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Influence of moisture on the photochemically induced polymerisation of epoxy groups in different chemical environment

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Abstract

The influence of atmospheric humidity on the photochemically induced cationic polymerisation of epoxy groups in different chemical environments is shown. With increasing humidity, the polymerisation rate of glycidylethers decreases, whereas for epoxides with endocyclic epoxy groups the rate of polymerisation increases and the rate for epoxides with exocyclic epoxy groups is nearly not influenced. The reasons for the different behaviour are energetic differences for the reactions between the positively charged chain ends with water and the following proton transfer. Furthermore the reaction rate is influenced by the different stereochemistry of the attack of the next monomer. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxide; Cationic polymerisation; Water

1. Introduction

In recent years, the processing and the applications of the cationic photopolymerisation of epoxides were developed and new initiators were found. Mainly diaryliodonium and triarylsulfonium salts with BF_4^-, PF_6^-, AsF_6^- and namely SbF_6^- counterions are appropriate initiators [1,2]. Although it is well known, that water and other hydrogen donating species influence the cationic polymerisation strongly, the effect of protic compounds on the photopolymerisation of epoxides is not fully understood. In the majority of publications it is not even mentioned in which atmosphere the experiments were carried out. Among others Decker and Moussa [3] discuss, that the advantage of the cationic photopolymerisation of epoxides is the insensitivity against air and namely oxygen compared to the radical photopolymerisation of acrylates. Their results show, that a formulation of a sulfonium salt and 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate polymerises with the same velocity at the beginning of the reaction independently whether the atmosphere is nitrogen or air. In air, the final degree of conversion is higher. The molecular reason for this observation was not explained in the literature up to now. If water is added, for the cationic photopolymerisation of vinyl ethers it is found that the rate of polymerisation decreases and the final degree of conversion increases [4]. This is explained by chain transfer reactions involving the −OH groups formed by the reaction of the growing chain ends with the water.

Water and other proton donors act in the cationic photopolymerisation of epoxides in a variety of ways. On one hand, a proton donor is required as co-catalyst for the formation of the super acid which initiates the polymerisation reaction [5], as long as the polymerisation is not initiated directly by the carbocation formed. On the other hand, we have shown [6] that an extensive contact of the monomer/photoinitiator mixture to humid air leads to a deactivation of the initiator by hydrolysis of the organic cation as well as the anion of the super acid. Furthermore the presence of water or alcohols leads to chain transfer reactions [3,5]. The basic reactions for the photochemical decomposition of a sulfonium salt are shown in Scheme 1. Usually the initiator is split of homolytically and the polymerisation is initiated either by the cationic species or the super acid. The basic reactions for the initiation, the chain growth and the chain transfer of the epoxide polymerisation are shown in Scheme 2 [3]. The initiation is shown for the formed acid as example. In our previous work [6] it is shown that a mixture of an iodonium salt as initiator and 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate as monomer polymerises with a higher rate in air with 40% relative humidity than in air with a relative humidity of 30%. This observation is similar to the findings of Crivello [7]. It is observed, that the addition of hydroxyl containing

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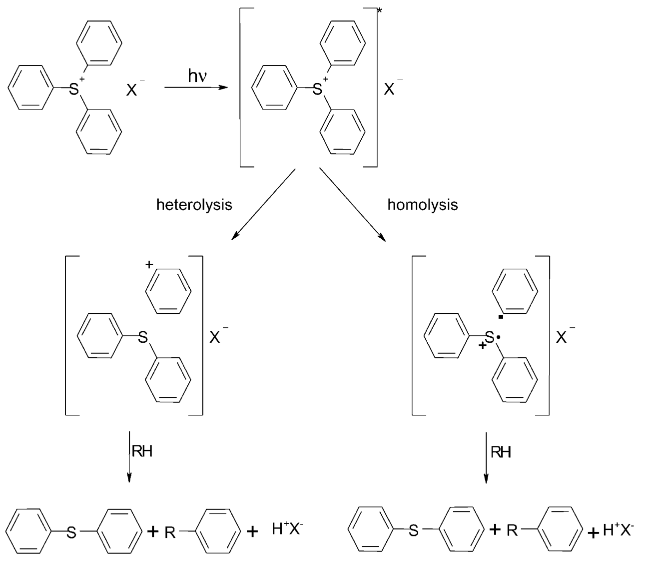
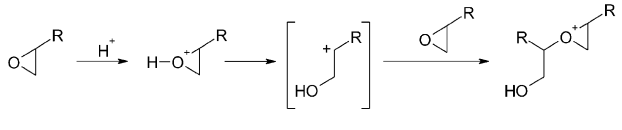
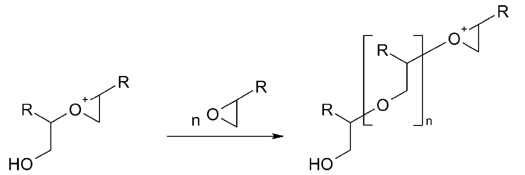


Scheme 1.

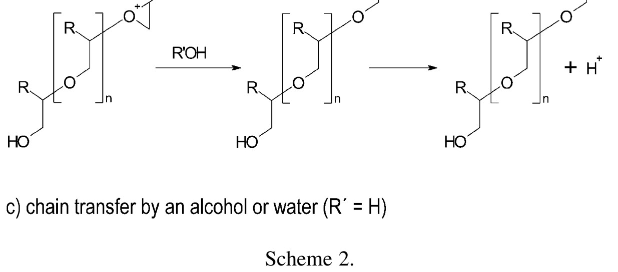
compounds (e.g. water and alcohols) results in an increased rate of polymerisation due to chain transfer. The aim of the work presented here is to show the effect of the humidity of the atmosphere on the photochemical polymerisation of epoxides with epoxide groups in a different chemical environment. Furthermore a model for the mechanistic explanation of the experimental findings is given.



a) initiation and reaction with the next monomer



b) chain growth



c) chain transfer by an alcohol or water (R′ = H)

Scheme 2.

2. Experimental

2.1. Materials

Bisphenol A diglycidylether (Epikote 234, Shell, viscosity 7000 mPa s), 4-vinyl-1-cyclohexene diepoxide (Aldrich, viscosity 32 mPa s), and 3,4-epoxycyclohexylmethyl-$3',4'$-epoxycyclohexane carboxylate (Degacure K126, Degussa, viscosity 300 mPa s) were used as epoxy resins. The initial water content of all epoxides was below 0.05% (Karl Fischer titration). A sulfonium salt with hexafluoroantimonate anion was used as photoinitiator (Sarcat CD-1010, Sartomer). This initiator is a 50 mass% solution of a mixture of the two components shown in Table 1 in propylene carbonate and is used as received. The structures of the components are shown in Table 1.

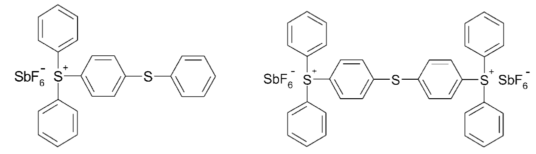
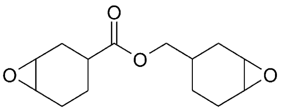
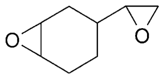
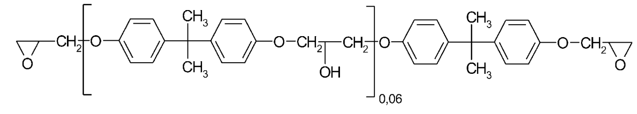
2.2. Polymerisation

Mixtures of the monomers with 0.2 mol% of the initiator were prepared and cast onto a gold-plated silicon wafer. The casting knife applied leads to a film thickness of 12 μm. The photopolymerisation was followed by real time IR spectroscopy (RTIR) with 50 spectra per second with a Bruker IFS66. The reaction was pursued for 415 s. During the IR experiments, the substrates were fixed on a HARRICK SEAGULL adjusted to a reflection angle of 20°. The light intensity of the mercury high pressure lamp (SUV-DC-P from Lumatec) was 80 mW cm^{-2} at the sample. The intensity was controlled with a calibrated SOLATELL SC10 UV spectroradiator. The samples were placed in a chamber covered with a potassium bromide window. Inside the chamber, the temperature was 25 °C and the air flow through the chamber was adjusted in a way, that the atmosphere was changed approximately once per second. The humidity of the air flow was measured by a calibrated testo 601 hygrometer. In advance of polymerisation the samples were equilibrated in the atmosphere with the chosen humidity for 5 min. Even at the highest humidities no increase of the water signals or other changes in the IR-spectra were observed during equilibration.

2.3. Molecular modelling

In this work, the density functional program DMol [8–11] is applied. This method works with numerically generated atomic orbitals as basis functions and a self-consistent solution of the Kohn–Sham equations with a conventional matrix diagonalisation. The gradient-corrected functional BP is used (exchange [12] and correlation [13]). The basis set we used is called double-numerical with polarised functions (DNP). A double-numerical (DN) basis is comparable with a split valence basis. The best convergence (eigenvector-following [14]) is achieved with non-frozen core orbitals and a fine integration grid.

Table 1
Structure of the compounds used

Sarcat™CD-1010 (Sartomer)	 50 mass-% in propylene carbonate $M_{eq} = 537.43$ g mol^{-1}
Degacure® K126 (Degussa)	 $M_{eq} = 126.16$ g mol^{-1}
4-Vinyl-1-cyclohexene diepoxide (Aldrich)	 $M_{eq} = 70.09$ g mol^{-1}
Epikote 234 (Shell)	 $\bar{M}_{eq} = 179.3$ g mol^{-1}

3. Results and discussion

During the polymerisation of the different epoxides the IR-signals which are characteristic for the epoxy group (790 and 750 cm^{-1} for the endocyclic and alicyclic epoxy groups and 915 and 764 cm^{-1} for the glycidyl ether) decrease whereas the characteristic band of the formed ether group (1100 cm^{-1}) increases. Due to the higher intensity and the unique position in the spectrum the band at 790 cm^{-1}, respectively, 915 cm^{-1} is used for the analysis of the epoxide consumption. If the polymerisation is carried out in a water containing atmosphere, an additional broad band is formed at 3300 cm^{-1} which can be attributed to hydroxyl groups formed. Fig. 1 shows the spectra of a Degacure K126 layer in advance of curing and after 415 s of irradiation in air with a relative humidity of 30% as example. As can be seen in the figure, the epoxy groups are not fully turned over after the chosen irradiation time. This is the case in most of the experiments carried out. The epoxy signals disappear if the samples are stored for some days. This shows that a post curing reaction takes place, which is characteristic for the cationic chain growing polymerisation of epoxides. The spectra in Fig. 1 show that a shoulder is formed at the low wavenumber side of the ester carbonyl band at 1740 cm^{-1}. Such a shoulder is characteristic for hydroxy esters and is caused by the interaction of the hydroxyl proton with the ester carbonyl. The formation of the shoulder therefore supports the formation of hydroxyl groups during polymerisation as detected by the formation of the band at 3300 cm^{-1}. Although the hydrolysis of esters is usually slower than the cationic polymerisation of an epoxide, it is imaginable, that the spectral changes are caused by carboxylic acid formed. As no carboxylic acid could be detected on the surface of the polymer films by the method of Chilkoti [15] this possibility can be excluded.

Fig. 2 compares the course of the polymerisation reactions for the three selected diepoxides at a relative air humidity of 20%. 4-Vinyl-1-cyclohexene diepoxide is the most reactive monomer, but the reaction slows down at a turn over of about 50% and appears to stop within the time of observation. The observation can be explained if mainly one of the two different epoxide functionalities of the monomer takes part in the reaction. The bisphenol A diglycidylether Epikote 234 is less reactive. The cycloaliphatic diepoxide Degacure K126 shows the lowest reactivity.

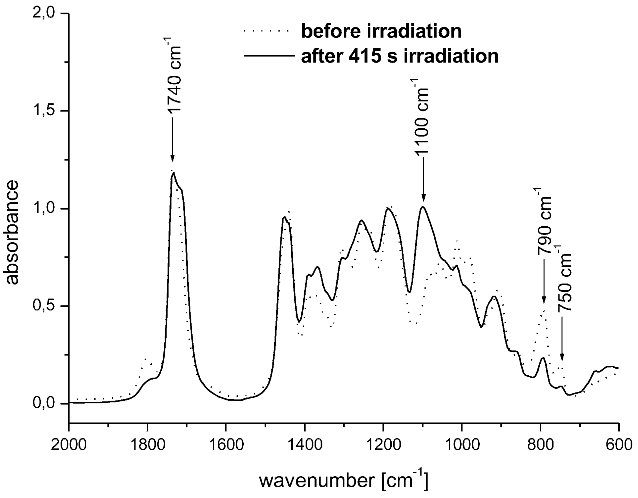


Fig. 1. IR-spectra of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate before and after photopolymerisation.

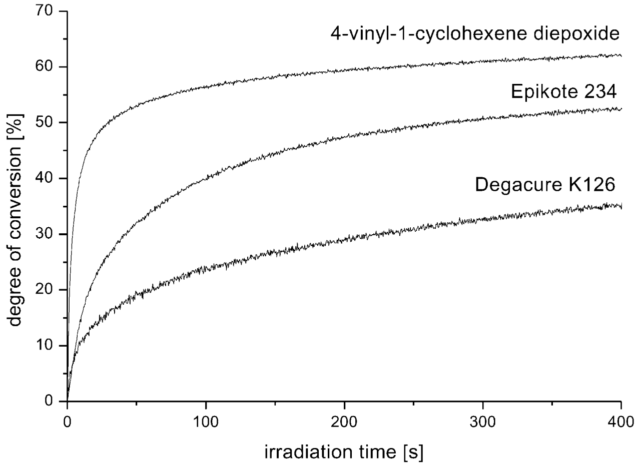


Fig. 2. Photopolymerisation of 12 μm thick films (order from top) of 4-vinyl-1-cyclohexene diepoxide, bisphenol A diglycidylether (Epikote 234) and 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (Degacure K126) in air with 20% relative humidity.

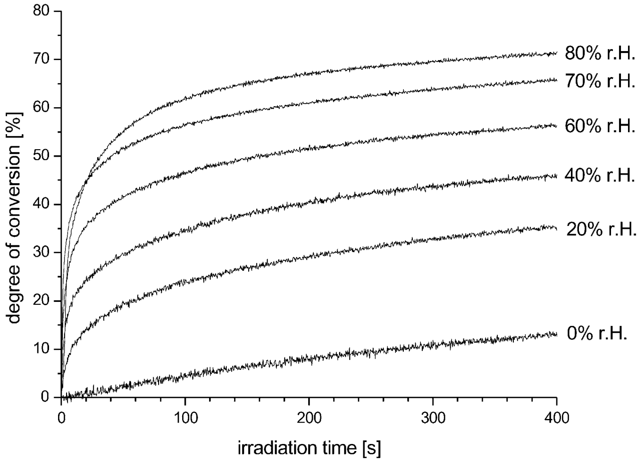


Fig. 4. Photopolymerisation of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate in air with 0, 20, 40, 60, 70 and 80% relative humidity.

The observed reactivity of the later two resins is in the reverse order of previously published results [16]. This might be explained with the lower humidity of the air in which our reactions are carried out, leading to a limited number of chain transfer reactions. As the Epikote 234 contains a small amount of hydroxyl groups, the reaction can be accelerated by chain transfer reactions, which is not the case for the cycloaliphatic diepoxide. If one compares the polymerisation properties of different monomers, not only the reactivity but also the viscosity might influence the reaction rate. One expects that the reaction rate decreases with increasing viscosity. This is also the reason for the decreasing reaction rate at higher degrees of conversion. The 4-vinyl-1-cyclohexene diepoxide has the lowest viscosity (32 mPa s) and highest reaction rate of the three monomers. The monomer with the highest viscosity (Epikote 234, 7000 mPa s) has the medium reaction rate and the monomer with the medium viscosity (Degacure K126, 300 mPa s) has the lowest reaction rate. The different orders of viscosity and reaction rate shows, that differences of the viscosity cannot explain the order of the reaction rates and turn over. Furthermore one has to take into account, that the viscosity increases strongly already at a low turn over, e.g. one can assume (unfortunately not measure, because the reaction cannot be stopped after a distinct turn over) that the viscosity of the 4-vinyl-1-cyclohexene diepoxide at a turn over of 20% or so is higher than the initial viscosity of the other monomers, but the reaction rate is still higher. The reasons for the different reactivities are the differences of the reaction mechanism of the side reaction with the moisture of the air, as discussed in the next chapters.

To examine the influence of moisture on the cationic polymerisation, the three diepoxides are photopolymerised in air with different humidity (Figs. 3–5). Fig. 3 shows that the polymerisation of the 4-vinyl-1-cyclohexene diepoxide is hardly influenced by the humidity of the surrounding atmosphere. With increasing humidity just a slight increase

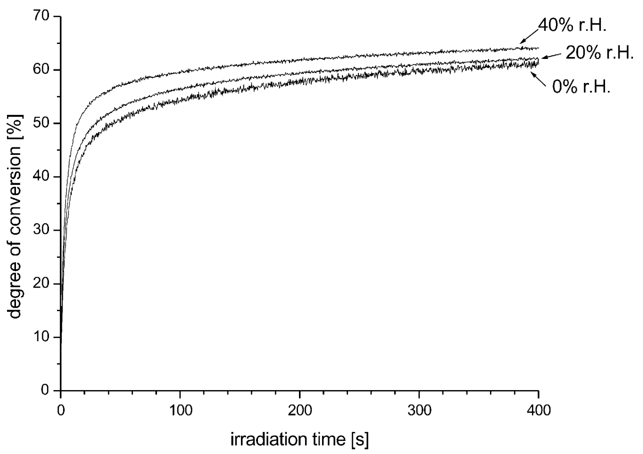


Fig. 3. Photopolymerisation of 4-vinyl-1-cyclohexene diepoxide in air with 0, 20 and 40% relative humidity.

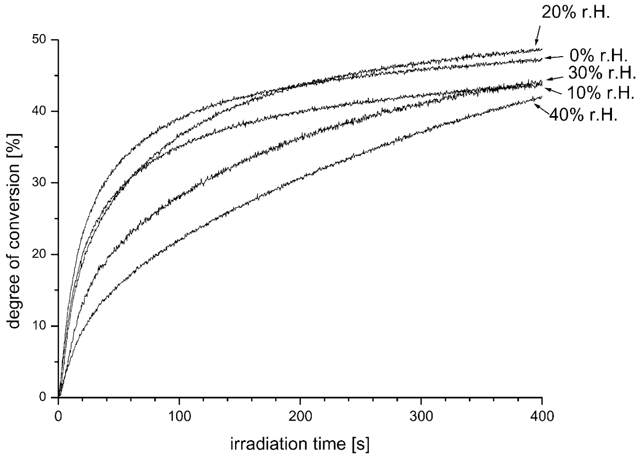


Fig. 5. Photopolymerisation of bisphenol A diglycidylether (Epikote 234) in air with 0, 10, 20, 30 and 40% relative humidity.

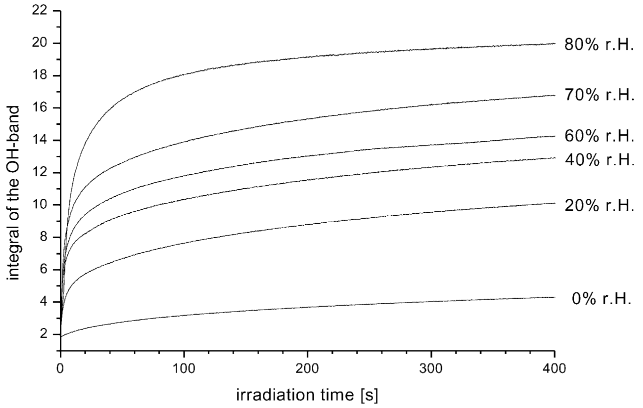
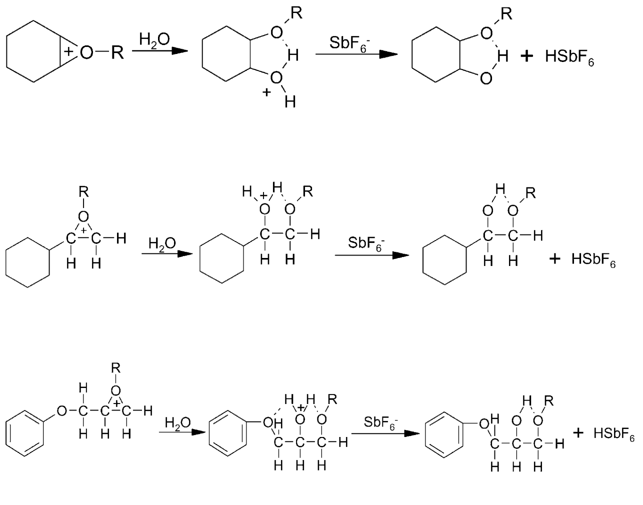


Fig. 6. Formation of –OH groups (integral over the band at 3300 cm^{-1}) during the photopolymerisation of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate in air with 0, 20, 40, 60, 70 and 80% relative humidity.

in the degree of conversion is observed. In contrast, the final degree of conversion as well as the polymerisation rate of the cycloaliphatic diepoxide Degacure K126 increase strongly with increasing humidity of the atmosphere (Fig. 4). On the other hand, the polymerisation rate of the diglycidylether Epikote 234 decreases with increasing humidity and the final degree of conversion is weakly influenced by the humidity within the duration of the experiment (Fig. 5).

Fig. 6 shows the dependence of the integral over the –OH band at 3300 cm^{-1} on the irradiation time of the cycloaliphatic diepoxide Degacure K126 at different humidities. The integral of the –OH band increases with increasing humidity of the air in which the reaction takes place. The relationship between the degree of conversion of the epoxide groups and the integral of the –OH band is linear. This shows that hydroxyl groups are formed due to the reaction with water, and not only the rate and final degree of conversion is influenced by the moisture but also the chemical composition of the resulting polymer.



Scheme 3.

Although it is well known, that moisture influences the initiation reaction (e.g. water may act as proton donor as shown in Scheme 1), this cannot be the reason for the differences measured, as the initiator is the same for the polymerisation of all three diepoxides. Therefore one must assume that differences in the chain growing or the chain transfer reactions of the epoxide groups in different chemical environment are the reason for the different behaviour. For the cationic polymerisation it is well known, that nucleophilic proton donors (e.g. water and alcohols) can attack the positive centre of the growing chain. Such an attack is the first step for a chain transfer shown in Scheme 2c. Formally the reaction between the growing chain and water leads to the formation of an oxonium ion. The formal oxonium ion transfers a proton to an appropriate reaction partner (e.g. water, anion, monomer, see below). Due to this reaction a hydroxyl group is formed which is also able to carry out a chain transfer reaction. This means that every water molecule reacting with the polymerising material can lead to two chain transfer reactions. The chain transfer reaction carried out by the formed alcohol is basically identical to the polymerisation of epoxides by the activated monomer mechanism described by Yagci and Schnabel [17].

To explain the different behaviour of the three diepoxides with epoxy groups in a different chemical surrounding, molecular modelling is used. As the molecules are quite complex, the following model structures were chosen for the calculations: cyclohexene oxide for cycloaliphatic epoxy groups, phenyl glycidylether for aromatic glycidylethers and vinyl cyclohexane oxide for an exocyclic epoxy group. A methyl group is used instead of the growing polymer chain (R in Scheme 3). The structure of reactants and products as well as the energy of the following reaction steps are calculated:

- attack of the positive end of the growing polymer chain by the water molecule forming an oxonium ion (Scheme 3);
- transfer of a proton to a water molecule (not shown);
- transfer of a proton to the hexafluoroantimonate anion (Scheme 3).

The conformations with the energy minima are calculated for the different reaction products. For cyclohexene oxide a 3D structure of the reaction product between water and the chain end is shown in Fig. 7 as example for the structures formed. It can be seen, that the protons of the added water are fixed via hydrogen bonds in a five-membered ring. The fixation of the protons by H-bonds within five-membered rings is shown for all model epoxides with standard structural formulas in Scheme 3. In each case the additional proton is located in the middle of the two oxygen atoms (bond lengths to the two oxygen between 0.10 and 0.15 nm). After abstraction of the additional proton the lengths of the hydrogen bond between the proton of the hydroxyl group formed and the neighbouring oxygen is in

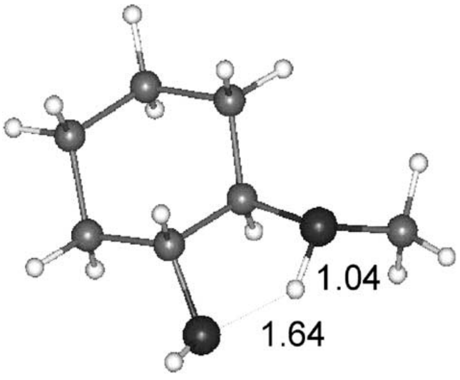


Fig. 7. Structure of the cyclohexene oxide cation after reaction with water. The numbers are the bond lengths in Å.

the range of 0.22 nm, whereas the O–H bond length is approximately 0.1 nm. The calculated energies are summarised in Table 2. The results show that the attack of the growing chain by water and the transfer of the proton to the hexafluoroantimonate anion are reactions with an energy release. In contrast to this, for the transfer of the proton to a water molecule forming an hydroxonium ion, energy is required. This result shows that, if an hydroxonium ion is present in the polymerising mixture, the proton will be transferred to a hydroxyl group but not vice versa. In addition to the energy gain by the transfer of the proton to a hexafluoroantimonate anion the transfer to the anion should be favoured by electrostatic reasons, because the anion is always close to the positive charge. From the preferred proton transfer to the hexafluoroantimonate compared to water, one can conclude that the initiation of the new polymer chain—as the final step of the chain transfer—is carried out by the magic acid $HSbF_6$ and not by H_3O^+.

Table 2 shows that the energy gain for the addition of water by the positive chain end is the highest for the glycidylether (Epikote 234). This is most likely caused by the fixation of both protons in a pair of five-membered rings (Scheme 3). At the same time the transfer of the proton to the hexafluoroantimonate anion is connected with the lowest energy gain for this compound. This means that the protons are fixed effectively by the hydration of the glycidylether cation and are therefore not accessible for the initiation of the next chain. In other words one step of the chain transfer reaction is inhibited and the result is the decrease of the polymerisation rate with increasing relative humidity of the atmosphere shown in Fig. 5.

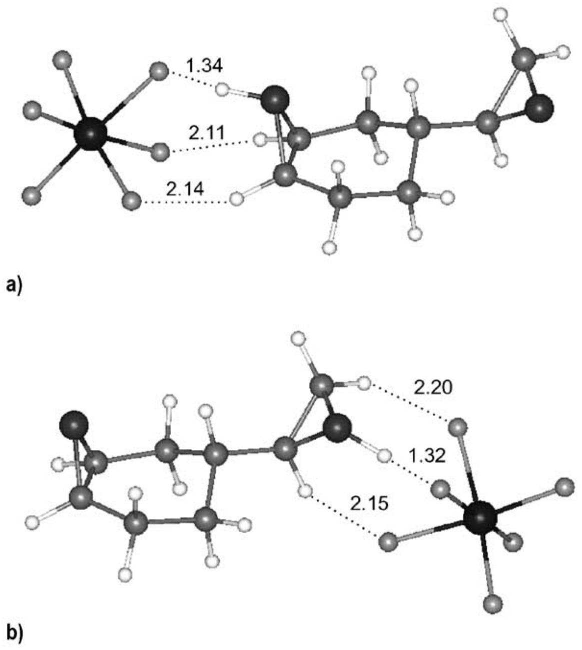


Fig. 8. Conformation of protonated 4-vinyl-1-cyclohexene diepoxide stabilised by the hexafluoroantimonate anion. (a) Protonation of the endocyclic epoxy group. (b) Protonation of the exocyclic epoxy group. The numbers are the bond lengths in Å.

But the different behaviour of the two other epoxides cannot be explained by the results shown in Table 2. The polymerisation rate of the monomer with only cycloaliphatic epoxy groups (Degacure K126, Fig. 4) increases with increasing humidity of the atmosphere. This increase can be explained with the aid of Fig. 8. For electrostatic reasons the hexafluoroantimonate anion is located close to the cation. Fig. 8 shows that the anion fits perfectly onto the protonated epoxide rings if the ion pair is in the conformation which corresponds to the energy minimum. The bond lengths between the fluorine atoms and the atoms of the epoxide ring are 0.13 nm (H bond to O), respectively, 0.21 nm (H bond to C). Compared to a single interaction between one of the fluorine atoms and the proton bond to the oxygen the conformation shown is more favourable by about $-48\ \mathrm{kJ\ mol^{-1}}$. Fig. 8(a) shows the conformation of the cycloaliphatic epoxy group (e.g. Degacure K126 and 4-vinyl-1-cyclohexene diepoxide). For the chain growth

Table 2
Energy required or released for different partial reactions

	ΔE (kJ mol^{-1})		
	Cycloaliphatic epoxide	Glycidylether	Exocyclic epoxide
Addition of H_2O	− 91	− 131	− 104
Proton transfer to H_2O	182	192	160
Proton transfer to SbF_6^-	− 147	− 136	− 169

the reaction with the next epoxide is required. This is obviously difficult by sterical reasons. As long as the hexafluoroantimonate anion is in the preferred configuration, the attack is only possible from the side of the cyclohexane ring. Since water is a small molecule it can attack the group and the turn over of the epoxide is increased by chain transfer reactions. By this reaction an alcohol is formed which is sterically not as exacting as the epoxide, too. The chain transfer by this alcohol again forms an alcohol, and so on. Due to this the polymerisation proceeds mainly due to the chain transfer. Therefore the turn over increases with increasing humidity of the atmosphere. As ether linkages are formed by the polymerisation as well as by the chain transfer, the polymer structure formed is the same in both cases, beside the OH-end groups in the case of the polymer formation by the chain transfer. In contrast to the protonated endocyclic epoxy groups, protonated exocyclic epoxy groups are free rotatable and the anion does not shield the group effectively. The conformation is shown in Fig. 8(b) for the exocyclic epoxy group of 4-vinyl-1-cyclohexene diepoxide. Such protonated epoxy groups can be attacked easily by the next epoxide from the other side. Due to the free rotatability the reaction of this group is quick without chain transfer reactions.

Additionally to the lower energy gain the attack of the exocyclic epoxy group of 4-vinyl-1-cyclohexene diepoxide by water is lowered compared to the other epoxides because of the quick reaction with the next epoxide. The lower number of reactions with water is confirmed by the much lower intensity (approximately by a factor of 10) of the hydroxyl band in the IR-spectra of the polymer formed by polymerisation of 4-vinyl-1-cyclohexene diepoxide (turnover up to 50%) compared to the purely cycloaliphatic diepoxide Degacure K126. This shows that the number of hydroxyl groups formed during polymerisation of the exocyclic epoxy group of 4-vinyl-1-cyclohexene diepoxide is low. From the discussion of the results one can assume, that the epoxy groups of the 4-vinyl cyclohexene diepoxide turned over during the time of the experiment are mainly the exocyclic epoxy groups of this monomer and not the cycloaliphatic epoxy groups. The structures of Fig. 8 are valid for the case that the epoxide groups are attacked by a proton. In other word a new polymer chain is started as the last step of a chain transfer reaction or the polymerisation is initiated by the hexafluoroantimonic acid as one of the decomposition products of the initiator. In the case of the conventional chain growth or the initiation by cationic species, the proton at the oxygen must be replaced by the polymer chain or the cationic species. In this case the positively charged epoxy group is not only sterically shielded by the hexafluoroantimonate anion but also by the organic rest. Although the structures are slightly different, the argumentation for the different reactivity of the different epoxy groups is the same as discussed for the structures shown in Fig. 8.

In advance of the reaction with the growing polymer chain the water must diffuse into the films. As the reaction rate as well as the turn over were the same for 6, 12 and 24 μm thick monomer layers, one can conclude, that the reaction with the atmospheric moisture is not diffusion controlled in this thickness range. Nevertheless one cannot exclude that the amount of water diffusing into the film is partially determined by the solubility of water in the polymerising film. If the solubility of water in the three reacting systems is different, this will have an influence on the absolute changes of the reaction rate and turn over by the water. But it will not change the fact discussed in this paper, that the reaction of some monomers is accelerated by the moisture and that of other monomers is decelerated or nearly not influenced.

4. Conclusions

It could be shown that the influence of moisture on the cationic photopolymerisation of epoxides depends strongly on the chemical environment of the epoxy group. The reasons for the different behaviour are given below.

- The retardation of the proton release as a step of the chain transfer reaction of the cationic structure formed by the reaction of water with the positively charged growing chain.
- Differences of the stereochemistry of the epoxy groups. After attack of the growing chain end by a water molecule the chain growth stops. A proton must be released to initiate the next chain. The release of the proton is retarded by the interaction with two oxygen atoms in a five-membered ring. If the reaction is carried out with glycidyl ethers, both protons of the added water are stabilised within a dual five-membered ring system. Therefore the reaction rate decreases strongly with increasing humidity; one step of the chain transfer is inhibited. The reaction of epoxides with a free rotatable exocyclic epoxy group which is not bound via an oxygen is hardly influenced by moisture. The reason is the lower energy release for the reaction with water and the lower stability of the five-membered ring compared to glycidylethers. Furthermore the reaction of monomers with exocyclic epoxy groups like 4-vinyl-1-cyclohexene diepoxide is already very quick without chain transfer reactions. Due to this quick reaction the probability for a reaction with water is low. The reaction rate of epoxides with endocyclic epoxy groups increases with increasing humidity. The main reason for this is the sterical hindrance of the growing polymer chain because the hexafluoroantimonate anion shields the cation in a way that the attack of the next monomer is only possible from the side of the cyclohexane ring or the hexafluoroantimonate anion has to move to a thermodynamically less stable position. The reaction of the shielded chain end with the small water molecules or the sterically less exacting alcohols (compared to the cycloaliphatic

epoxide) is not hindered as strong. Therefore the reaction proceeds mainly due to chain transfer reactions caused by the water. As the chemical composition (formation of –OH groups) of the resulting polymer is different if the polymerisation is carried out in atmospheres of different humidity, one can assume, that the properties of the polymers are different. This will be published soon.

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