melt processed and full advantage taken of its high melting point. Why are these polymers more heat stable than poly(vinyl chloride) since they both can split out HCl? Presumably this is due in part to the chlorine in our polymers being primary rather than the less stable secondary type as with poly(vinyl chloride).²⁷ Also, some of the weak links which are reported to facilitate the decomposition of poly(vinyl chloride) such as tertiary chlorine, and especially allylic chlorine, should not occur in our polymers.²⁸

Glass transition (Fig. 8). The glass transition temperature, T_g , of CD homopolymer is 95°C and is much higher than the T_g of TD homopolymer (55°C). This result is no doubt due to the previously noted helical conformation of CD homopolymer in the solid state. The helical chain conformation should be more rigid and give a higher T_g than the *trans* zig-zag conformation of the TD homopolymer.

The effect of copolymer composition on T_g is instructive (Fig. 8). Since the comonomer units are nearly identical, one would expect the linear, dotted theoretical

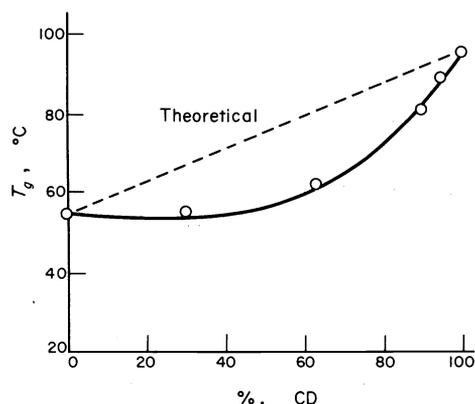


Fig. 8. Effect of CD-TD copolymer composition on T_g .

relationship of T_g vs % CD.²⁹ Actually T_g , as determined by DTA, does not change until 50% CD is reached, at which point T_g increases rapidly with % CD. These data were all obtained at high molecular weight so that molecular weight is not a factor. The unusual dependence of T_g on copolymer composition is probably related to the tendency of successive CD units with the same stereochemistry to form a helical conformation. Since one does not have appreciable successive CD chain units in a random copolymer until the CD content of the copolymer exceeds 50%, the shape of curve may be very reasonable. This result suggests that as soon as you have two successive CD chain units with the same stereochemistry, there is a strong tendency to form a helical chain conformation, even in the amorphous state.

General. The specific gravity of these polymers is high (Table 11) in keeping with their 50% chlorine content. The rate of crystallization of the CD homopolymer from the melt is very rapid; the half-time of crystallization at 130°C is 30 sec. Indeed under some fabrication conditions, such as orientation, the high rate of crystallization can be a problem. This result is further evidence that our CD polymer is highly stereoregular and also that the helical conformation persists in the melt. On the other hand, the very low rate of crystallization of the TD homopolymer indicates poor stereoregularity and/or random conformations in the melt. The rate of crystallization of the TD homopolymer is so low that melt fabricated specimens are usually in the amorphous state. Thus, the properties given for the TD homopolymer are for the amorphous state and are very similar to what we find for generally amorphous CD-TD copolymers except for T_g -dependent properties in copolymers with over 50% CD.

Water absorption of these polymers is low. Most significant is the high Limiting Oxygen Index, 28%, of these polymers. This result is in the range generally accepted as good for flame resistance. Oxygen permeability of these polymers is low and in the extrudable Saran range. Water vapor transmission is also low. Films and moldings of these polymers, including the crystalline CD polymer, are clear. Electrical properties are good and much like oriented polyester (such as Mylar).

The melt rheology of these polymers is also interesting. Limited studies have indicated that the crystalline CD polymer has an unusually high melt viscosity compared with TD homopolymer. This no doubt results from the stiffer chain of the CD homopolymer, due to its helical conformation persisting in the molten state as well as in solutions, as noted earlier. Even so, the CD polymer

Table 11. General properties

	Homopolymers	
	CD	TD
Specific gravity	1.45	1.50
Crystalline m.p., °C	235	150
Rate of crystallization from melt	Very High	Very Low
Water absorption (24 hr) %	0.06	—
Flammability	Self-extinguishing	
Limiting Oxygen Index (% Oxygen)	28.1	27.2
U.L. 646 rating	SE-1	
Permeability (1 ml, biaxially oriented)		
O ₂ , cc/100 in ² /24 hr/atm	6	2.6
WVT, g/100 in ² /24 hr	2.2	0.15
Clarity	Transparent	
Molding qualities	Good	
Electrical properties	Like mylar	

appears to be readily fabricated if the molecular weight is not excessive (preferably η_{inh} of 0.6–0.7).

Mechanical and related properties

Unoriented tensile properties (Table 12) are good for both homopolymers except for the low elongation which leads to the low impact strength noted. The higher strength properties of the CD homopolymer on injection molding are probably due to orientation effects. Mold shrinkage is low. Hardness of these polymers is high.

Uniaxial orientation of these polymers (Table 13) greatly enhances tensile properties and improves toughness as indicated by the higher elongations. Biaxial orientation also increases strength and toughness and still gives clear products.

The heat distortion temperature of CD homopolymer (Table 14) is high, but not as high in the 264 psi test as one might expect based on the melting point of this polymer. This result is no doubt due to the somewhat low crystallinity levels, about 30–35%, that are attained with this polymer. Thus, the high load properties are determined by the glass transition temperature. The low load (66 psi) heat distortion temperature is much higher and does reflect the high crystalline melting point of the CD polymer.

The oxidation resistance and light stability of CD polymer are excellent and greatly exceed those of most simple polyepoxides (Table 14). TD polymer and copolymer also have similar properties.

Presumably, this enhanced oxidation- and light-stability

Table 12. Mechanical properties unoriented

Compression molded	Homopolymers	
	CD	TD
Tensile strength, psi	7500	5100
Tensile modulus, psi	320,000	320,000
Elongation at break, %	2.7	2.2
Injection molded		
Tensile strength, psi	9300	
Tensile modulus, psi	550,000	
Elongation at break, %	2.0	
Impact,† in lb	1.9	
Mold shrinkage, in/in	0.006	
Hardness		
Rockwell, R	126	
M	100	

†Miniaturized test. In a comparable test general purpose polystyrene gives 3.7 in lb.

Table 13. Mechanical properties oriented

Uniaxial	Homopolymers	
	CD	TD
Draw	6.7×	3.6×
Tensile strength, psi	30,000†	13,000–23,000
Tensile modulus, psi	660,000	260,000–600,000
Elongation at break, %	12	40
Biaxial		
Draw	2.5×	3.25×
Tensile strength, psi	10,500	12,700
Tensile modulus, psi	330,000	450,000
Elongation at break, %	27	75

†1.5 g/Denier.

Table 14. Environmental resistance of CD homopolymer

Heat	
Distortion temp., °F	
264 psi	205
66 psi	316
Stability in air	1 week or more at 175°C†
	Light

hr in fade-0-meter ca. 200

†Dependent on stabilizer formulation and use conditions.

is due to having an electron withdrawing group on every main chain atom. It is, however, desirable to add both an antioxidant and an acid acceptor to our polymers in order to achieve maximum oxidation- and heat-resistance. Indeed, the data cited here are based on polymers stabilized with 0.5% Irganox 1010 and 2% of the diglycidyl ether of bisphenol A.

Chemical resistance has not been extensively studied, but is good to weak acids and bases and aliphatic solvents. CD polymer should have at least moderate resistance to aromatics, ketones, and chlorinated aliphatics.

Uses

Certainly, CD homopolymer is by far the most interesting material in this new family of polyethers. It has a useful combination of properties. I believe that there are numerous market areas where it would find application, depending, of course, on price. Some of the most promising areas are high performance plastic, fiber, film, bottles, pipe and coatings. The high performance plastic and fiber areas appear particularly interesting since there is an important market need for flame resistance in both areas.

The properties of CD homopolymer are compared in Table 15 with two large volume, high performance plastics, acetal and polycarbonate. Tensile properties are similar except for our low elongation and thus poor impact properties. Mold shrinkage is equal to polycarbonate and better than acetal. Heat distortion temperature is inferior in the 264 psi test, but in the same range as acetal and polycarbonate for the 66 psi test. The Limiting Oxygen Index is as good or better and no doubt can be easily improved with appropriate additives such as antimony oxide, based on the high chlorine content of our polymer. Hardness is somewhat higher and water absorption markedly lower than for either acetal or polycarbonate. CD polymer should have large advantages in chemical resistance over acetal and polycarbonates. Our greatest deficiency is, of course, impact strength which can be greatly improved by orientation. In general, the properties of CD polymer are sufficiently attractive to acquire volume usage in the high performance plastic area, assuming that the impact problem is eliminated and that the cost is reasonable.

In the fiber area, we have done limited work on preparing melt spun fibers (Table 16) from crystalline CD polymer, actually a 99-1 CD-TD copolymer. Properties, although not optimized, are in a useful fiber range with tensile strength at about the level of some important commercial fibers such as wool and rayon. The fibers have excellent resilience and are dyeable with disperse dyes.

In the coatings area, limited studies have shown that these polymers have attractive properties for protecting steel from corrosion. This conclusion applies to amorphous copolymers in solution coatings. This ability to

Table 15. Properties compared to high performance plastics

	CD polymer	Acetal	Polycarbonate
Tensile, psi	7-9000	11,000	8700
Modulus, psi $\times 10^{-3}$	320-560	40	350
Elongation, %	2.5	15	80
Mold shrinkage, in/in	0.006	0.020	0.006
Heat distortion temp., °F			
264 psi	205	255	270
66 psi	316	338	280
Limiting Oxygen Index (% oxygen)	28.1	15.0	26-28
Hardness, Rockwell R	126	120	120
Water absorption, %	0.06	0.25	0.18

Table 16. Fiber properties of crystalline CD polymer

Tensile, gpd	1.8-2.4
Modulus, gpd	32-42
Elongation, %	19-12
Zero strength temp., °C	200
Elastic recovery, %	
at 2%	100
3%	98-100
10%	98
Dyeability	Disperse dyes

protect steel from corrosion is surprising in view of the known steel corrosion problem which has been experienced with epichlorohydrin elastomers.³⁰

CONCLUSIONS

A new class of polyethers containing 50% chlorine have been described. These new polymers are prepared by the cationic homo and copolymerization of the *cis* and *trans* isomers of 1,4-dichloro-2,3-epoxy-butane.

The crystalline, racemic diisotactic polymer from the *cis* monomer is especially significant. It crystallizes with a helical chain conformation which appears to persist, under some conditions, in solution and in the melt and also influences the crystallization and glass transition behavior of the CD polymer and copolymers.

The crystalline CD polymer has an interesting combination of properties. It has a high melting point (235°C), crystallizes readily from the melt, is unusually stable to heat and light, can be melt-processed up to 270°C, is flame resistant, has good mechanical properties, and has good barrier properties for air and water. Its main deficiency is poor impact strength which can be overcome by orientation and other methods. This polymer is derived from low cost raw materials, i.e. Cl₂, butadiene, and O₂, and should ultimately be of moderate cost. The combination of properties of the CD polymer should lead to such uses as flame-resistant plastic, fiber, film, and coatings.

The cationic polymerization of CD to highly stereoregular racemic, diisotactic polymer has unusual mechanism aspects. Possible polymerization mechanisms are proposed. Further work is needed to elucidate the detailed mechanism aspects, particularly to explain the excellent copolymerization of CD with TD.

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