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Photopolymerization of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate and tri (ethylene glycol) methyl vinyl ether

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Abstract

Photopolymerizations of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (ECH) and triethyleneglycol methyl vinyl ether (TEGMVE) and their mixtures catalyzed with diaryliodonium hexafluoroantimonate (IA) were studied. Rates of polymerizations for mixtures of monomers are different from those for both homopolymerizations. The photocured mixtures showed a single not dual glass transition temperature over all composition ratios. During SEC analysis, the soluble fraction of the photocured equimolar mixture did not show any peaks that the homopolymer of TEGMVE showed, which means that TEGMVE was incorporated into a polymer network. Real-time FT-IR spectroscopy showed that ECH and TEGMVE did not polymerize independently for polymerizations of mixtures of ECH and TEGMVE. ^{13}C NMR spectroscopy showed strong evidence that cross-propagation reaction occurs. All of the above suggest that the copolymerization takes place during the photoinitiated cationic polymerization of ECH and TEGMVE mixtures.

Keywords: Cationic photopolymerization; Cycloaliphatic epoxide; Mono vinyl ether

1. Introduction

Vinyl ethers and cycloaliphatic diepoxides are among the most reactive monomers polymerized by cationic polymerization. Photopolymerization studies for vinyl ethers and cycloepoxides have been frequently reported in the literature [1–12], and the copolymerizations of vinyl ethers with cycloaliphatic diepoxides have been also studied [13–15]. It is known that vinyl ether monomers are used as diluents for photopolymerization of epoxides to reduce viscosity of the polymerizing system and enhance physical properties (toughness) of the resulting polymer. However, the reports on a (co)polymerization mechanism are still conflicting. Dougherty and Crivello [14] proposed that the photoinitiated cationic polymerization of a blend of triethyleneglycol divinyl ether and 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (ECH) proceeds largely independently to form an interpenetrating polymer network. However, they observed increased reaction rate of ECH and decreased reaction rate of vinyl ether in that system in comparison to the reaction rates for the homopolymerizations. The same research group also reported [15,16] that propenyl ether did not react until almost all of epoxy groups were consumed in the system composed of MCEPr (6-methyl-3,4-epoxycyclohexylmethyl propyl ether) and CP (3,4-cyclohexenylmethyl 1-propenyl ether). Also they observed again that polymerization of ECH in a mixture of ECH and butyl vinyl ether was much faster than independent polymerization of ECH. Lapin [3] reported that vinyl ethers and epoxides may homo-polymerize but there was little evidence of copolymerization of vinyl ethers and epoxides. However, Decker [17] suggested that the copolymerization takes place during the photoinitiated cationic polymerization of blends of vinyl ethers and epoxides. He indicated that the acetal group detected in NMR spectroscopy is the evidence of cross-propagation. The objective of this work is to investigate the (co)polymerization of a cycloaliphatic diepoxide and a mono-vinyl ether with different composition ratios.

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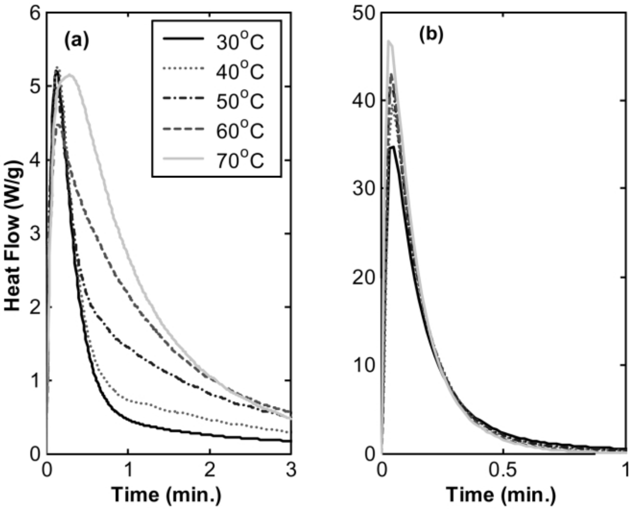

Fig. 1. Photopolymerization profiles of ECH (a) and TEGMVE, (b) at various temperatures.

2. Experimental

2.1. Materials

3,4-Epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (ECH) and triethyleneglycol methyl vinyl ether (TEGMVE) were purchased from the Aldrich Chemical Company. These monomers were used without further purification. Diaryliodonium hexafluoroantimonate (IA, CD1012) is a product of the Sartomer Company.

2.2. Photopolymerization and characterization

Polymerizations were carried out in bulk in a Photo-DSC (TA Instruments) at temperatures ranging from 30 to 70 °C for mixtures containing 1 wt% IA as a photoinitiator. A 60 ml/min. flow of ultra-high purity (UHP) nitrogen was maintained in the irradiation chamber, even though photoinitiated cationic polymerization is not sensitive to oxygen. Samples were exposed for 12 min to the UV radiation of a medium pressure mercury lamp and the sample size was about 3 mg. The light intensity was 40 mW/cm^2, which was measured by a radiometer (International Light IL-1400A).

Number average and weight average molecular weights and molecular weight distributions of polymers were determined by size exclusion chromatography (SEC). The chromatograph utilized four Styragel columns (HR 0.5, HR 2, HR 4 and HR 5; Waters) and was equipped with a refractive index detector and a photodiode-array UV detector. The solvent was tetrahydrofuran flowing at 1 ml/min.

Dynamic mechanical analysis (DMA) was used in order to investigate the glass transition temperature (T_g) of polymers after UV irradiation in the photo-DSC and also after postcuring in the DMA. The monomer mixture was placed on a glass fabric (40 × 12 mm, clamp distance: 11 mm) and irradiated for 12 min. in the photo-DSC. Then the sample was placed between the DMA clamps and temperature was increased to 200 °C at a rate of 10 °C/min. After the postcure, T_g of copolymer was measured again by using the same procedure but a lower heating rate (5 °C/min.).

FT-IR spectra for photopolymerizations were collected on a real-time FTIR spectrometer combined with a Photo-DSC instrument. A diamond reflection ATR module was used in a ReactIR 2000 spectrometer and the probe was installed in a Photo-DSC instrument. The spectrometer was equipped with a MCT detector and the spectra were recorded with a resolution of 8 cm^{-1} at a time resolution of 3.5 sec. Samples (0.36 mm thick) were put on the top of the probe at a room temperature (∼25 °C) and irradiated with the UV light in air atmosphere. The UV light intensity used in these experiments was 3 mW/cm^2. When a higher intensity of the light was used, proper measurements by the FT-IR spectrometer could not be obtained for the polymerization of highly reactive TEGMVE. A region of 2383–1850 cm^{-1} for each spectrum was excluded due to a cutoff of the diamond probe. Thus, for our experiments any functional group absorbance peaks cannot be observed in this cutoff range. Usually, nitrile or sulphur containing groups can be detected in this range.

^{13}C NMR analysis was used for the polymers resulting from polymerizations of ECH, TEGMVE and equimolar mixture of them. ^{13}C NMR spectra were recorded on a Bruker AC 300. In order to obtain an uncrosslinked sample for NMR analysis, polymerization of an equimolar mixture of ECH and TEGMVE was performed at low UV light intensity (3 mW/cm^2) and was stopped at conversion ∼50%. The sample was dissolved in THF immediately after the polymerization. After 4 days of THF dissolution/extraction, the soluble fraction of the sample was analyzed using the ^{13} C NMR spectrometer. Homopolymers of TEGMVE and ECH were treated in the same manner for comparison. The homopolymer of TEGMVE dissolved completely in the solvent, but the homopolymer of ECH and the polymer of the mixture of ECH and TEGMVE were extracted from insoluble crosslinked networks. Unreacted monomers were separated by using a SEC column.

3. Results and discussion

3.1. Photoinitiated cationic polymerization of a cyclic diepoxide and a mono vinyl ether and their mixtures

Photo-DSC was used to record reaction rate vs. time profiles. The photo-DSC has the advantage that the rate of reaction can be followed in real time as it is assumed that the heat produced by the polymerization is proportional to the number of monomer units reacted [18]. Another advantage is that a good temperature control can be maintained when a small amount of sample is used.

When ECH containing 1% of IA was exposed to UV

Table 1
Heat of polymerizations for monomer mixtures at various compositions and temperatures

	ECH/TEGMVE (%mole ratio)	Heat of polymerization (J/g)		
		30 °C	60 °C	70 °C
ECH	100/0	212	400	438
ECH75	75/25	405	458	476
ECH50	50/50	572	547	557
ECH25	25/75	480	470	486
TEGMVE	0/100	441	440	454

irradiation, the total heat of reaction was highly dependent on the polymerization temperature due to crosslinking leading to vitrification which restricts the mobility of propagating active chains (Fig. 1(a) and Table 1). However, for the polymerization of TEGMVE, the total heat of reaction did not depend on the temperature (as shown in Table 1) because polymerization of this mono-vinyl ether monomer does not result in network formation and the glass transition temperature of the resulting polymer is well below the polymerization temperature.

The heat of polymerization for mixtures of ECH and TEGMVE was higher than that of ECH as shown in Table 1. This phenomenon can be explained by the increased mobility of the polymer chain if the copolymerization results in a lower glass transition temperature of the polymer than that of ECH homopolymer. The notation for monomer mixtures is shown in Table 1 (i.e. ECH75 = mixture of 75 mol% of ECH and 25 mol% of TEGMVE, etc.).

Increasing the amount of ECH in the monomer mixtures significantly decreased the reaction rate from that of pure TEGMVE at a polymerization temperature of 30 °C (Fig. 2(a)). This suggests that the monomers do not react independently as the heat evolution rate is much different than might be anticipated for a combination of individual homopolymerizations (Fig. 2(a)). At a polymerization temperature of 60 °C, the overall heat evolution rate increases but it is still slow in comparison to the rate of homopolymerization of TEGMVE, as shown in Fig. 2(b).

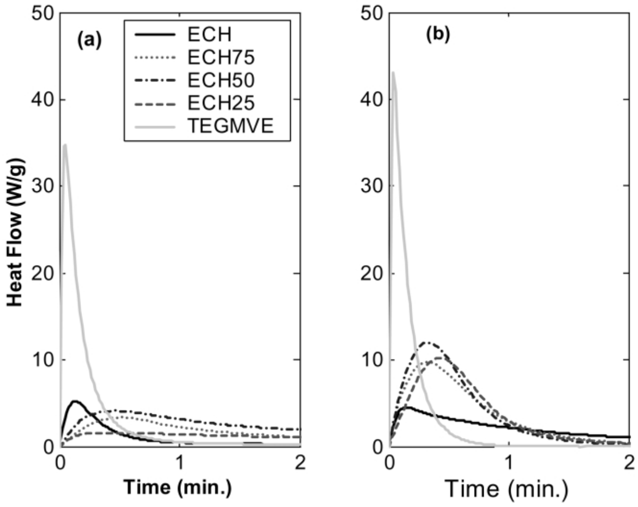

Fig. 2. Copolymerization of ECH and TEGMVE with various compositions at 30 °C (a) and 60 °C (b).

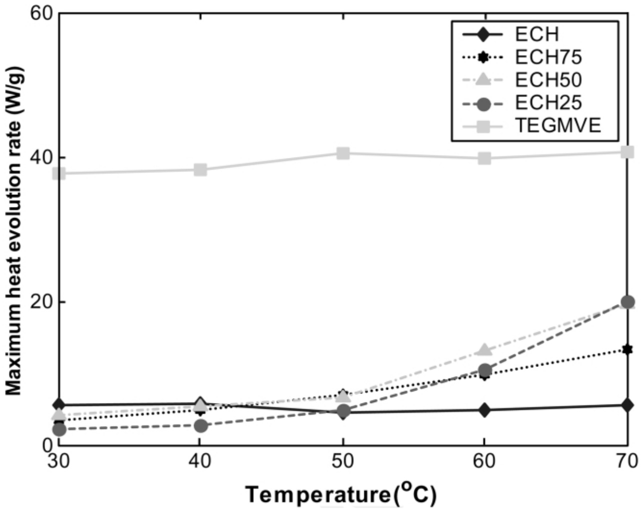

Fig. 3. Comparison of maximum heat evolution rates at different temperatures for copolymerization of ECH and TEGMVE.

From all investigated by photo-DSC ECH/TEGMVE mixtures, the highest efficiency is observed for polymerization of the equimolar mixture (Fig. 2). It might be hypothesized that this occurs due to the formation of ECH-TEGMVE 1:1 complexes. Such complexes might have a form of a “sandwich” with the vinyl ether inserted between two cyclohexane rings bearing epoxy groups. Of course, these complexes would be quite weak and exist in equilibrium with the monomers but still can facilitate copolymerization between epoxy and vinyl groups.

The maximum heat evolution rate for homopolymerizations of ECH and TEGMVE was almost constant even when

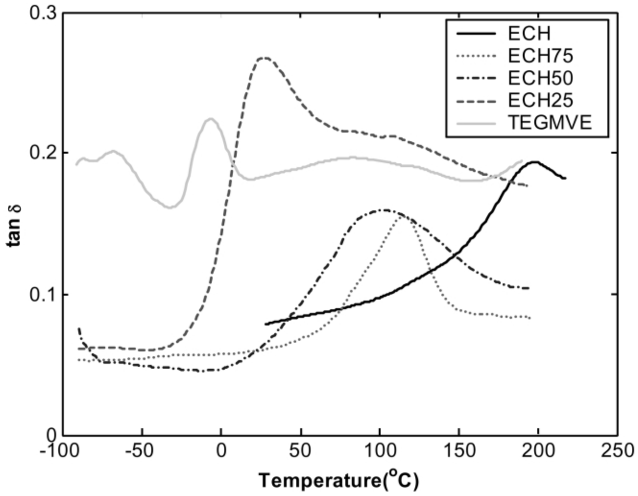

Fig. 4. DMA analysis for the products of copolymerization of ECH and TEGMVE at different compositions. (Maximum peak: -7 °C, TEGMVE; 27 °C, 25ECH; 97 °C, 50ECH; 115 °C, 75ECH; 197 °C, ECH).

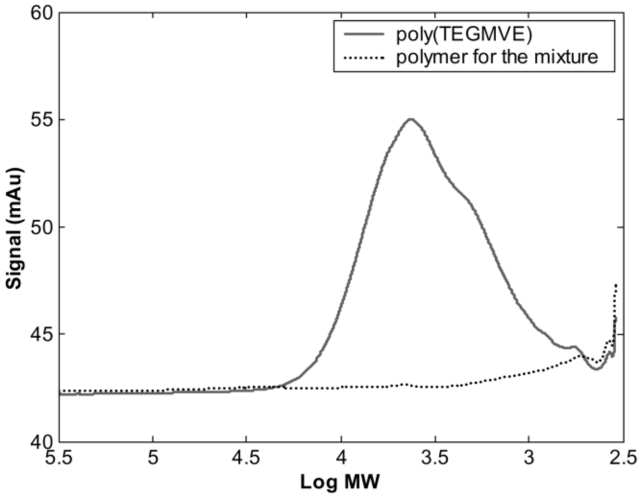

Fig. 5. SEC curves for polyTEGMVE and a soluble part of polymer of the equimolar mixture of ECH and TEGMVE.

the temperature was increased, but that for the polymerization of ECH and TEGMVE mixtures increased with temperature (Fig. 3). This might indicate that cross-propagation reactions take place and that these reactions have activation energies different from homo-propagations. This suggests again not only that the monomers do not polymerize independently but also that copolymerization is probably taking place.

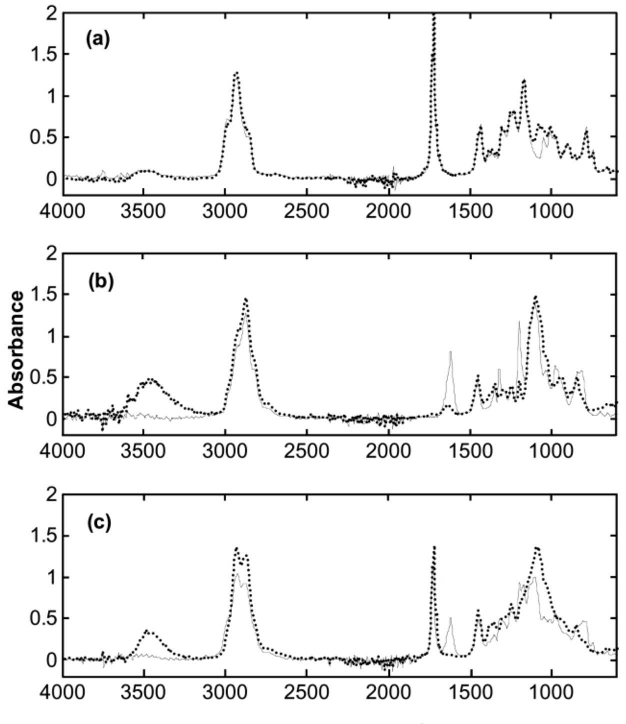

Fig. 6. The corrected ATR FT-IR spectra of (a) ECH, (b) TEGMVE and (c) ECH50 during the polymerization. Continuous line: initial, broken line: after 30 min.

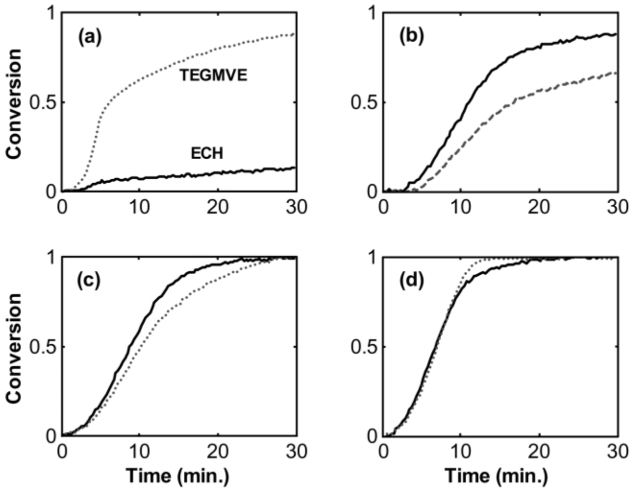

Fig. 7. Conversion of the two monomers for polymerizations of mixtures of ECH and TEGMVE. (a) homopolymerizations of ECH and TEGMVE; (b) ECH75; (c) ECH50; (d) ECH25. (Continuous lines: ECH; broken lines: TEGMVE).

3.2. Glass transition temperature of polymers

It is well known that when two monomers copolymerize randomly, the resulting polymer shows a single glass transition temperature. If polymerization of mixtures of ECH and TEGMVE produced two mixed homopolymers, a DMA scan of the polymerized mixtures would show two glass transition temperatures for the individual homopolymers. However, the DMA scans of the polymerization products showed a single not dual glass transition temperature for all the compositions used as shown in Fig. 4. The figure shows the glass transition temperatures after post-curing. The glass transition temperature for polymerized mixtures of ECH and TEGMVE increased with the increasing ratio of ECH to TEGMVE.

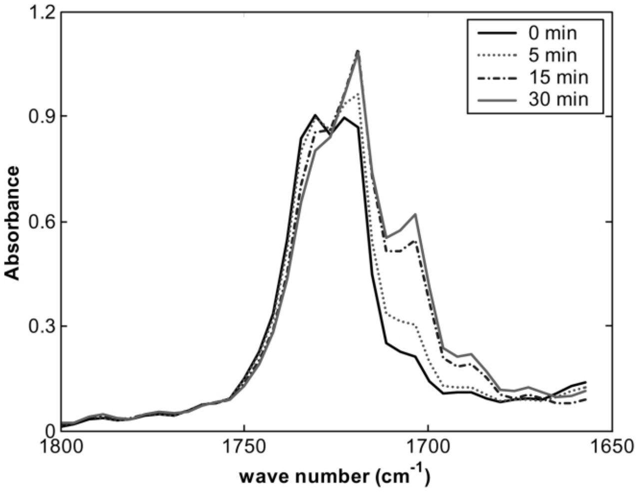

Fig. 8. Spectral changes during polymerization of the equimolar mixture of ECH and TEGMVE.

3.3. SEC analysis of polymers

After a mixture of equimolar amounts of ECH and TEGMVE had been irradiated under the UV light, the resulting polymer sample was put immediately into THF for dissolution. For comparison, homopolymers of TEGMVE and ECH were also treated in the same manner. PolyTEGMVE dissolved completely in THF but polyECH was not soluble in THF because of the network formation. The soluble fraction of the photocured mixture of ECH and TEGMVE was taken for SEC analysis after 4 days of THF extraction, and this solution was compared with the solution of homopolymer of TEGMVE. While polyTEGMVE showed a SEC peak with the weight average molecular weight of 4260 daltons according to PS calibration, the soluble fraction of the photocured equimolar mixture of ECH and TEGMVE did not show any peaks in the molecular weight range of the TEGMVE homopolymer as shown in Fig. 5. If ECH and TEGMVE in the mixture polymerized independently, homopolymer of TEGMVE would have been seen in the SEC graph. Clearly, no measurable amount of TEGMVE homopolymer was produced during the polymerization of the mixture of ECH and TEGMVE again supporting the hypothesis that the polymerized TEGMVE was incorporated into the polymer network by copolymerization with reactive groups of ECH.

3.4. Real time FT-IR spectroscopy

Individual conversions of functional groups were calculated from the decay of the absorption band of $-CH{=}CH_2$ at 1618 cm^{-1} for TEGMVE and the absorption band of the epoxy ring at 745 cm^{-1} for ECH. The absorption bands at 788 cm^{-1} and 745 cm^{-1} are both related to the epoxy ring in ECH but only the absorption band at 745 cm^{-1} was used because the one at 788 cm^{-1} overlapped with some absorption bands from TEGMVE for the polymerizations of mixtures of ECH and TEGMVE. To reduce variability, experiments for different composition ratios were performed on the same day and under the same conditions. For each composition ratio experiments were performed at least in triplicate.

As the homopolymerization of ECH proceeds, the intensity of the absorption bands for the epoxy ring at 787.66 and 745.15 cm^{-1} is decreasing while the intensity of the absorption band for the C–O ether group in the region of 1150–1000 cm^{-1} is increasing with the reaction time. This results from the break-up of the epoxy ring and formation of the ether group during the polymerization. On the other hand, the intensity of the absorption band for $-CH{=}CH_2$ vinyl group at 1618.5 cm^{-1} is decreasing with reaction time for the polymerization of TEGMVE. Fig. 6 shows initial and final FT-IR spectra for the polymerizations of ECH, TEGMVE and the equimolar ratio of ECH and TEGMVE. The spectra were corrected for the depth of infrared penetration related to the wavenumber.

The depth of penetration for each wave number is calculated from the following equation:

$$d_p = \frac{1}{2\pi W N_p (\sin^2\theta - N_{sp}^2)^{1/2}}$$

where, W : the wave number, N_p : the refractive index of the crystal, θ : the angle of incidence, N_{sp} : the ratio of the refractive index of the sample to the crystal, $N_{sample}/N_{crystral}$. Then the spectra were corrected for the penetration depth as follows:

$$d_{p,min} = \frac{d_p}{\min(d_p)}, \qquad \mathrm{Abs}_{corrected} = \frac{\mathrm{Abs}}{d_{p,min}}$$

where, $d_{p,min}$: the minimum value of the penetration depth, Abs: the absorbance.

Changes between the initial and the final FTIR spectra for neat ECH were relatively small, but it is easily seen that the absorption band of C–O group (1150–1000cm^{-1}) increased with reaction time. The $CH{=}CH_2$ vinyl group band (1618.5 cm^{-1}) was greatly decreased after 30 min for the polymerization of neat TEGMVE. Fig. 7 shows conversion versus time plots for the two monomers during polymerizations of mixtures of ECH and TEGMVE with different composition ratios. For homopolymerization of ECH, the final conversion after 30 min was around 15% while the final conversion was around 85% for homopolymerization of TEGMVE. When polymerizations of mixtures of ECH and TEGMVE were performed, the polymerization of TEGMVE was slowed down and at the same time the reaction of ECH was accelerated and its final conversion was greatly increased. In addition, for the polymerizations of the mixtures ECH25 and ECH50 the final conversion of TEGMVE was higher than the conversion for the homopolymerization. Thus, for polymerizations of ECH25 and ECH50 both the absorption band for the epoxy ring and the absorption band for the vinyl group completely disappeared after the polymerization. This indicates that-generally speaking-there is a synergism in the case of the polymerization of ECH/TEGMVE mixtures in comparison to the homopolymerizations of the two monomers.

The discussed changes in the reaction rates for a mixture of ECH and TEGMVE can be affected by changes in viscosity of the mixture since increasing the content of TEGMVE reduces the viscosity of the mixture. Therefore, the reduced viscosity of the system would account for the increased reaction rate of ECH. However, it seems that this explanation is valid only at the beginning of the reaction and for systems containing small amounts of TEGMVE.

On the other hand, addition of a flexible ether moiety from TEGMVE to a polymer chain should reduce the glass transition temperature of the polymer. Thus, in comparison with homopolymerization of ECH the polymer having some TEGMVE units should become more flexible and mobile,

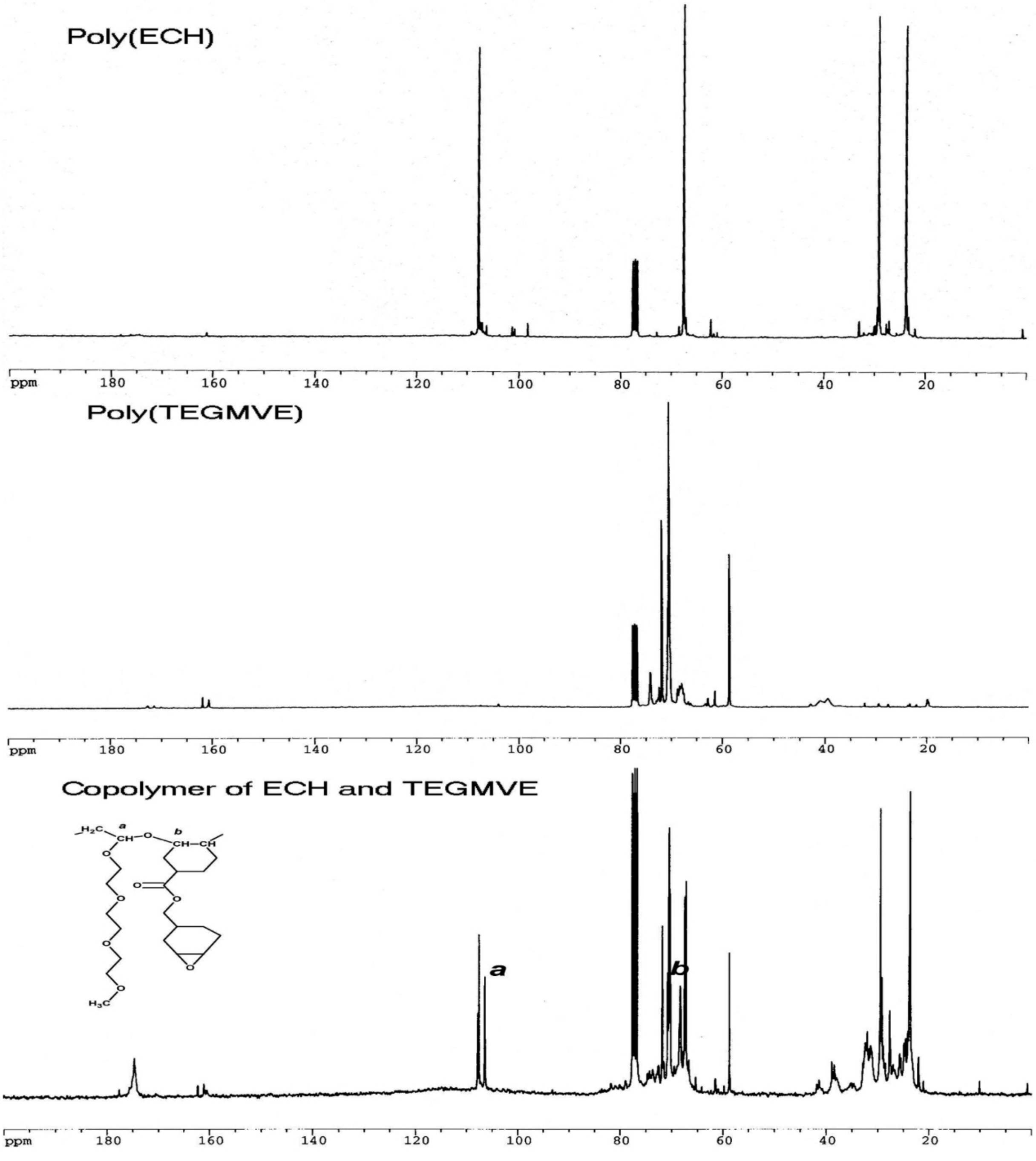

Fig. 9. ^{13}C NMR spectra for polymers of ECH, TEGMVE and the equimolar mixture of ECH and TEGMVE.

which should account for the enhanced reaction of ECH during polymerization of ECH/TEGMVE mixtures.

The increased reaction rate for ECH in the mixture might be also explained to some extent by a chain transfer reaction with hydroxyl group and moisture in the air. The formation of hydroxyl groups in the polymerization of TEGMVE as indicated by the IR absorption band at ca. 3400 cm^{-1} seems to come from a side reaction resulting in de-alcoholation of ether polymer chains. It is well known that protonated ether could decompose into cation and alcohol. In our studies, even if the polymerization of TEGMVE was performed under a nitrogen atmosphere the resulting polymer still showed the presence of hydroxyl groups.

Some interesting observations were also made by scrutinizing changes in the carbonyl band during polymerization of ECH/TEGMVE mixtures. Generally, a carbonyl group shows a very strong absorbance in FTIR spectra and sometimes it is hard to see absorbance changes. When we carefully examined the carbonyl band in the spectra for the polymerizations of the mixtures of ECH and TEGMVE, we noticed that there was a shift in the position for some of the carbonyl groups indicating the transformation of the

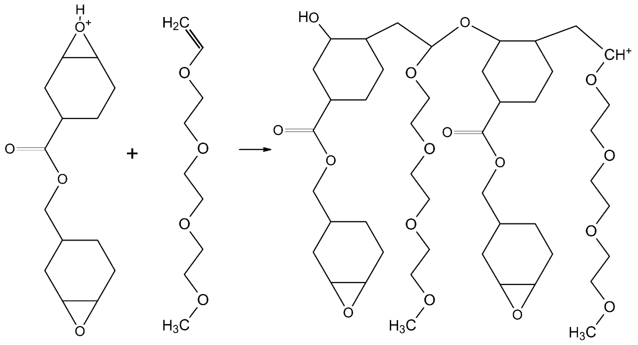

Fig. 10. Cross-propagation of ECH and TEGMVE.

chemical environment from ester to carboxylic acid. As the polymerization of the mixtures of ECH and TEGMVE proceeds, intensity of the band of the carbonyl group at 1734 cm^{-1} decreases, while the band at 1703 cm^{-1} increases, as shown in Fig. 8. The band at 1734 cm^{-1} comes from the C═O stretching of the ester group and the band at 1703 cm^{-1} comes from the stretching vibration for carboxylic acid. The formation of carboxylic acid might result from the hydrolysis of ester with moisture in the air. On the other hand, the transformation was not found for the homopolymerization of ECH even if the polymerization of ECH was performed under higher UV light intensity (40 mW/cm^2) giving a final conversion of 35%. Probably the hydrolysis of ester groups in ECH units in the polymer chain is accelerated in the presence of TEGMVE which is more polar and may be enhanced by hydroxyl groups resulting from de-alcoholation of TEGMVE. The formation of carboxylic acid during the polymerization of ECH/TEGMVE mixtures was also confirmed by ^{13}C NMR results as shown below (a peak with chemical shift at 174.6 ppm).

3.5. ^{13}C NMR spectroscopy

To confirm that a cross-propagation reaction occurs, ^{13}C NMR spectroscopy was used for the two homopolymers and for polymer produced from an equimolar mixture of ECH and TEGMVE. Fig. 9 shows the ^{13}C NMR spectra for poly(ECH), poly(TEGMVE) and the (co)polymer of ECH and TEGMVE. If cross-propagation reaction occurs, the resulting polymer has the structure as shown in Fig. 10. When compared with the spectra for the two homopolymers, the ^{13}C NMR spectrum for the (co)polymer of ECH and TEGMVE shows two new distinct peaks *a* and *b* (Fig. 9). The carbon adjacent to two oxygens in acetal grouping resulting from cross-propagation (Fig. 10) gives a resonance at 107 ppm (peak *a*). This is additional strong evidence that the cross-propagation occurs during polymerization of ECH and TEGMVE mixtures.

4. Conclusions

This work provides one of the most detailed kinetic and analytical studies yet performed on the photopolymerization of epoxides and vinyl ethers.

Strong experimental evidence implies that copolymerization indeed takes place during photopolymerization of ECH and TEGMVE mixtures. Rates of polymerization for the mixtures of monomers are different from those for homopolymerizations of ECH and TEGMVE. DMA analysis shows that the polymerized mixtures display a single not dual glass transition temperature over all composition ratios and that the glass transition temperatures follow the changing composition ratio of the two monomers. SEC analysis also demonstrates that TEGMVE is incorporated into a polymer network during copolymerization. Furthermore, real time FT-IR spectroscopy shows that ECH and TEGMVE do not polymerize independently for the polymerizations of mixtures of ECH and TEGMVE. Finally, ^{13}C NMR spectroscopy shows convincingly that a structure resulting from the cross-propagation is present in the polymer produced by polymerization of ECH and TEGMVE mixtures.

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