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# Cationic polymerization of a cycloaliphatic diepoxide with latent initiators in the presence of structurally different diols

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## Abstract

The influence of different polyether based diols on the photochemically and thermally induced cationic polymerization of a cycloaliphatic diepoxide is examined. If the polymeric diol is a 1,2-diol based polyether the polymerization is retarded compared to the pure diepoxide, whereas the polymerization is not influenced or even enhanced if the diol is a polyether based on a 1,4-diol or a low molecular weight 1,2-diol. The different behavior is explained by the complexation of protons in a crown ether like structure in the presence of the polyethers based on 1,2-diols. This leads to an effective reduction of the acid concentration available to initiate the polymerization. The model was verified by the addition of a small amount of 12-crown-4. In the presence of the crown ether the polymerization is also strongly retarded.

*Keywords:* Epoxide; Cationic polymerization; Polyetherdiol

## 1. Introduction

The cationic photopolymerization of epoxides is widely used for printing inks, adhesives or coatings. Appropriate initiators are diaryliodonium and triarylsulfonium salts with $BF_4^-$, $PF_6^-$, $AsF_6^-$ and particularly $SbF_6^-$ counterions [1,2]. During the last few years latent thermal initiators for the cationic polymerization of epoxides were also developed [2]. The polymerization of the epoxide is initiated by the super acid or carbocation formed during the photochemically or thermally induced decomposition of the initiator. The basic reactions for the photochemical decomposition of diaryliodonium [3] and triarylsulfonium salts [4] are described in the literature as well as the initiation, chain growth and chain transfer of the epoxide polymerization [5]. Although it is well known that hydrogen donors strongly influence the cationic polymerization, the effect on the polymerization of epoxides with latent initiators has received little attention. If the reaction is not directly initiated by the carbocations formed by the decomposition of the initiator, a proton donor is required as co-catalyst for the formation of the initiating super acid [3,4]. As long as the monomer is not dried extensively and the reaction is not carried out in a dry atmosphere, the amount of water naturally present in the monomer is high enough to work as a proton donor for the initiation. Furthermore, the presence of water or alcohols leads to chain transfer reactions. The alcohol attacks the positively charged end of the growing polymer chain forming an ether bond and a hydroxyl group. The released proton initiates the growth of the next polymer chain. This is also called 'polymerization by the activated monomer mechanism' and was examined with conventional initiators by Penczek and Kubisa [6]. Analogous work for the photochemically induced polymerization of epoxides was published by Yagci and Schnabel [7] and showed that a 'copolymerization' between the diepoxide and the alcohol takes place via a chain transfer reaction. If a diepoxide is polymerized with a diol or triol, the system becomes cross-linked, whereas the reaction with a monoalcohol leads to dead ends in the polymer network [8]. Crivello et al. [9] measured, that the rate of the photochemically induced polymerization of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate increases if ethylene glycol or 1,4-butanediol are added. At the same time, the conversion of epoxy groups increases within the first three minutes of UV irradiation. The curing rate was examined semiquantitatively using the irradiation time required to receive a tack free coating. No quantitative measurements are available in

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the literature. This is also the case for the comparison of diols with different chemical structures. Corresponding measurements for the cationic photopolymerization of vinyl ethers show that for amounts up to 5% by weight alcohols did not influence the polymerization rate, but they increased the final conversion of double bonds [10]. Since the network density is changed by the reaction between epoxide and alcohol, the mechanical properties of the resulting polymer are also influenced. This can be used for example, in the flexibilization of dental materials with poly(1,4-butanediol) [11] or coatings with polyester polyols [12]. The aim of the work presented here is to show the effect of different polyether diols on the photochemically and thermally induced polymerization of the cycloaliphatic diepoxide 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate and to explain the different behavior of the examined diols.

## 2. Experimental

### 2.1. Materials

The diepoxide used for the experiments was 3,4-epoxycyclohexylmethyl-3′,4′-epoxycylohexane carboxylate (ERL4221, Union Carbide). Poly(1,4-butanediol) ($M_n$ 1400), poly(ethylene glycol) ($M_n$ 200 and 600), diethylene glycol, ethylene glycol and polyethylene glycol-*ran*-propylene glycol) ($M_n$ 2500, 20 mol% propylene glycol) from Aldrich were used as diols. The photoinitiator for the cationic polymerization was Cyracure UVI 6974 (Union Carbide), which is a 50% solution of an aromatic sulfonium salt in propylene carbonate [13]. The counterion of the sulfoniumsalt is hexafluoroantimonate. 0.2 mol% of the initiator was used in all experiments with respect to the diepoxide. The thermal initiator benzyl tetrahydrothiophenium hexafluoroantimonate was prepared according to the literature [14]. This initiator (0.5 mol%) was dissolved in the epoxide to examine the influence of the above mentioned diols and 12-crown-4 (Aldrich) on the thermal polymerization of the cycloaliphatic epoxide. The thermal polymerization was examined by DSC (TA Instruments DSC 2920, 10 K/min, 20–200 °C).

### 2.2. Photopolymerization

The diepoxide/initiator/diol mixtures were prepared and applied onto a gold-coated silicon wafer. The thickness of the reactive epoxide coating was 12 μm. The photopolymerization was examined by real time IR spectroscopy (RTIR) with 50 spectra per second with a Bruker IFS66. The polymerization was followed for 415 s. The substrates were fixed on a HARRICK SEAGULL with the reflection angle adjusted to 20°. The light intensity of the mercury high pressure lamp (SUV-DC-P from Lumatec) was 80 mW/cm$^2$ at the sample. The light intensity was controlled with a calibrated SOLATELL SC10 UV spectroradiator. The samples were placed in a chamber covered with a potassium bromide window. The temperature was 25 °C and the atmosphere inside the chamber was changed approximately every second. The relative humidity of the air flow was 30% and was measured by a calibrated testo 601 hygrometer. In advance of polymerization the samples were equilibrated in this atmosphere for 5 min. During polymerization of the different mixtures the IR-signals which are characteristic for the epoxy group (790 and 750 cm$^{-1}$) disappear and the characteristic band of the formed ether group (1100 cm$^{-1}$) increases. Due to its higher intensity and unique position in the spectrum the band at 790 cm$^{-1}$ is used for the analysis of the epoxide consumption. The degree of conversion is determined after calibration [15] with the monomer and polymers with a complete turn over of the epoxide groups.

## 3. Results and discussion

The cycloaliphatic diepoxide 3,4-epoxycyclohexylmethyl-3′,4′-epoxycylohexane carboxylate was polymerized in the presence of different polymeric diols. The reaction was initiated either photochemically or thermally. The alcohol was inserted into the polymer network by a chain transfer mechanism. During this reaction a proton is released and starts a new chain through the attack of an epoxide ring [7]. The result of this reaction is a new polymer chain containing a hydroxyl end group. This means that the number of hydroxyl groups stays constant during the polymerization of the epoxide with the alcohol. The highest amount of alcohol which can be inserted into the polymer is an equimolar amount relating to the epoxide. In this case, a polymer with alternating epoxide and alcohol units results.

The photoinduced copolymerization was examined by real time infrared spectroscopy (RTIR). Fig. 1 shows the effect of different amounts of poly(1,4-butanediol) on the

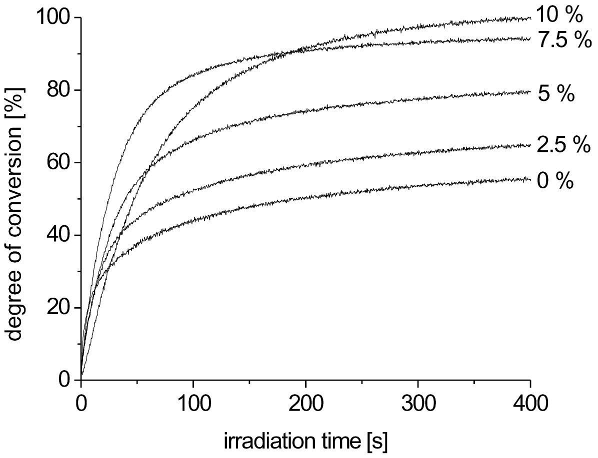


Fig. 1. Degree of conversion of epoxide during the photopolymerization between the epoxide and different amounts of poly(1,4-butanediol) with a $M_n$ of 1400.

course of the polymerization. The polymerization of the diepoxide without alcohol is quick at the beginning of the reaction but slows down already at low degrees of conversion. During the examination time, the final degree of conversion of the epoxide is only approximately 55%. The reason for this is the formation of a dense polymer network with reduced mobility of the reactive groups still present in the mixture. The final degree of conversion increases with increasing amount of diol present in the monomer. This is due to the lower network density of the resulting polymers and the higher mobility of the residual epoxide groups. At low degrees of conversion the rate of the reaction is constant, as long as the content of poly(1,4-butanediol) is below 10 mol%. At a content of 10 mol% the polymerization rate decreases. It seems that the epoxide consumption becomes determined by the alcohol content through the chain transfer reaction carried out by the hydroxyl group, whereas at lower alcohol contents the epoxide consumption is mainly determined by the chain growth reaction.

Fig. 2 shows the degree of conversion of the epoxide groups after the examination time of 415 s for the diepoxide with a poly(1,4-butanediol) content of up to 10 mol%; the curve has a S-like shape. At higher contents of diol it levels to a degree of conversion of 100%. At low contents of diol the degree of conversion of the epoxide increases only little. Obviously the molecular mobility is not increased noticeably at diol levels of less than about 2.5 mol%.

The effect of structurally different diols on the final degree of conversion of the epoxide, as well as on the reaction rate, is shown in Fig. 3. The content of the diols is 7 mol% in each case. It can be seen that for each diol the degree of conversion during the observation time is approximately 80%. Due to the cationic character of the polymerization, postcuring takes place. The experiments are, therefore, not representative for the final state of the samples after a longer reaction time. After a postcuring time of 5 days the gel content of the samples was determined by the extraction with acetone for 48 h. For all samples, the gel content was above 95%. Due to the small differences, the results are not further discussed.

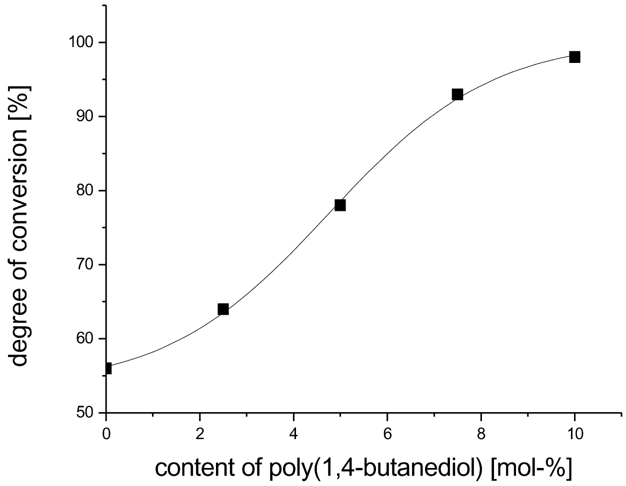


Fig. 2. Dependence of the degree of conversion of the epoxide after 415 s irradiation on the amount of poly(1,4-butanediol) in the reaction mixture.

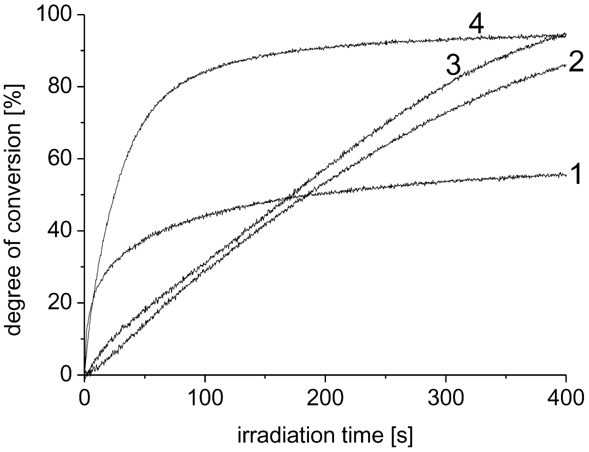
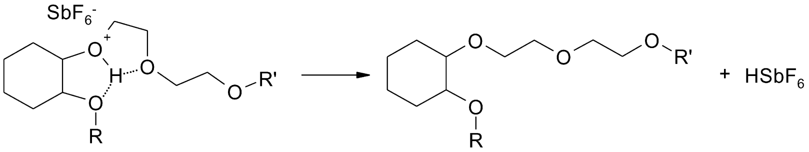


Fig. 3. Dependence of the degree of conversion of the epoxide in the presence of 7 mol% of different diols during irradiation with UV light (80 mW/cm$^2$, humidity of the air 30%): (1) without diol, (2) poly(ethylene glycol-*ran*-propylene glycol) ($M_n$ 2500), (3) poly(ethylene glycol) ($M_n$ 600), (4) poly(1,4-butanediol) ($M_n$ 1400).

Although the final degree of conversion is not greatly influenced, poly(ethylene glycol) and poly(ethylene glycol-*ran*-propylene glycol) influence the polymerization in a different way compared to poly(1,4-butanediol). The rate of epoxide conversion is decreased by the two diols containing two $CH_2$-groups between the ether oxygens (Fig. 3, graphs 2 and 3), but not by poly(1,4-butanediol) (Fig. 3, graph 4) which contains four $CH_2$-groups between the ether bonds. The origin of this effect cannot be the molecular weight of the diols, as the molecular weights of the two diols showing retardation of the polymerization rate are quite different. Furthermore, the ethylene glycol unit cannot by itself be the cause for the retardation, since the diol with propylene glycol units behaves in the same way. The structural unit present in both retarding polymers is the 1,2-linkage of the oxygens compared to the 1,4-positions in poly(1,4-butanediol). One possible explanation for the different behavior of the alcohols lies in the chain transfer reaction. Each attack of a hydroxyl group onto the positive end of the growing polymer chain is the first step of a chain transfer reaction. During this attack a structure like the one shown on the educt side of Scheme 1 is formed. In this scheme the cyclohexane ring represents the basic structure of the cycloaliphatic diepoxide, R the grown polymer chain and R′ the diol. To initiate the growth of the next polymer chain, the proton from the hydroxyl group must be released together with the anion, which is always present close to the cationic chain end [15]. The formed super acid is the initiator for the next chain. If the diol contains oxygen in the 1,2-positions the proton might be fixed within two five-membered rings, as can be seen in Scheme 1. In the case of oxygen in 1,4-positions the proton cannot be stabilized by a



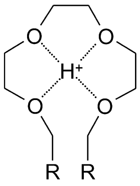
Scheme 1.

second five-membered ring and the formation of the super acid $HSbF_6$ is not as hindered as in the first case. This model suggests that the observed difference between the polymerization of the epoxide with the different alcohols is the deceleration of one step of the chain transfer reaction in the case of oxygen in 1,2-positions of the diol. This is very similar to the retardation of the cationic polymerization of glycidyl ethers by moisture, whereas the polymerization of other epoxides is not retarded [15]. On the other hand, the complexation of protons by polyethers based on 1,2-diols seems to be a possible explanation for the reduced epoxide consumption. In this case, the proton of the acid is fixed in a crown ether like structure (Scheme 2), also leading to a reduced concentration of protons available to initiate the next polymer chain.

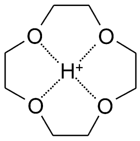
To check if the retardation of the polymerization by polyethers with oxygen in 1,2-positions is specific for the photopolymerization or if it takes place for any method of initiation, additional experiments were carried out. In these experiments, the polymerization was induced by a thermally active latent cationic initiator. 0.5 mol% benzyl tetrahydrothiophenium hexafluoroantimonate was dissolved in the cycloaliphatic diepoxide as a thermal initiator and 7 mol% of the respective diols were added. The thermal polymerization was examined by DSC with a heating rate of 10 K/min. The starting temperatures of the reactions (first noticeable deviation from the base line) and the temperatures of the peak maxima are listed in Table 1. The polymerization in the absence of diols starts at about 99 °C and the peak maximum is at 135 °C. The addition of ethylene glycol or diethylene glycol leads to a decrease in the start temperature to about 91 and to 94 °C, respectively. In contradiction to the decrease in the start temperature the temperature of the peak maximum increases to 137 and 144 °C, respectively. The addition of poly(ethylene glycol) 200, which corresponds approximately to tetraethylene glycol, leads to a start temperature of 102 °C and a peak maximum of 141 °C. The presence of polyetherdiols with the oxygen in 1,2-position and higher molecular weight leads to a further increase of both temperatures to about 108 and 155 °C, respectively. If poly(1,4-butanediol) is added, the start temperature decreases to about 92 °C and the temperature of the peak maximum increases only to 145 °C.

The different behavior of the polymeric diols corresponds with that observed for the photochemically induced polymerization, which shows that the influence of the diols has nothing to do with the fragmentation mechanism of the initiators or the thermal versus photochemical process.

Interestingly the start temperature is reduced due to the presence of the low molecular weight ethylene glycols and the poly(1,4-butanediol). With increasing molecular weight of the ethylene glycols however the start temperature increases. This shows that the presence of the hydroxyl group leads to an activation of the reaction, but if the number of oxygens in 1,2-position in the molecule increases a deactivation mechanism becomes effective. The activation by the hydroxyl group can be explained by its function as a proton donor in the formation of the super acid during initiation and also the increased consumption of the epoxide due to the activated monomer mechanism. Both functions of the alcohol are well known [7], but the deactivation by the 1,2-diols with higher molecular mass has not been previously described. Most likely this behavior is caused by the fixation of the protons in a crown ether like structure, either like the one shown in Scheme 1 or that in Scheme 2. If this is the case, the addition of a crown ether to the epoxide/diol mixture should have a similar effect. As shown in Table 1 this is actually the case. Since a high number of 1,2-ether linkages are already present in the formulations containing the polyethylene glycol 600, the start temperature for the polymerization is not greatly influenced by the addition of the 12-crown-4. But the temperature at which the polymerization of the formulation with poly(1,4-butanediol) starts, increases with increasing amount of the crown ether. For the experiments, 12-crown-4 was chosen as the crown ether with the smallest ring, which should have the highest proton affinity. The ability of crown ethers to form complexes with protons and hydronium ions is well known in the literature [16–18]. A typical structure is shown in Scheme 3. Stabilization of cationically curable epoxides is usually carried out by the addition of amines. The present work shows that crown ethers are also appropriate compounds to stabilize cationically curable epoxide formulations due to



Scheme 2.



Scheme 3.

Table 1

Influence of different diols and 12-crown-4 on the thermal polymerization of the cycloaliphatic epoxide (PEG–poly(ethylene glycol), PPG–poly(propylene glycol), PTHF–poly(1,4-butanediol))

| Compounds added to the cycloaliphatic epoxide | Start of the reaction (°C) | Peak maximum (°C) |
|---|---|---|
| Only epoxide | 98.9 | 135.3 |
| 7 mol% ethylene glycol | 90.5 | 137.4 |
| 7 mol% diethylene glycol | 93.6 | 143.6 |
| 7 mol% PEG 200 | 102.3 | 141.4 |
| 7 mol% PEG 600 | 108.6 | 155.7 |
| 7 mol% PEG/PPG 2500 | 107.6 | 154.9 |
| 7 mol% PTHF 1400 | 91.8 | 145.5 |
| 7 mol% PEG 600 + 1 wt% 12-crown-4 | 106.4 | 156.9 |
| 7 mol% PEG600 + 5 wt% 12-crown-4 | 105.8 | 152.0 |
| 7 mol% PTHF 1400 + 1 wt% 12-crown-4 | 102.4 | 146.1 |
| 7 mol% PTHF 1400 + 3 wt% 12-crown-4 | 101.8 | 144.6 |
| 7 mol% PTHF 1400 + 5 wt% 12-crown-4 | 105.8 | 145.9 |

their ability to fix protons. The same effect can however be achieved by the addition of polyethers with oxygens in the 1,2-position. Actually the compositions containing poly(1,4-butanediol) only start to gel after about three days at room temperature, whereas the other mixtures are stable for more than a month.

The peak maximum is almost independent from the type of diol present in the epoxide. It increases with the molecular weight and therefore the total amount of diol in the mixture. The addition of the crown ether does not influence the peak temperature. The reason for the increasing peak temperature with increasing molecular weight of the diols is, therefore, most likely the dilution of the reactive groups present in the mixtures.

It is occasionally mentioned that the initiation of the cationic polymerization of epoxides is carried out by a formed carbocation in the case of benzyl tetrahydrothiophenium salts (thermal initiator in this study) and similar compounds as initiators and by the super acid in the case of iodonium and sulfonium salts (photoinitiator in this study). However, this is discussed contradictorally in the literature. In the case discussed here, a high amount of alcohol is present and one can assume that a carbocation formed reacts very quickly with the alcohol forming an acid which initiates the polymerization. In the case of the polymerization in the absence of alcohol the formation of the super acid is not necessarily the case. Therefore, one cannot exclude a change in the initiation mechanism by addition of the alcohol. Whether this is the case or not cannot be concluded from the experimental results. But the possible difference only exists for the consumption of the first epoxide group per polymer chain and is, therefore, not relevant for the consumption of the epoxide discussed here.

## 4. Conclusions

From the point of view of a formulator of epoxide compounds it is a technical rule, that cationically curing epoxides react quicker if alcohols are added. For the photochemically curing mixtures, it could be shown that this is only true with respect to the final degree of conversion, within a limited time of observation. If polyetherdiols with oxygen in the 1,2 positions are used as alcohols, the reaction rate decreases, whereas the reaction rate is not greatly influenced by polyetherdiols with the oxygen in the 1,4 positions. Similar results are observed for the thermally induced cationic curing of epoxides. Additionally it could be shown that the polymerization is activated simply by the presence of any alcohol. If the molecular mass of the polyethers with the oxygens in the 1,2 position increases, a deactivation becomes dominant and the start temperature of the polymerization increases. The same effect can be observed in the presence of 12-crown-4 irrespective of the type of diol present in the mixture. As crown ethers are able to complex protons (Scheme 3), one can conclude that this ability is the reason for the inhibition of the cationic polymerization. 1,2-Polyethers are also able to form conformations with crown ether like structures. One can suggest that such structures are formed by the complexation of the proton as shown in Scheme 2. In both cases, the protons formed during the decomposition of the initiators, or released during the chain transfer reaction, are fixed and are temporarily not available for the start of the next chain reaction. On the other hand such a complexation can already take place during the chain transfer reaction, as shown in Scheme 1. If this is the dominant reaction, compared to the complexation by the polyether chain itself, a strong retardation should be observed for diethylene glycol. The reaction product between the chain end of the polymerizing epoxide and this diol has four oxygen atoms in the 1,2 positions and the proton is already present in this complexing environment. Since no inhibition, but an acceleration, can be observed in the presence of diethylene gylcol, one can conclude that the retardation of the chain transfer process is not the limiting factor for the whole reaction.

Furthermore, one can conclude that crown ethers, especially 12-crown-4, are appropriate stabilizers for cationically curable monomers and are an alternative to the conventionally used amines for this purpose. The results show that one should be able to adjust the reactivity of cationically curing epoxide formulations by the choice of the appropriate diol.

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