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Od Redakcji

Kontynuując utrwaloną już od bardzo wielu lat w naszym czasopiśmie tradycję wydawania zeszytów tematycznych, niniejszy podwójny numer „Polimerów" poświęcamy tematyce żywic epoksydowych. Za cenną pomoc w zaprogramowaniu i realizacji tego zeszytu zespół redakcyjny serdecznie dziękuje Panu prof. dr. Piotrowi Penczkowi z Instytutu Chemii Przemysłowej. Pragniemy przypomnieć P.T. Czytelnikom, że ostatnim epoksydowym zeszytem „Polimerów" był numer 4—5 w 1993 roku.

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Study of the Structure-Reactivity Relationships in the Photoinitiated Cationic Polymerization of Epoxide Monomers

Summary — The rates of the photoinitiated cationic polymerization of a variety of different structurally diverse open-chain, terminal, internal and cycloaliphatic epoxide monomers were determined using real-time Fourier transform infrared spectroscopy. The results were compared and an attempt was made to correlate the reactivity of the monomers with their structures. The effects of such factors as steric hindrance, intramolecular side reactions and the formation of crosslinked networks are discussed. A general conclusion can be made that the polymerizations of cycloaliphatic epoxides are more rapid than all the other types of epoxy monomers and that within this class of monomers, steric hindrance plays a major role in determining the order of reactivity.

Key words: epoxide monomers, photoinitiated cationic polymerization, chemical structure, reactivity, real-time FTIR studies.

There has been a marked growth in the interest and applications of photoinitiated polymerizations during the past decade [1]. This technology has many advantages and is rapidly making considerable impact in areas such as printing inks, coatings, and adhesives [2, 3]. The photoinitiated cationic polymerization (PCP) of epoxide, vinyl- and 1-propenyl-ether monomers is presently under especially intensive development in industry and

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academia [4—6]. In particular, the PCP of multifunctional epoxide monomers is very attractive because the resulting polymers possess excellent adhesion, low shrinkage and superior chemical resistance which are of importance for coatings on metal, plastics and wood [7].

One important parameter upon which the use of the PCP of epoxide monomers depends in many applications is the polymerization or cure rate. High PCP cure rates result in greater throughputs and consequently more favorable economics. It is, therefore, imperative to employ monomers with the highest cure rates possible. Surprisingly, there are very few reports in the literature concerning the relative reaction rates of various epoxide monomers in cationic polymerization in general and PCP in particular. Initial work in this laboratory focused on the use of commercially available epoxide monomers for applications involving PCP. Our studies showed that the polymerization rates for the ring-opening PCP of those epoxides is highly dependent on the structure of the monomers [8, 9]. The presence of ester, ether, amide or urethane groups in epoxide monomers were observed to markedly depress the reaction rates [10]. Although early work centered about the use of commercially available epoxides, it was recognized that these monomers were most commonly used in condensation polymerization reactions together with hardeners such as amines and anhydrides. They were not intended for use in catalytic PCP polymerization and further, often contain small amounts of impurities which can inhibit PCP. In view of the considerable acceleration of activity in this field, it appeared worthwhile to synthesize monomers expressly for PCP. To optimally design monomers with the highest reactivity possible in PCP, it is necessary to develop detailed information concerning the structure-reactivity relationships of this class of monomers.

In this communication, we report the results of systematic studies conducted to determine the reaction kinetics of structurally diverse model epoxide compounds in PCP. The behavior of three general classes of monomers; cycloaliphatic epoxides, linear 1,2-epoxyalkanes, and linear α,ω-diepoxyalkanes are reported. The effects of such features such as ring-size, steric environment around the epoxide bond and geometric isomerism on the rate of polymerization are discussed. The influence of physical parameters such as sample preparation, photoinitiator concentration and UV-light intensity are also reported.

EXPERIMENTAL

Materials and Analytical Procedures

Epoxycyclopentane, epoxycyclohexane, epoxycycloheptane, epoxycyclooctane, epoxycyclododecane, 1-methyl-1,2-epoxycyclohexane, *cis*-2,3-epoxybutane, *trans*-2,3-epoxybutane, 1,2-epoxyhexane, 1,2-epoxyoctane, 1,2-epoxyhex-5-ene, 1,2-epoxydec-9-ene, 1,12-dibromododecane, *m*-chloroperbenzoic acid and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from the „Aldrich Chemical Co." (Milwaukee, WI). α-Pinene oxide, 1,2-epoxydecane, 1,2-epoxydodecane, 1,2-epoxytetradecane and 1,2-epoxyhexadecane were obtained as gifts from the „Elf Atochem Company" (King of Prussia, PA). The photoinitiator, (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-10), was prepared and purified as described in a previous paper [11]. Polypropylene film used in the RTIR studies was a gift from the Capacitor Department of the „General Electric Corp." (Hudson Falls, NY).

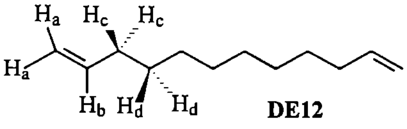
^{1}H-NMR spectra were obtained on a Varian XL-200 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as an internal reference. Gas chromatographic analyses were performed on a Hewlett Packard HP-5840A Gas Chromatograph equipped with a 15 m x 0.53 mm x 1.5 mm film thickness crosslinked methyl silicone gum column and a flame ionization detector. Routine IR spectra and real-time FTIR (RTIR) spectra were recorded on a MIDAC M-1300 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector.

Synthesis and Purification of Model Compounds

Dehydrobromation of 1,12-Dibromododecane

1,12-Dibromododecane (5 g, 0.076 mol) and 27.5 g (0.183 mol) of DBU were placed in a 250 mL three-necked round-bottom flask, equipped with an overhead stirrer, a nitrogen inlet and a reflux condenser. The reaction mixture was heated and stirred at 120°C for 2 h under an atmosphere of nitrogen until a white to caramel colored viscous suspension formed. After cooling the reaction mixture, the product was separated from the reaction mixture by extraction with anhydrous ether. The solvent was removed on a rotary evaporator and the product was distilled at 85—87°C/15 mm Hg (2 kPa). The yield of dodeca-1,11-diene, **DE12** was 2.99 g (0.019 mol, 24% theory). GC analysis showed one major product with a purity of > 99.5%.

^{1}H-NMR ($CDCl_3$) δ (ppm) 5.85 (m, 2H, H_b); 5.05 (m, 4H, H_a); 2.20 (m, 4H, H_c); 1.4—1.8 (m, 12H, H_d).



DE12

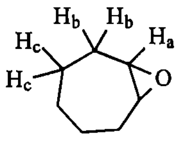
General Procedure for Epoxidation

Described below is a typical experimental procedure for the epoxidation of cycloheptene. All the other olefins were epoxidized by analogous procedures [12].

Epoxidation of Cycloheptene

Into a 500 mL three-necked round bottom flask equipped with a magnetic stirrer, thermometer, reflux condenser and dropping funnel was placed 51.8 g (0.23 mol) of *m*-chloroperbenzoic acid. Dichloromethane (350 mL) was added into the flask and the reaction mixture was cooled to 6°C in an ice bath. Cycloheptane 19.2 g (0.2 mol) was added using an addition funnel, at a rate sufficient to maintain the temperature below 10°C. After the addition was complete, the mixture was stirred at room temperature for an additional 2 h. The *m*-chlorobenzoic acid that formed was removed by suction filtration and the filtrate was washed with 100 mL 10% $NaHSO_3$, followed by two 50 mL portions of saturated $NaHCO_3$ and dried over Na_2SO_4. The solvent was removed on a rotary evaporator and the product was purified by fractional distillation (79—80°C/13 mm Hg = 1.73 kPa). The yield of epoxycycloheptane was 16.2 g (0.145 mol) or 72% theory. GC analysis showed one major product with a purity of > 99.5%.

^{1}H-NMR ($CDCl_3$; δ (ppm) 3.05 (m, 2H, H_a); 1.95 (m, 4H, H_b); 1.1—1.7 (m, 6H, H_c).



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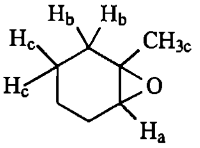
Epoxidation of 1-Methylcyclohexane

1-Methyl-1,2-epoxycyclohexane **6ME** was prepared as described above in 67% yield (16.9 g, 0.176 mol) after purification. The compound was purified by fractional distillation at 65—67°C/20 mm Hg (2.66 kPa). GC analysis showed one major product with a purity of > 99.5%.

^{1}H-NMR ($CDCl_3$) δ (ppm) 2.95 (m, 1H, H_a); 1.6—1.9 (m, 5H, H_b); 1.1—1.6 (m, 7H, H_c).

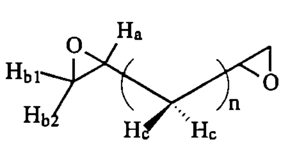


6ME

Epoxidation of 1,2-Epoxyhex-5-ene

1,2-Epoxyhex-5-ene was epoxidized using *m*-chloroperbenzoic acid as described above. The yield of 1,2,5,6-diepoxyhexane **DI6** was 6.37 g (0.056 mol or 69% theory). The product was purified by fractional distillation at 126—128°C. GC analysis showed one major product with a purity of > 99.5%.

^{1}H-NMR ($CDCl_3$) δ (ppm) 2.95 (m, 1H, H_a); 2.75 (m, 1H, H_{b1}); 2.45 (m, 1H, H_{b2}); 1.4—1.8 (m, 4H, H_c).



n = 2 (DI-6), 6 (DI-10), 8 (DI-12)

Epoxidation of 1,2-Epoxydec-9-ene

The yield of 1,2,9,10-diepoxydecane **DI10** after purification by fractional distillation at 101°C/13 mm Hg (1.73 kPa) was 13.05 g (0.084 mol) or 84% theory. GC analysis showed one major product with a purity of > 99.5%.

^{1}H-NMR ($CDCl_3$) δ (ppm) 2.85 (m, 1H, H_a); 2.7 (m, 1H, H_{b1}); 2.4 (m, 1H, H_{b2}); 1.1—1.6 (m, 12H, H_c).

Epoxidation of Dodec-1,11-diene DE12

1,2,11,12-Diepoxydodecane **DI12** was prepared in 53% yield (2.01 g, 10.1 mmol) by epoxidation of dodec-1,11-diene. After purification by fractional distillation at 62—65°C/1.0 mm Hg (0.13 kPa), GC analysis showed one major product with a purity of > 99.5%.

^{1}H-NMR ($CDCl_3$) δ (ppm) 2.85 (m, 1H, H_a); 2.7 (m, 1H, H_{b1}); 2.4 (m, 1H, H_{b2}); 1.0—1.6 (m, 16H, H_c).

Studies of Reaction Rates by Real-Time Infrared Spectroscopy

The kinetics of the UV-induced cationic epoxide ring-opening polymerizations were followed by real-time infrared spectroscopy (RTIR). The instrument was fitted with a UVEX Model SCU-110 mercury arc lamp in which the light was carried through a flexible optic wand to the sample compartment. The end of the wand was placed at a predetermined distance and directed at an incident angle of 45° onto the sample window. The UV light intensity was measured using UV Process Supply Inc. Control Cure Radiometer. Evaluation of the received spectra and the calculations of peak integrals or curve fittings were performed using MIDAC GRAMS/386 for Windows Version 3.01b software. The sample temperature was recorded with the aid of an Omega DP25-TC-A IR optical pyrometer. The detector of the optical pyrometer was placed at distance of 10 cm from the sample.

To make reproducible comparisons between various monomers, all monomers were freshly distilled before use and their purities established by GC. All samples were prepared using the following procedure. A homogeneous solution of a defined concentration of the photoinitiator, **IOC-10**, and the monomer was prepared. The solution was spread as a thin film of ~ 30 μm between two layers of 30 μm polypropylene film. To maintain consistent sample thickness, the sample was smoothly coated onto the matte side of the polypropylene film and covered with another identical layer of polypropylene film. The peak to peak distance taken by the interferometer of the FTIR spectrometer was held at a constant value. The sample temperature at the start of the polymerization reaction was also held constant at between 24—26°C. Data was collected at a rate of three complete spectra per second. Unless otherwise noted, all photopolymerizations were conducted at a light intensity of 20 mW/cm^2.

The reaction rates were determined from the areas of the infrared absorption band at 1050—1150 cm^{-1}. This band is assigned to the linear ether bond formed on ring-opening of the epoxide moiety. The conversions were calculated from the integrations of the peak areas assigned to the epoxide absorption band at wavelengths between 765—930 cm^{-1}. Potential interference of a band at 841 cm^{-1} due to one of the absorption of polypropylene film was eliminated by a curve fitting routine using a Gaussian function to separate overlapping peaks. Once the polypropylene peak was separated in the first frame (i.e. spectrum), the peak characteristics were held constant in order to calculate the curve fit in the last frame. Systematic errors using this method of determining the epoxide conversions can be estimated at ±5%. The relative rate for a given monomer can be calculated by using the equation:

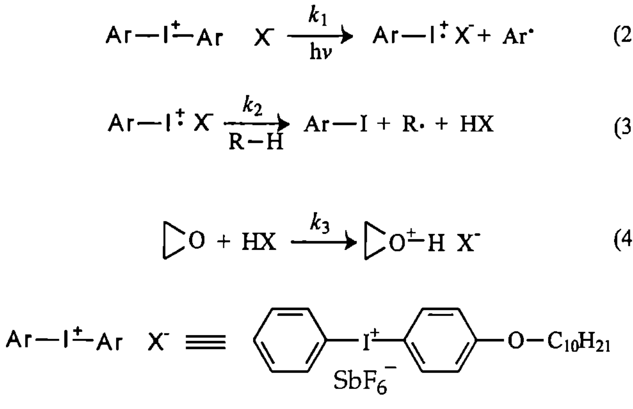
$$R_p/[M_o] = ([\%\ \text{conversion}]_{t2} - [\%\ \text{conversion}]_{t1})/(t_2 - t_1) \qquad (1)$$

In this equation Rp is the rate of polymerization and $[M_o]$ the initial monomer concentration. t_2 and t_1 are the times between collecting conversion data. A plot of percent conversion, which is related to the peak intensity of the ether formation, versus the irradiation time provides a kinetic curve for the polymerization. The slope of the initial linear portion of the curve corresponds to the factor $R_p/[M_o]$. To insure reproducibility of the data for conversion and reactions rates, all polymerizations were repeated a minimum of five times.

RESULTS AND DISCUSSION

General Considerations

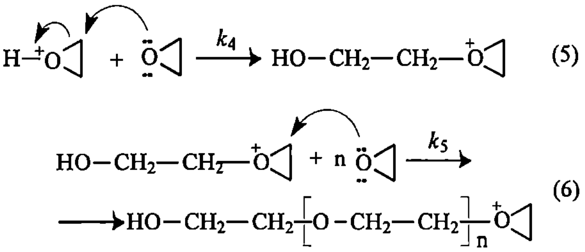
To understand more about PCP and outline the dominant kinetic and structural factors involved in the polymerizations of epoxide monomers, a brief discussion of the mechanism of this polymerization is necessary. The initiation of PCP is a multistep process as depicted in Scheme 1 with three major steps and three individual kinetic rate constants. In the example given in this scheme, the photolysis of diaryliodonium salts is depicted, however, very similar schemes may be written for other onium salt photoinitiators.



Scheme 1

The photolysis step [equation (2)] is dependent on the quantum yield of the photoinitiator as well as the intensity and wavelength of the light used. As in several previous studies [8, 9, 13, 14], we employed (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (**IOC-10**) as the photoinitiator. This photoinitiator has a high quantum yield (Φ = ~ 0.7) and shows good solubility in all the epoxide monomers described in this study. Usually, the photolysis is conducted at a relatively high light intensity (20 mW/cm^2) such that the decompositions of **IOC-10** is fast and k_1 is large. In addition, the concentration of the photoinitiator is generally kept below 1.0 mol % based on the monomer so that the optical density is sufficiently low to permit penetration of the light to the bottom of the sample. This is necessary to ensure rapid and homogeneous photolysis throughout the sample since diaryliodonium salt photoinitiators do not bleach. On irradiation, an aryliodonium cation-radical is formed by cleavage of the diaryliodonium salt. There is also evidence for the formation of aryl cations as well [15, 16]. Both of these highly reactive species abstract protons from the monomer or impurities (R-H) in the reaction mixture to generate a Brönsted acid as shown in equation (3). The actual initiation reaction involves the direct protonation of the epoxide oxygen by the Brönsted acid as shown in equation (4). Photolysis **IOC-10** generates the very powerful acid, $HSbF_6$. From kinetic studies of the cationic polymerization of epoxides it is known that protonation of an epoxide with such „super acids" is rapid, quantitative and, therefore, may be assumed to have a low activation energy [17, 18]. Thus, all rate constants, k_1, k_2 and k_3, are expected to be large.

Both of the chain-propagation steps shown in equations (5) and (6) of Scheme 2 involve bimolecular S_N2 mechanisms in which the nucleophilic oxygen of the epoxide monomer attacks the active oxiranium ion chain end and opens the ring to form an ether bond. As depicted in equation (5), the initial attack by an epoxy monomer occurs on a secondary oxonium ion while the main propagation step shown in equation (6) involves attack at a tertiary oxonium ion. Because of steric hindrance considerations, reaction (5) would be expected to be faster than reaction (6) ($k_4 > k_5$). In addition, since a proton is less able to stabilize a positive charge than an alkyl group, the secondary oxonium species shown in equation (5) would be expected to be more reactive than the tertiary oxonium species shown in equation (6). Both reaction steps are slow compared to the initiation reactions [equations (2)—(4) in Scheme (1)] and equation (6) is probably rate limiting. Since either reaction (5) or (6) is the rate limiting step, it is most important to consider the major parameters influence these reactions and also what measures can be taken to increase their rates. Both reactions are highly dependent on the electronic nature and steric requirements of both the monomer and the activated oxiranium chain end. Thus, a detailed understanding of the effects of monomer structure on the propagation steps of the polymerization is crucial to the subsequent design of more reactive monomers.



Scheme 2

Termination of PCP occurs by ion-splitting reactions involving reactions of the growing cation with the anion, by chain transfer reactions or by reactions with impurities.

There are many factors which influence the rates of reactions (5) and (6). For example, when the epoxide ring bears substituents, there are steric, electronic and stereochemical effects generated which have a large impact on both the chain end and on the incoming monomer. The presence of substituents also affects the direction (i.e. which carbon-oxygen bond in the oxiranium chain end is cleaved) that ring-opening polymerization takes place. Besides the steric effects, thermodynamic factors also influence the polymerization rate by changing the activation energy of the propagation reaction. For example, the heats of formation for epoxides are sensitive to the epoxide ring strain [19]. With higher ring strain, the reactivity usually increases. The structure of the monomer also predetermines the physical properties such as the glass transition temperature of the polymer formed by affecting the chain mobility. If there are more than one epoxide functional group per monomer, competing intramolecular cyclization reactions or other side reactions can occur. Unfortunately, all these effects are interdependent so it is very difficult to separate purely steric, kinetic and thermodynamic contributions to the overall rate of polymerization. It was, therefore, necessary to conduct carefully controlled kinetic investigations using several series of closely related monomers in which the structural features can be varied incrementally.

Our kinetic investigations of the reactivities of the epoxy monomers were carried out using real-time infrared spectroscopy (RTIR). This technique was especially useful in these studies because it is a simple, direct method which can be applied to very fast photopolymerizations on a time scale of 1—5 seconds. Moreover, we have shown that the run-to-run reproducibility in well-controlled experiments can be held to within ±5%. This analytical technique involves monitoring the decrease of an infrared band characteristic of the functional group undergoing polymerization. Alternatively, the increase in the intensity of the IR band of a functional group being formed during polymerization may be monitored. For these studies, a FTIR spectrometer oriented with the IR beam in the vertical direction was employed. PCP was carried out by impinging a UV beam onto the sample while simultaneously monitoring the changes in the infrared spectrum as function of the time as polymerization takes place.

The samples consisted of a thin films of pure subject monomers in which the photoinitiator is homogeneously dissolved. A sample film was deposited on a carrier film and then immediately covered with another carrier film. This minimizes the potential contamination of the monomer during the polymerization. The „sandwich" was mounted in a standard 5 cm x 5 cm slide holder and then placed in the sample compartment of spectrometer. The properties of the carrier film are important to success and reproducibility of the measurements. For these studies, the carrier film should be thin and of uniform thickness, it should be transparent to UV and reasonably thermally stable. Although many different polymer and glass or quartz films were examined, oriented poly(propylene) film showed the best overall properties. To maintain consistent conditions, continual UV irradiation at a specified intensity was carried out during the entire time of polymerization. In separate experiments, the effects of light intensity and photoinitiator concentration were investigated for selected monomers.

Since the ultimate objective of these studies was to develop optimally reactive epoxy monomers, monomers such as glycidyl ethers, glycidyl esters, and epoxy urethanes which have been previously shown to undergo slow PCP were excluded from this investigation. Consequently, we have confined the focus of this study to three classes of the most reactive monomers namely; cycloaliphatic epoxides, 1,2-epoxyalkanes and α,ω-diepoxyalkanes.

Polymerization of Cycloaliphatic Epoxides

Effect of Light Intensity

Figure 1 shows a comparison of the polymerization kinetics for epoxycyclohexene carried out under different light intensities using 1 mol % **IOC-10** as the photoinitiator. It can be seen that even using low light intensities, the reaction rate after an initial induction period remains nearly the same. The decrease in the induction period as the UV intensity is increased can be explained by the reaction of the initiator species (the Brönsted acid) with a low concentration of impurities. These impurities such as water and other basic materials are at levels which are not detectable by GC or NMR. Once the initiator concentration exceeds a threshold above the initiator concentration, the polymerization proceeds rapidly.

Effect of Initiator Concentration

The effect of the initiator concentration at a constant UV light intensity on the rates of PCP of epoxycyclohe-

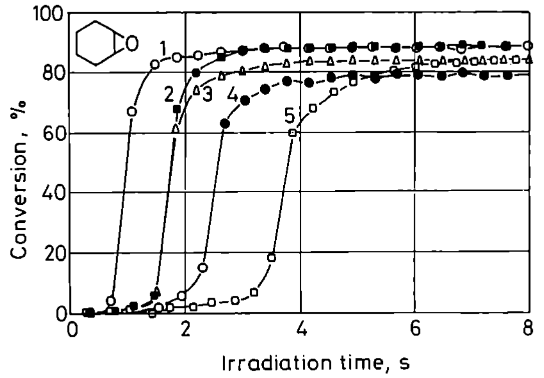


*Fig. 1. Comparison of the rate of polymerization of **6** at different UV irradiation intensities: 1 — 27 mW/cm², 2 — 15.27 mW/cm², 3 — 10 mW/cm², 4 — 5.0 mW/cm², 5 — 3.2 mW/cm²*

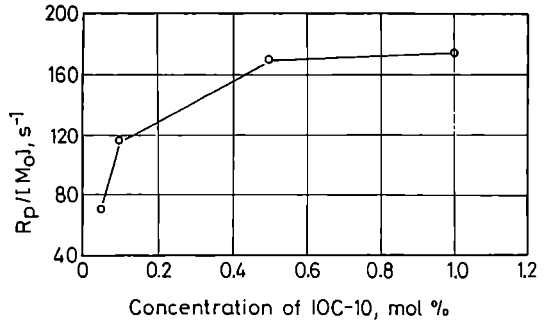


*Fig. 2. Plot of the rate ($R_p/[M_O]$) of polymerization of **6** as function of the IOC-10 concentration*

xane, **6**, is shown in Figure 2. The rates increase markedly as the concentration of **IOC-10** increases from 0.05—0.5 mol % while from 0.5—1 mol % further changes are small. The same observation can be made with respect to the induction period. Ultimate conversions (after 100 s) at photoinitiator concentrations from 0.1—1 mol % are nearly constant. A summary of these data are given in Table 1. Based on these results, the subsequent PCP reactions were carried out at 25 +/- 1°C and the UV irradiation intensity was held at 20 mW/cm² throughout the entire polymerization time. A photoinitiator concentration of 0.5 mol % **IOC-10** was employed for all monomers.

Table 1. Polymerization of epoxycyclohexane with different concentrations of IOC-10*)

Concentration mol % IOC-10	Reaction rate $R_p/[M_O]$, s^{-1}	Conversion %	Induction period, sec
1.0	174.5	89	0.7
0.5	169.2	84	1.0
0.1	115.2	86	2.2
0.05	70.5	77	2.8

*) The flux was held constant at 20 mW/cm².

Effect of Ring Size

To examine the effect of the ring strain in the epoxide group on the polymerization rate, a series of cycloaliphatic epoxides with different ring sizes (**5**—**12**) was investigated. Cycloaliphatic epoxy monomers are easily prepared by the direct epoxidation of the corresponding cycloalkenes and the thermodynamic properties such as the heats of formation, ΔH_f, ring strain energies, E_s, and steric energies, E_{steric}, of these epoxides have been reported in the literature [19—21]. A comparison of the kinetic curves for the PCP of cycloaliphatic epoxy monomers with ring sizes from **5**—**8** and **12** are shown in Figure 3. The reaction rates calculated from the slopes of the curves together with the available thermodynamic data for monomers **5**—**8** and **12** are summarized in Table 2.

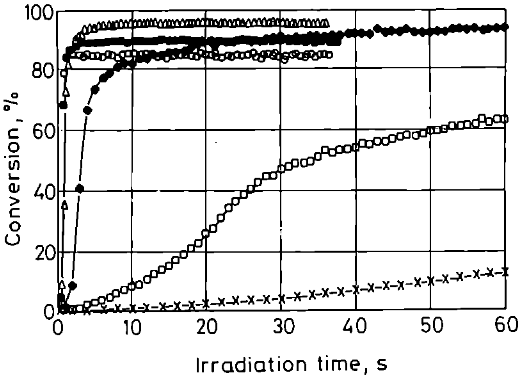
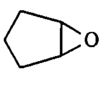


Fig. 3. Comparison of the RTIR curves for cycloaliphatic epoxy monomers with different ring sizes: O — 5, ■ — 6, △ — 7, ◆ — 8 at 60°C, □ — 12 at 60°C, x — 12 at 25 °C

Table 2. Polymerization of cycloaliphatic epoxides with different ring sizes

Monomer	Conversion %	$R_p/[M_O]$ s^{-1}	$-\Delta H_f$[20] kJ/mol	E_s[21] kJ/mol	E_{steric}[19]d) kJ/mol
5	85	171	131	120	–
6	89	169	166	112	68.4
7	95	95.2	198	106	–
8	95	29.9a)	–	114	102.1
8	70	1.18b)	213c)	–	–
12	82	2.15d)	–	–	–
12	83	0.48	–	–	–

a) Measured at 60°C.
b) Reaction in solid state.
c) $-\Delta H_f$ calculated for the solid state.
d) Calculated by molecular mechanics with extended MM2 force field.



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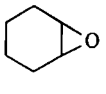

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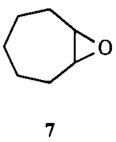

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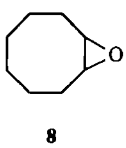

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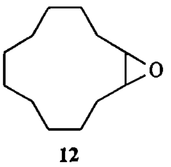

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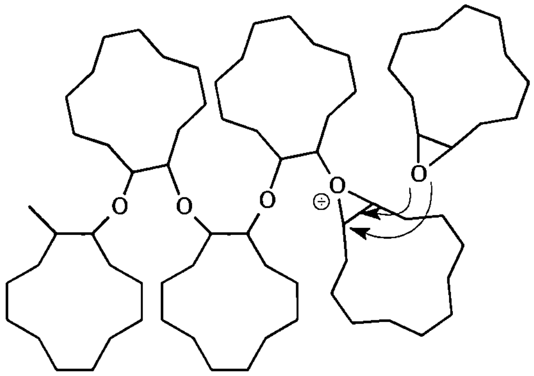
Monomer **8** is a solid melting at 53°C. Accordingly, the polymerization of this monomer was carried out at in the solid state at 30°C and in the melt at 60°C. The conversion after 400 s is about 70% at both temperatures, but the reaction rate increases from $R_p/[M_0]$ = 1.18 s^{-1} at 30°C to $R_p/[M_0]$ = 29.9 s^{-1} at 60°C in the melt. The reason for this increase can be ascribed to the limitations of diffusion and mobility of the monomer in the solid state. To evaluate the effect of temperature on the rates of ring-opening polymerization, epoxy monomer **12** was polymerized at different temperatures. The increase in the reaction rate is not nearly as marked as in the case of **8** in which there is a phase change. In this case, the reaction rate increases from $R_p/[M_0]$ = 0.48 s^{-1} at 25°C to 2.15 s^{-1} at 60°C.

As many be noted in Table 2, the most reactive epoxy monomers in PCP are those with the smallest cycloaliphatic rings. Reaction rates drop markedly with larger ring sizes. The reaction rates of monomers **5—7** at 25°C are much higher than monomer **8** at the same temperature and even at 60°C. Monomer **8**, in turn, is more reactive than monomer **12** at both 25°C and at 60°C. This observation is opposite to the increase of the reported heats of formation with larger ring sizes [20, 21]. The ring strain energies, which are calculated from the corresponding acyclic compounds [19], decrease from **5—7** and the ring strain energy of is higher than of monomer **6**. This suggests that in the heats of formation depend on additional factors beside the ring strain of the epoxide group. One of those factors is the steric environment around the epoxide bond. In addition to influencing the ring strain in cycloaliphatic epoxides, the ring size also has a considerable influence on the rate of reaction due to steric requirements at the reaction site. In general, the steric hindrance about an epoxide group increases with larger rings due to the greater bulkiness of the ring substituents and to their greater conformational freedom.

Raber *et al* [19] applied molecular mechanics to cycloaliphatic epoxides and found that their calculated heats of formation are in a good agreement with the experimentally measured data. Using this method, structural parameters were obtained which are presented as the steric energies, E_{steric}, in Table 2. These data shown that **8** has a much higher steric energy than **6**. It appears that a higher steric energy depresses the rate of a PCP even when the ring strain energy is high. Unfortunately, no thermodynamic data for **12** could be found, but it is quite evident that the formation of the polymer from this monomer is sterically hindered (Scheme 3). This also suggests that steric hindrance of the chain growth also plays a major role in determining the reaction rate PCPs.



Scheme 3

Effect of Geometric Isomerism

In the case monomer **12**, both *cis-* and *trans*-epoxide groups are present and the ratio of the two isomers was

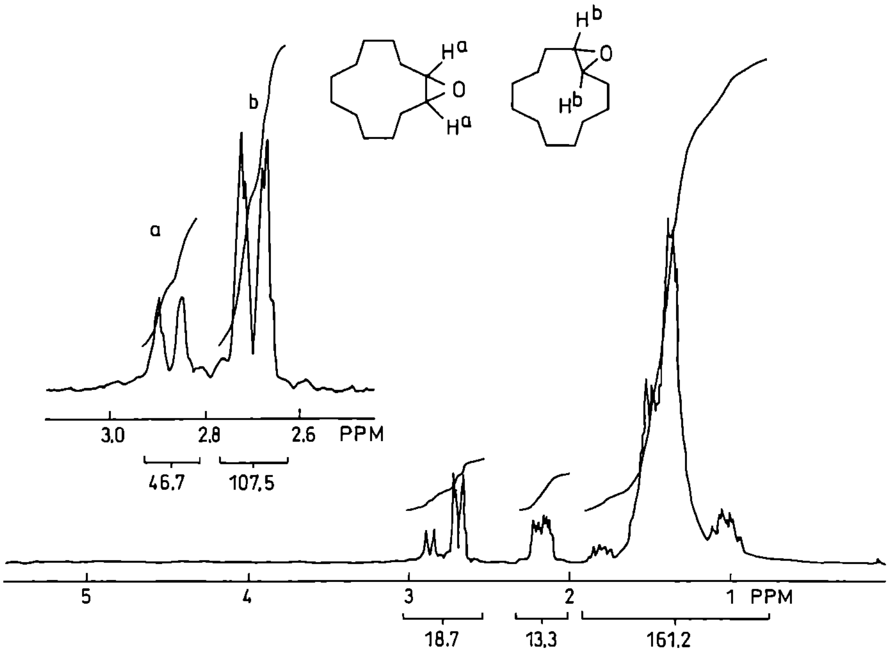


Fig. 4. ^{1}H-NMR spectrum 12. Insert shows a magnification of the epoxide region

determined by ^{1}H-NMR to be 2.3 (*cis/trans*, mol:mol). The ^{1}H-NMR spectrum for monomer **12** is shown in Figure 4. In the infrared, the absorption band at 754 cm^{-1} was assigned to the *cis*-epoxide bond while the band at 804 cm^{-1} was assigned to the *trans*-epoxide bond. A three dimensional plot of the RTIR spectra acquired during the PCP of **12** is shown in Figure 5. Figure 6 shows conversion versus time plots taken from the data shown in Figure 5. From this figure, it can be noted that the *cis*-epoxide reacts faster and proceeds to higher conversions than the *trans*-epoxide when the two isomers are copolymerized together. The average reaction rate presented in Figure 6 was determined by monitoring the appearance of the peak at 1078 cm^{-1}, which was assigned to the linear ether bond in the polymer. The overall conversions of the two polymerizations were calculated by averaging the integrals of the two epoxide peaks shown in Figure 5.

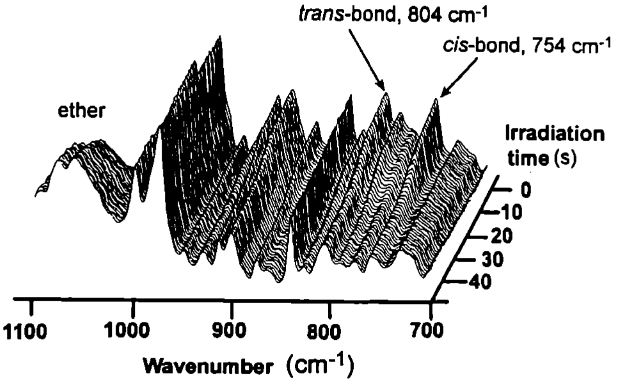


Fig. 5. Three dimensional plot of the RTIR spectra during the PCP of ***12***

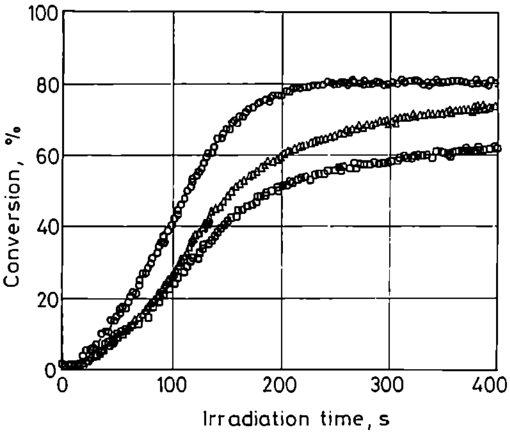


Fig. 6. Polymerization kinetics of the cis- and trans-epoxide isomers of ***12****: ○ — cis-epoxide bond absorption 754 cm^{-1}, □ — trans-epoxide bond absorption 804 cm^{-1}, △ — ether bond absorption 1077 cm^{-1}*

To further examine and to demonstrate the effects of geometrical isomerism in PCP, the polymerization of a 1/1 molar mixture of 2,3-*cis*- and 2,3-*trans*-epoxybutane isomers was carried out. The data are presented in Figure 7 which demonstrates again that the *cis*-2,3-epoxybutane isomer reacts faster and with higher conversion than the *trans* isomer. In the case of monomer **12** containing a large cycloaliphatic ring, the ring strain energy of the *cis* and *trans* isomers should not be significantly different. In this case, it can be postulated that steric factors are mainly responsible for the overall slower rate of polymerization of this monomer as compared to other members of the series. In addition, as shown in Scheme 3, the approach of a *cis*-epoxide to an active chain end would be expected to be more sterically favored than the approach of the corresponding *trans*-epoxide.

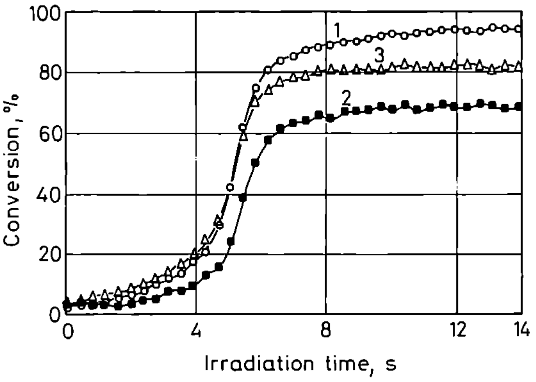


Fig. 7. Comparison of the RTIR curves of a 1/1 (mol:mol) mixture of cis-2,3- and trans-2,3,-epoxybutane: 1 — cis-epoxide bond absorption 756 cm^{-1}, 2 — trans-epoxide absorption 810 cm^{-1}, 3 — linear ether bond absorption 1081 cm^{-1}

Effect of Steric Hindrance

To obtain more information about the influence of structural parameters in PCPs, cycloaliphatic epoxides with different degrees of steric hindrance about the epoxide group were polymerized. The PCP curves for 1,2-epoxycyclohexane, **6**, 1-methyl-1,2-epoxycyclohexane, **6ME**, and α-pinene oxide, **6PI**, are illustrated in Figure 8. As expected, the reaction rates decrease with an increase

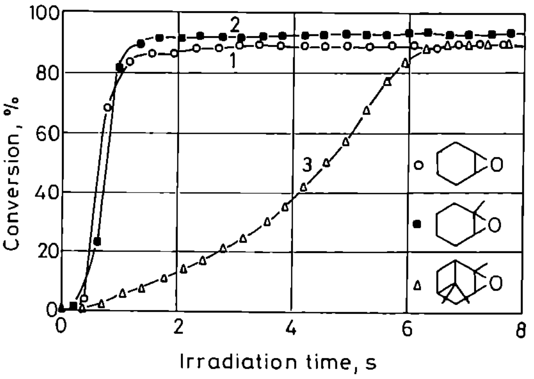
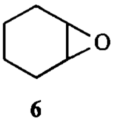
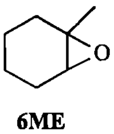
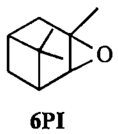


Fig. 8. Comparison of the reaction kinetics of the PCP of cycloaliphatic epoxides with different degrees of steric hindrance around the epoxide bond: 1 — ***6****, 2 —* ***6ME****, 3 —* ***6PI***

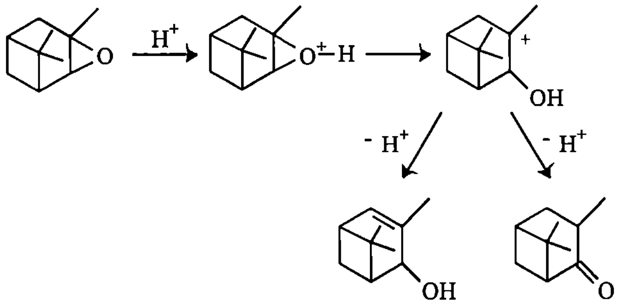
in the steric hindrance about the epoxide bond; **6**, $R_p/[M_o]$ = 168 s^{-1}; **6M**, $R_p/[M_o]$ = 109 s^{-1}; **6PI**, $R_p/[M_o]$ = 24.0 s^{-1}. This can be explained by an increase in the steric barrier provided by both the methyl group on the epoxide ring and the two geminal methyl groups on the bridge of the bicyclic ring system. In the case of α-pinene oxide, the bulky bridge group at the chain end allows the approach of the incoming epoxy monomer to the activated chain end to take place only from the side of the ring opposite to the bridge. Similar considerations apply to the orientation of the incoming monomer during its attack at the chain end. Both of these factors combine to markedly depress the polymerization rate of **6PI**.


6


6ME


6PI

Besides the steric hindrance which is provided by the methyl substituent on the epoxide ring in monomers **6ME** and **6PI**, the electronic environment around the epoxide bond also changes as compared to monomer **6**. This results in side reactions such as the acid catalyzed rearrangement of the epoxy group to form ketones and allylic alcohols as shown in Scheme 4 for **6PI**.


Scheme 4

These same rearrangements are not observed during the PCP of the unsubstituted cyclic epoxides **5**—**8** and **12**. In a 3D chart of the RTIR of **6PI** (Figure 9), the appearance of bands assigned to both carbonyl and hydroxyl groups appear and clearly increase as the polymerization proceeds. The selective isomerization of various epoxides to ketones under mild Lewis acid conditions ($LiClO_4$ in diethylether) has been reported [12] and the results are summarized in Table 3. Unsubstituted cycloaliphatic epoxides and terminal *n*-epoxyalkanes did not rearrange under these conditions to form either ketones or alcohols. The same observations was made in the PCP of the cyclic monomers **5**—**8** and **12** and in the 1,2-epoxyalkenes which are described the later in this communication. It was also shown that under similar conditions, the more highly substituted the epoxide, the greater the extent of isomerization that takes place. The infrared spectra of **6ME**, show that although there is some small amount of ketone and alcohol formation taking place, the PCP rate is very high and this is the dominant reaction. It should be noted that the conversions were calculated by following the integration of the IR band areas assigned to the epoxide group. Since the amount of isomerization is small in the case of monomers **6ME** and **6PI**, the contribution of this side reaction was not included in the calculations of the conversions in this study.

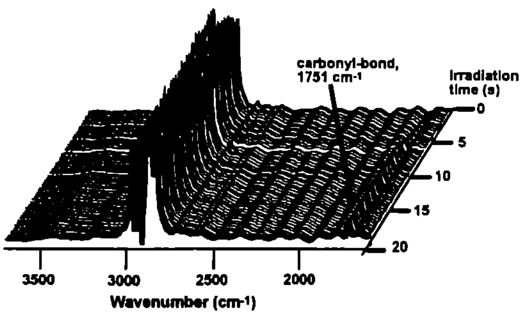
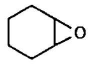
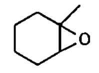
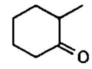
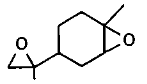
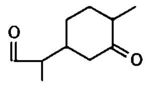
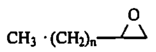
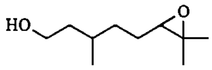
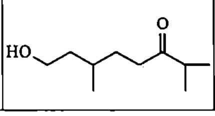
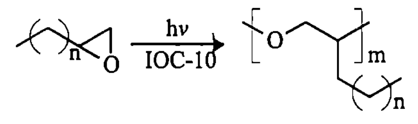


Fig. 9. Three dimensional plot of the RTIR spectra during the PCP of 6PI

T a b l e 3. **Conversion of epoxide to ketones under mild Lewis acid conditions ($LiClO_4$ in Et_2O) [12]**

Epoxide	Product	Duration	Yield
	–	24 h	no reaction
		2 h	83%
		4 h	70%
	–	24 h	no reaction
		4 h	79%

Polymerization of 1,2-Epoxyalkenes

 (7)

n = 3 (N-6); 5 (N-8); 7 (N-10); 9 (N-12); 11 (N-14); 13 (N-16)

In the third series of these systematic studies, the PCP rates of linear, 1,2-epoxyalkenes were investigated. It was of interest to study the steric effect of the length of the aliphatic side chains on the rate of polymerization of these monosubstituted terminal, epoxy monomers. The RTIR curves of a series of these monomers are compared in Figure 10. As noted in this figure, all the PCPs of the 1,2-epoxyalkenes follow essentially the same reaction kinetics. The average reaction rate for these monomers is $R_p/[M_o]$ = 1.6 s^{-1} and the conversions are

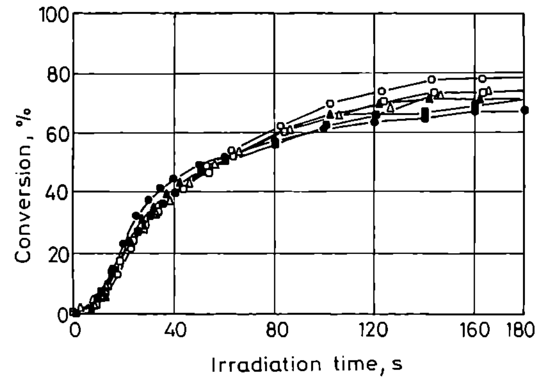
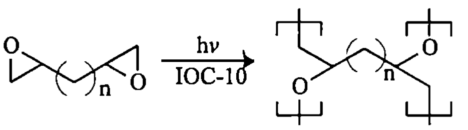


*Fig. 10. Comparison of the reaction kinetics of the PCP of 1,2-n-epoxyalkenes: ● — **N-6**, ■ — **N-8**, ▲ —**N-10**, O — **N-12**, □ —**N-14**, △ —**N-16***

all approximately 75% after 300 s irradiation time. The rates of polymerization of these monomers are significantly lower than the corresponding cycloaliphatic epoxides with the same number of carbon atoms. There are two possible reasons for these results. First, the epoxide bond is not as strained and, therefore, not as reactive as in cycloaliphatic epoxides. Second, even though the epoxy groups are terminal and relatively unhindered, the flexible side chains can adopt conformations which effectively sterically hinder the approach of the incoming epoxide oxygen to the activated chain end. This also partially explains the lower reaction rates for these monomers. Side reactions such as the acid catalzed rearrangements to ketones and alcohols were not observed by IR spectroscopy.

Polymerization of α,ω-Diepoxyalkanes



(8)

n = 0 (DI-4); 2 (DI-6); 4 (DI-8); 6 (DI-10); 8 (DI-12)

In this study, linear α,ω-difunctional epoxide monomers (**DI-4** to **DI-12**) were prepared and photopolymerized. As in the previous series **N-6** to **N-16**, both epoxide groups are monosubstituted and are placed at the terminal position of the aliphatic chain. However, in comparison to the previous series in which linear, soluble polymers are formed, the polymerizations of these difunctional monomers lead to crosslinked networks. The focus in this investigations is to determine both the influence of the structure of the monomer and the effect of the change of the polymer physical state on the reaction rates and the conversions. The kinetics of the polymerizations of a series of these monomers are illustrated in Figure 11 and the data derived from these curves presented in Table 4.

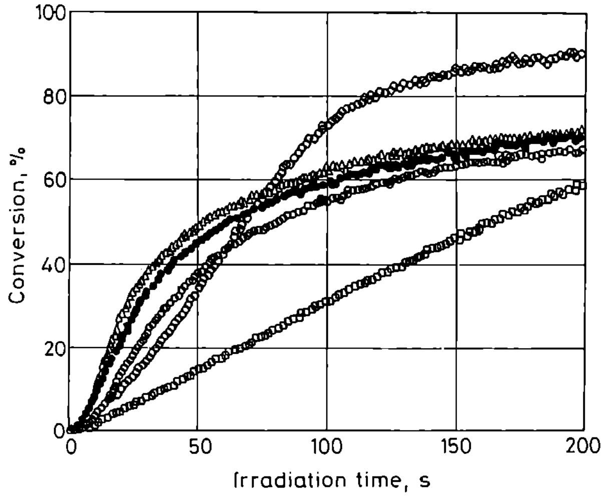


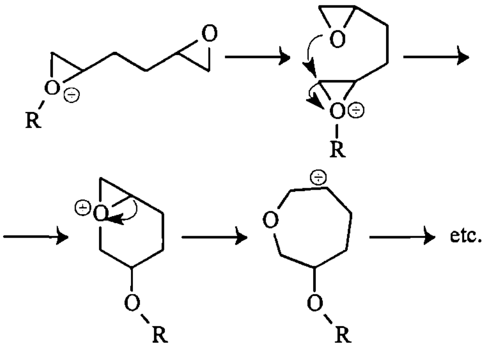
*Fig. 11. Comparison of the reaction kinetics of the PCP of α,ω-diepoxyalkenes: ◇ — **DI-4**, □ — **DI-6**, △ — **DI-8**, ● — **DI-10**, O — **DI-12***

T a b l e 4. Conversions and polymerization rates of the PCP of α,ω-diepoxyalkenes

Compound	Conversion$^{a)}$, %	$R_p/[M_0]$, s^{-1}
DI-4	91	0.78
DI-6	81	0.34
DI-8	69	2.02
DI-10	75	1.34
DI-12	68	0.96

$^{a)}$ Conversions were taken after 300 s irradiation time.

In this series, monomer **DI-8** is the most reactive. It is apparent that **DI-4** and **DI-6** follow very different reaction kinetics than the other monomers. A possible explanation for the slower rates of polymerization of these two monomers is that intramolecular side reactions occur. In Scheme 5 a proposed mechanism for the intermolecular cyclization reaction of **DI-6** is shown. A similar reaction would be possible for **DI-4** by forming a cyclic intermediate with a bridged five membered ring. The higher conversions observed for monomers **DI-4** and **DI-6** compared to the other model compounds also agree with this hypothesis. The intramolecular cyclization reaction occurs with a higher probability than intermolecular reactions. In addition, intramolecular cyclization results in polymers with a more linear



Scheme 5

structure which consequently also have greater solubility and mobility and, therefore, proceed to higher conversions.

The reaction rates of monomers **DI-8**, **DI-10** and **DI-12** decrease as the methylene chain between the two terminal epoxide groups is lengthened. This may be due to an incremental increase in the steric hindrance of the epoxide bond by the methylene chain. Further, the functional groups can be considered to be undergoing a dilution since the ratio of the mass of the functional group to the total molecular mass decreases. The formation of a crosslinked network seems to have little influence on either the reaction rate or the conversion. The reaction rates **DI-8** and **DI-10** are comparable to those of the monofunctional 1,2-epoxyalkenes. One explanation for this observation is that the epoxide functional groups are sufficiently distant from one another that they behave independently. In addition, the T_g of the resulting networks would be expected to be low in both cases so that mobility within the developing crosslinked network remains high. Accordingly it may be noted that the conversions of these two monomers are also as high as those obtained with monofunctional monomers **N-6—N-16**. It can also be observed that other difunctional monomers in which the two epoxy groups are separated by stiff spacer groups display marked rate deacceleration effects at low conversions due to the immobility of the functional groups in the glassy matrix which is formed.

Figure 12 shows a direct comparison of the kinetic curves of representative epoxide monomers taken from the three different structural classes which were examined during the course of this investigation. In summary, it can be concluded that the most reactive monomer is the simple, unsubstituted cycloaliphatic monomer epoxycyclohexane, **6**. The high reactivity of this monomer is due to the fact that it is relatively free of steric hindrance and side reactions, but contains considerable ring strain. **6PI** is less reactive despite the higher ring strain as a consequence of the steric hindrance due to the bicyclic structure. Lower reactivity is observed for linear monofunctional monomer **N-6**. In comparison, **DI-8** displays unexpectedly high reactivity which can be attributed to the presence of a long spacer group which essentially isolates the epoxide groups allowing them to behave independently. **DI-6** and cyclic monomer **12** are the least reactive monomers shown in Figure 12. A combination of unfavorable effects, including cyclization, and immobilization and steric hindrance appear to be responsible.

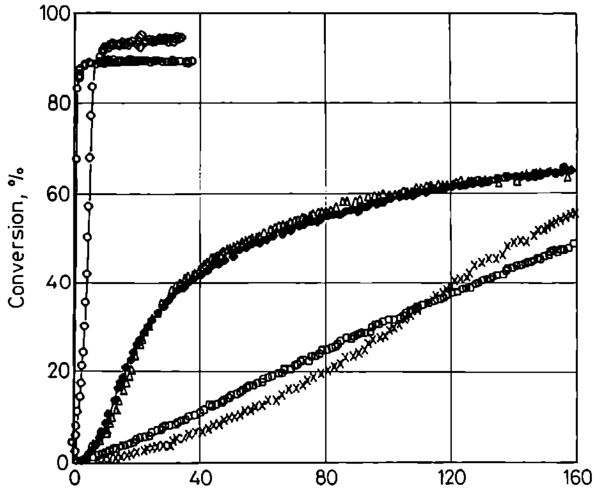


Fig. 12. Comparison of the reaction kinetics of the PCP of different aliphatic epoxides: O — 6, ◇ — 6PI, △ — N-6, ◆ — DI-8, □ — DI-6, x — 12

COCNLUSIONS

Three different series of epoxide monomers were prepared and subjected to kinetic studies of their PCP by RTIR. A special experimental apparatus for these investigations was used to make a comparison within and between these series possible. Within the three classes of epoxides examined, a wide range of reactivity was observed. Cycloaliphatic epoxides show high reactivities which lead to very high PCP polymerization rates. Cycloaliphatic epoxy monomers **5—7** and **6ME** are the most reactive monomers and, therefore, given the fastest reaction rates. Ring strain in cycloaliphatic epoxy monomers is not the only controlling factor in determining the reactivity of a monomer. Steric bulk is also a very important determinant. This was shown for monomer **12**, which due to its bulky structure, reacted significantly slower than the other cyclic monomers. Steric factors are also responsible for the observation that *cis* epoxides react faster and with higher conversions than *trans* epoxides. It was also shown that greater substitution on the epoxide ring leads to side reactions such as isomerization to ketones and alcohols. Thus, whereas this reaction is negligible for terminal (monosubstituted) and 1,2-substituted epoxides, it occurs to an appreciable extent for tri- and tetrasubstituted epoxides.

1,2-Epoxyalkanes react slower and with lower conversions than the cycloaliphatic epoxides. In a series of these monomers, the reaction rates of PCP were observed to be independent of the aliphatic chain length. Terminal epoxides do not undergo rearrangements to ketone, aldehyde or hydroxyl groups as side reactions. α,ω-Diepoxyalkenes react at rates similar to 1,2-epoxyalkanes. In a series of these former monomers, **DI-4** and **DI-6** followed slower reaction kinetics than the rest of the monomers. We suggest that these two monomers undergo intramolecular cyclizations as side reaction which lead to lower reaction rates. As the aliphatic chain is further lengthened from **DI-8** to **DI-12**, the reaction rates decrease. The formation of a crosslinked network seems not to have a major influence on reactivity rate or conversion for these specific two monomers. Monomer **DI-8** displays the highest reactivity in this series.

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