

# Polyepoxides; formation and properties of their network structure

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# Polyepoxides; formation and properties of their network structure

E. W. Meijer

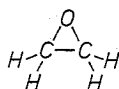
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*Polyepoxides are polymer materials widely used in the electronics industry, and there is much interest today in a better understanding of their structure at the molecular level. The article below discusses two methods — phosphorescence spectroscopy and nuclear magnetic resonance spectroscopy — that can be used to give 'a closer view' of polyepoxides.*

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## Linear-chain polymerization

Polyepoxides are obtained by the polymerization of epoxide monomers<sup>[1]</sup>. Epoxides have the structural feature of a three-membered ring, consisting of two carbon atoms and one oxygen atom. The simplest monomer is ethylene oxide:



The ideal bond angles of carbon and oxygen cannot be realized in a three-membered ring. The bonds in an epoxide ring are forced to take up 'unusual' angles averaging 60° (instead of about 109°), which results in a structure possessing an internal ring strain and a corresponding strain energy of about 60 kJ/mol.

A chemical reaction that opens the epoxide ring (*fig. 1*) gives a gain in energy because of the loss of ring strain. This energy gain provides the thermodynamic basis for the 'ring-opening polymerization' of epoxides<sup>[2]</sup>.

Apart from the fulfilment of this thermodynamic condition, a good kinetic route has to be found along which the polymerization can take place sufficiently rapidly. This usually requires a catalyst or initiator. By a catalyst we mean a compound that greatly increases the rate of polymerization but is not used up in the reaction. An initiator may be necessary to start the polymerization in some cases, but does take part in the reaction, usually becoming incorporated in the polymer.

Various monomers are of importance in the applications of epoxide-based polymers. In these complex monomers one or more hydrogen atoms in ethylene oxide are replaced by other atoms or groups of atoms. Steric interaction between these substituents in the epoxide ring increases the ring strain. However, this may not give an increased reactivity in polymerizations; this depends on the nature of the reaction mechanisms for the various types of polymerization.

The polymerization can take place in the form of an addition reaction between compounds of the same kind, 'chain polymerization', or in the form of a step reaction — a succession of individually catalysed reactions between different kinds of compounds — 'condensation polymerization'<sup>[2]</sup>.

Chain polymerizations can be initiated by activating the epoxide ring of a monomer by a catalyst in such a way that it can react with a non-activated monomer. The resultant dimer remains activated, and so do the trimer, tetramer and so on. In this way hundreds or thousands of monomers can be concatenated to form a polymer in the 'propagation step' of the polymerization. In a 'termination reaction' the chain is deactivated and the catalyst is re-formed. It can then be used again to catalyse the formation of another chain. The catalyst can be an acid (a cationic catalyst) or a base (an anionic catalyst). *Fig. 2a* shows the progress of an acid-catalysed polymerization. The polymerization of epoxides started by an initiator can be regarded as a repetitive reaction in which the initiator is lengthened by one monomer unit at each repetition. The initiator may be for example an organo-

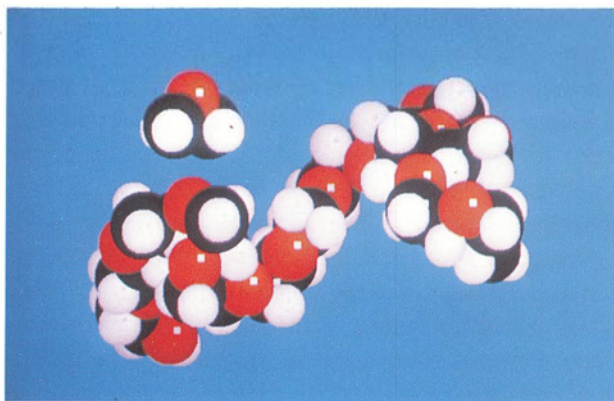


Fig. 1. Three-dimensional computer model of ethylene oxide (a) and polyethylene oxide (b). The spheres represent the Van der Waals radii of the various atoms. The models were produced by 'molecular-mechanics optimization'.

metallic compound (coordinative initiation). In this case the polymerization is terminated without the initiator being re-formed.

The reaction rates of these chain polymerizations may differ considerably. For instance, polymerizations catalysed by an acid like  $\text{BF}_3$  may often have to be carried out at a temperature below  $-50^\circ\text{C}$  to sustain the reaction, which is exothermic. On the other hand, polymerizations catalysed by a base, such as imidazole, only reach an acceptable rate at a temperature of about  $100^\circ\text{C}$ .

The second form of polymerization, condensation polymerization, is of great practical importance, since it is the basis for the widely used epoxy resins. Although it is mainly polymer networks that are produced in this way, the principle will be discussed here for linear chains. To synthesize such polymers a mixture of two kinds of compounds is used. One kind has two epoxide rings and the other contains two functional groups that can react with epoxide rings, e.g. amines, hydroxides or phenolic hydroxyl groups. Multiple repetition of the ring opening, catalysed each time, produces a polymer in a succession of steps (fig. 2b).

The macroscopic (physical, chemical and mechanical) properties of the polymeric end-product depend on the way in which the polymers are formed. In chain polymerization a cyclic ether (an epoxide) is converted into a linear — and much more stable — ether, built up by a regular repetition of a C-C-O unit in the main chain of the polymer (fig. 2a). Such regularly structured polymers have a strong tendency to crystallize. In condensation polymerizations of epoxides the main chain always contains polar side chains in the form of hydroxyl groups. These polymers are not so highly regular, and therefore tend to have the properties of amorphous glassy systems.

For completeness it should be mentioned that there are also combined forms of the two modes of polymerization described above, which can result in highly complicated systems.

### Formation of three-dimensional networks

A recent article in this journal dealt with the applications of polymer chemistry in the electrical industry<sup>[3]</sup>. An important feature in this chemistry is making polymer material insoluble. This can be done by linking linear polymers together, or by simultaneously polymerizing and cross-linking multifunctional monomers<sup>[4]</sup>. The latter method is widely used for making polyepoxides from bisepoxides containing two epoxide rings. Some examples are shown in fig. 3.

The many and various ways in which the chemical structure of these bisepoxides can be modified, and the diversity in polymerization reactions, ensure that materials can be produced to fit the particular speci-

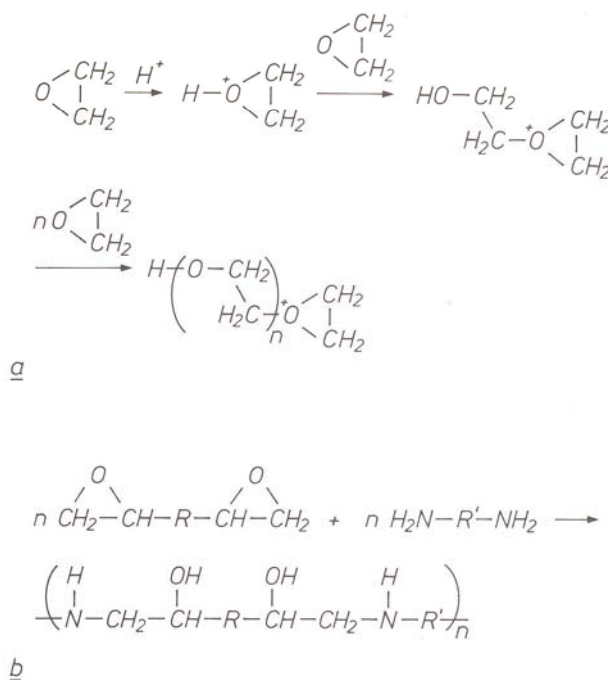
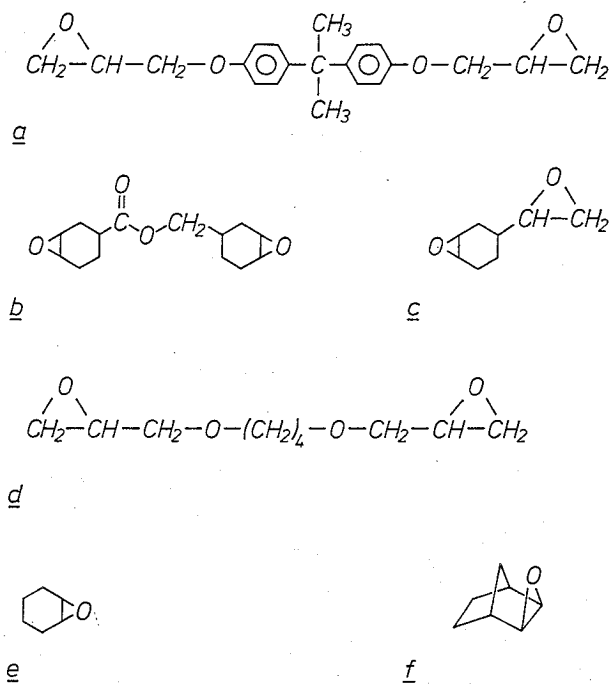


Fig. 2. a) Mechanism of an acid-catalysed chain polymerization of epoxides. b) Reactions for a condensation polymerization of a bisepoxide with a diamine. R and R' represent linking chains.

- [1] Y. Ishii and S. Sakai, in: Ring-Opening Polymerization, K. C. Frisch and S. L. Reegen (eds), Marcel Dekker, New York 1969, pp. 13-109.
- [2] S. Inoue and T. Aida, Cyclic ethers, in: Ring-Opening Polymerization, part 1, K. J. Ivin and T. Saegusa (eds), Elsevier, Barking 1984, pp. 185-298.
- [3] L. K. H. van Beek, Polymer chemistry in the electrical industry, Philips Tech. Rev. 42, 149-159, 1986.
- [4] J. G. Kloosterboer, G. J. M. Lippits and H. C. Meinders, Photopolymerizable lacquers for LaserVision video discs, Philips Tech. Rev. 40, 298-309, 1982.



**Fig. 3.** Four examples of widely used bisepoxides and two monoepoxides that we used as models. *a*) bisphenol-A diglycidyl ether, *b*) (3,4-epoxycyclohexyl)-methyl 3',4'-epoxycyclohexane carboxylate, *c*) 1-epoxyethyl-3,4-epoxycyclohexane, *d*) 1,4-butanediol diglycidyl ether, *e*) cyclohexene oxide, *f*) exo-2,3-epoxy-norbornane.

cations for any application. For most purposes condensation polymerization of two different compounds is used, because this is the method that offers the most variations in molecular structure. Examples are the epoxy resins for the encapsulations of ICs and discrete components, laminated resins for printed-circuit boards, and many adhesives, some of them conductive.

The formation of a three-dimensional network is described in this article by taking the chain polymerization of bisepoxides as an illustration. The illustration has more general validity, however. Polyepoxide networks are formed in a series of repeated reactions in which the low-viscosity bisepoxide is gradually converted into a hard end-product. This increase in viscosity during the reaction reduces the mobility of the monomers and their functional groups. The effect is intensified after the 'gel point' has been passed. The reduced mobility of the monomers and their functional groups has little influence, however, on the reaction rate of polymerization and cross-linking. Because the collisions between molecules become slower, fewer collisions are required on average to cause a reaction<sup>[5]</sup>. The rate of conversion is not in fact limited until 'vitrification' occurs. At this point the mobility of the functional groups that have not yet

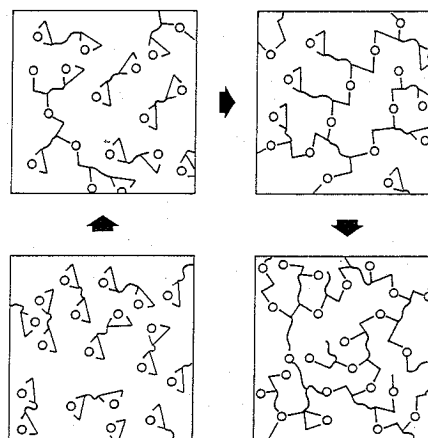
reacted is virtually zero because of the well-advanced cross-linking and the associated loss of free volume. In this 'glassy' state the reaction comes to a virtual standstill, without all the epoxides necessarily having reacted. The transition from the initial situation to the end-product is shown schematically in *fig. 4*.

In practice it is often advantageous if the polyepoxide networks are formed rapidly at the lowest possible temperature. Since this conflicts with other practical requirements — for durable and workable monomers without premature reaction — use is often made of 'latent catalysts'. In a latent catalysis an inert compound first has to be converted into a highly active catalyst before the polymerization can proceed. Latent catalysts can be formed by both thermal and photochemical methods.

Proper control of polymer formation requires not only a general understanding of what happens during the formation process but also a closer understanding of events on a molecular scale. Ultimately, local chemical variables determine the macroscopic physical and mechanical properties. It would be desirable to know the degree of homogeneity of the structure during the polymerization process, the precise reaction mechanisms in the different local situations, the probability of isomers being formed in the various mechanisms, and — not least — the ultimate mobility of individual polymer segments and the associated ultimate degree of conversion.

The insolubility of polymer networks makes it difficult to acquire this information, and in some cases even impossible. In the following sections two examples will be discussed that illustrate the way in which an investigation of this kind can be tackled.

Both examples deal with the formation and structure of polyepoxide networks, formed by chain polymerization with simultaneous cross-linking of bis-



**Fig. 4.** Diagram of the formation of a polyepoxide network from a bisepoxide.

epoxides. In the first example the way the polymerization process takes place is broadly known and we can therefore concentrate on more detailed aspects, such as the molecular mobility. It will be shown how phosphorescence spectroscopy can be used to monitor the change in the molecular mobility of polymer segments during the formation of a network. If the mechanism of polymerization is entirely unknown, however, this must be established first. The second example will show how the mechanism of network formation for model compounds can be studied by means of nuclear-magnetic-resonance spectroscopy, a powerful method for the spectroscopic investigation of organic molecules [6].

### Molecular mobility of polyepoxide networks [7]

#### Phosphorescence spectroscopy as an investigative method

A diaryl-iodonium compound can be used as the latent catalyst or photoinitiator for the formation of a polyepoxide network if the network is to be formed at room temperature while being exposed to light or other radiation (fig. 5) [8]. We have studied this network formation and the microstructure of the net-

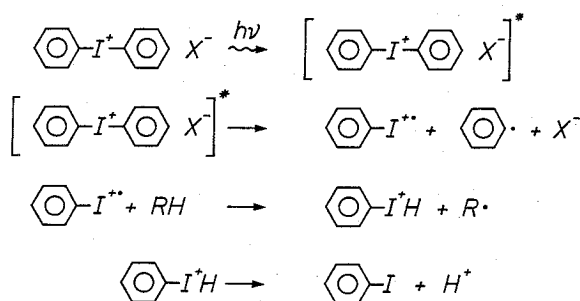


Fig. 5. The photochemical formation of an acid from a diaryl-iodonium salt [8], where X<sup>-</sup> represents AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, etc. In the first reaction step the diaryl-iodonium salt is brought into an excited state (\*), which then decays into reactive particles, mainly cations (+), radicals (•) and radical cations (+•).

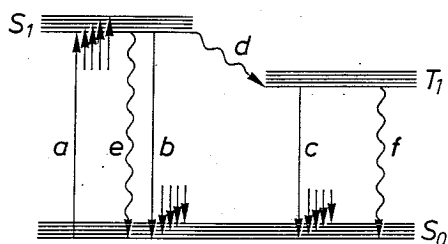


Fig. 6. Simplified representation of the Jablonski diagram for S<sub>0</sub>, S<sub>1</sub> and T<sub>1</sub> of an organic compound. Absorption (a), fluorescence (b), phosphorescence (c), intersystem crossing (d) and non-radiative transitions (e and f) are represented. The small arrows indicate the fine structure of the vibration.

works formed with the aid of phosphorescence spectroscopy, a method that has previously only been used in research on linear polymers.

Since most organic compounds possess a singlet ground state S<sub>0</sub>, the absorption and emission of light by these compounds can be represented in a simplified Jablonski diagram (fig. 6). In the case of phosphorescence the radiative transition takes place from an excited relatively long-lived triplet state (T<sub>1</sub>). Its long lifetime makes this triplet state extremely sensitive to non-radiative decay, which can occur as a result of molecular vibrations or collisions with other molecules in a triplet state (e.g. oxygen molecules). To record phosphorescence spectra it is therefore always necessary to limit the molecular mobility as far as possible. One way of doing this is by performing the measurements at low temperatures on an amorphous glass in which the molecule of interest has been dissolved.

As noted in the introduction, during polymer formation the product gradually becomes more viscous. This means that its molecules become less mobile. In the cured network the molecular mobility is low but is still subject to temperature-dependent changes. In this stage the lifetime of the triplet state and the intensity of the phosphorescence can provide important information about dynamic changes in the network.

The half-life  $\tau$  of the triplet state is given by:

$$\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1},$$

where  $\tau_r$  is the lifetime of the triplet state in the radiative decay and  $\tau_{nr}$  is its lifetime in the non-radiative decay. The temperature dependences of intensity and

[5] P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y., 1953, pp. 69-104.

[6] The following books should interest those who would like to know more about this subject;

on polymer chemistry:

G. Odian, Principles of Polymerization, 2nd edition, McGraw-Hill, New York 1981;

F. W. Billmeyer, Jr., Textbook of Polymer Science, Wiley Interscience, New York 1971;

D. W. van Krevelen, Properties of Polymers, Elsevier, Amsterdam 1976;

P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y., 1953;

on photochemistry and photophysics:

J. E. Guillet, Polymer Photophysics and Photochemistry, Cambridge University Press, Cambridge 1985;

N. J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings, Menlo Park, Cal., 1978;

on nuclear magnetic resonance spectroscopy for organic molecules:

H. Günther, NMR-Spektroskopie, Thieme Verlag, Stuttgart 1973;

J. B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York 1972.

[7] E. W. Meijer and R. J. M. Zwieters, in: Crosslinked Epoxies, B. Sedláček and J. Kahovec (eds), Walter de Gruyter, Berlin 1987, pp. 27-40.

[8] J. V. Crivello, Cationic polymerization — iodonium and sulfonium salt photoinitiators, Adv. Polym. Sci. 62, 1-48, 1984.

half-life are well known from work on linear polymers, and are given by<sup>[9]</sup>:

$$(I_f/I_p)(I_{p,0}/I_{f,0}) - 1 = A \exp(-E_a'/RT),$$

$$\tau^{-1} - \tau_0^{-1} = B \exp(-E_a''/RT),$$

where  $I_f$ ,  $I_{f,0}$ ,  $I_p$  and  $I_{p,0}$  are respectively the intensities of the fluorescence at the temperatures  $T$  and  $T = 0$ , and of the phosphorescence at the temperatures  $T$  and  $T = 0$ .  $\tau$  and  $\tau_0$  are the lifetimes at  $T$  and  $T = 0$ .  $A$  and  $B$  are constants;  $E_a'$  is the energy term denoting the temperature-dependence of the intensity of the phosphorescence and  $E_a''$  is the energy term denoting the temperature dependence of its lifetime.

Fig. 7 shows emission characteristics of a polyepoxide network that we have studied. Intermediates that occur during the photoinitiated decomposition of the diaryl-iodonium compounds used as a latent cat-

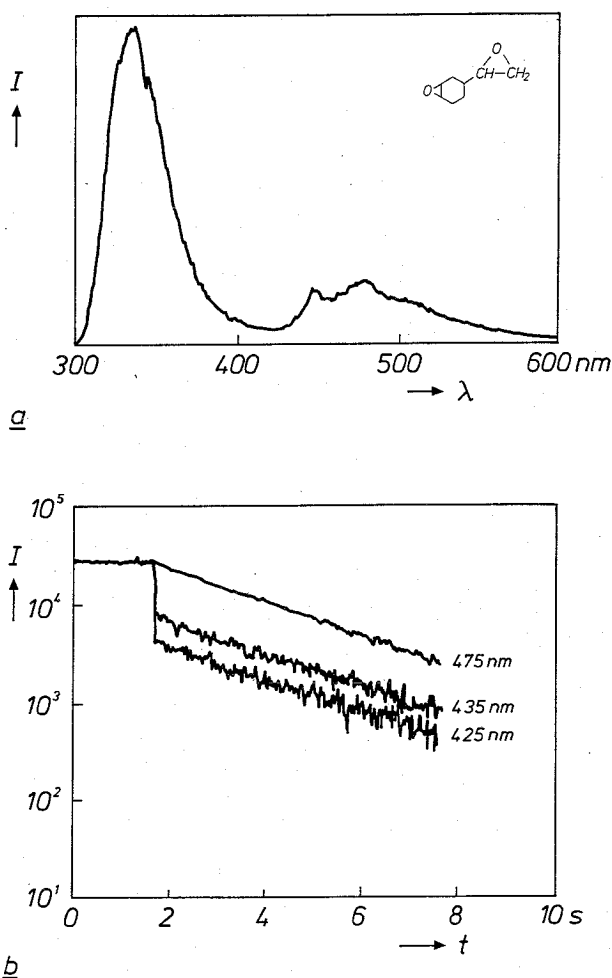


Fig. 7. *a*) The emission spectrum (intensity  $I$  against wavelength  $\lambda$ ) of a network of 1-epoxyethyl-3,4-epoxycyclohexane (fig. 3c), recorded at an excitation wavelength of 254 nm at room temperature. *b*) The decay of the excited triplet state for the same network, detected at three different wavelengths indicated in the figure. The excitation wavelength was 290 nm.

alyst are found to give rise to fluorescence with a maximum at a wavelength of 340 nm and to phosphorescence with a maximum at a wavelength of 480 nm (fig. 7*a*). The phosphorescence decays almost exponentially with a half-life of 1.6 s at room temperature (fig. 7*b*). In our investigations we used the diaryl-iodonium compound di(4-*tert*-butylphenyl)-iodonium-hexafluoroarsenate as latent catalyst and emission source. Although the nature of the emitting species has not been identified in detail, this is no objection to using the compound as a 'probe'.

#### Molecular mobility as a function of polymerization time<sup>[10]</sup>

If the fluorescence and phosphorescence intensities are measured as a function of the time in which the polymerization and cross-linking take place, an exponential increase is observed in both cases. The immediate rise in intensity of the fluorescence at the start of polymerization is followed, after an induction period dictated by the monomer used, by a rise in the intensity of the phosphorescence. In the case of the phosphorescence the induction period and the slope of the increase in intensity are interrelated (fig. 8).

As stated, all these effects are determined by the rate at which the molecular mobility in the continuously cross-linking polymer matrix is slowed down. This slowing down of the mobility is determined by the reaction rate of the polymerization and the change in viscosity on a micro-scale brought about by each step in the polymerization. It is the combination of these factors that interests the polymer chemist and can be investigated with this method of phosphorescence spectroscopy.

The end of the induction period indicates that the molecular mobility has reached a certain threshold value. The slope of the increase in phosphorescence is a measure of further changes in mobility.

Small variations in the composition of the original materials are found to give rise to changes in the polymerization processes that can readily be measured. Fig. 9 shows the result of phosphorescence measurements on mixtures of 1-epoxyethyl-3,4-epoxycyclohexane and 1,4-butanediol-diglycidyl ether. The first bisepoxide has a rigid structure and reacts rapidly, whereas the second is flexible and reacts relatively slowly. This has the result that when the proportion of the flexible monomer in the original mixture increases, it takes longer for the molecular mobility to slow down sufficiently for phosphorescence to occur. This is reflected in a longer induction period and not so steep a rise in the intensity curve.

We have compared the results of this new method of studying the processes of polymerization and net-

work formation with results of microcalorimetric experiments (DSC for Differential Scanning Calorimetry) on the same epoxides. In these experiments we monitored the progress of the reaction by measuring the heat of reaction produced per unit time. A com-

parison of fig. 8 and fig. 10 shows that both methods lead to corresponding conclusions: listing the various bisepoxides in order of polymerization rate as measured with the microcalorimeter gives exactly the same sequence as listing them in order of network formation as determined by phosphorescence spectroscopy.

The phosphorescence measurements had therefore taught us something about the rate of polymerization, but the method still had more to offer.

We also wanted to monitor the progress of the polymerization from measurements of the half-life of the excited triplet state. To determine this half-life we made a 'time-resolved' measurement of the phosphorescence. It was then found that the *half-life* of the triplet state is *not* dependent on the polymerization time, unlike the *intensity* of the phosphorescence, which does depend on the polymerization time. We assume that the explanation for this remarkable effect must reside in the inhomogeneous structural formation of the polyepoxide network. It seems to us that the increase in the degree of cross-linking does not take place homogeneously but is localized. This is to say that during the formation of the network the matrix consists of areas with a relatively high degree of conversion (giving phosphorescence with a long half-life) and areas with a relatively low degree of conversion (no phosphorescence). Extension of the regions with a high degree of conversion at the expense of areas with a low degree of conversion will then *increase* the intensity of the phosphorescence, but will not affect the half-life.

Other indications of the inhomogeneous polymerization postulated here have been found from electron-resonance-spectroscopy measurements on trapped free radicals in these polyepoxides [10]. Inhomogeneous polymerizations have also been postulated in other polymer networks [11].

*Molecular mobility as a function of temperature* [12]

As well as information about the rate of polymerization, phosphorescence spectroscopy can also provide information about dynamic-structural as-

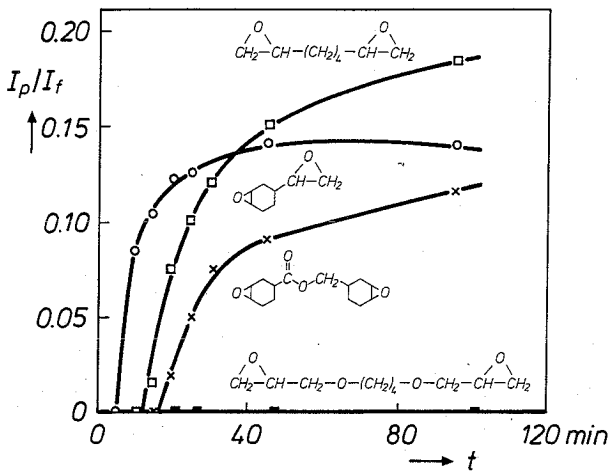


Fig. 8. Relative increase  $I_p/I_t$  in the phosphorescence intensity as a function of the polymerization time  $t$  for four polyepoxides at room temperature.

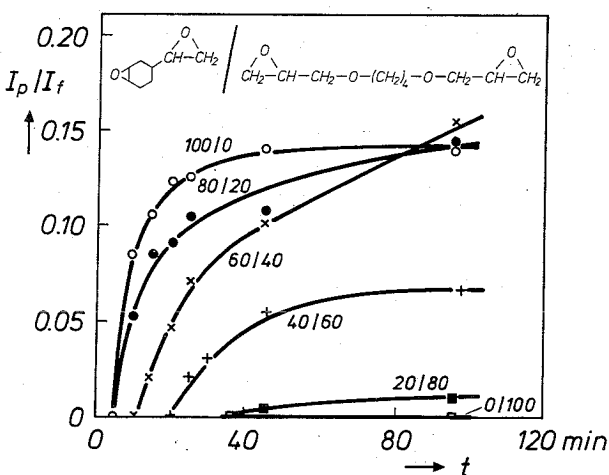


Fig. 9. As in fig. 8., for mixtures of two epoxides.

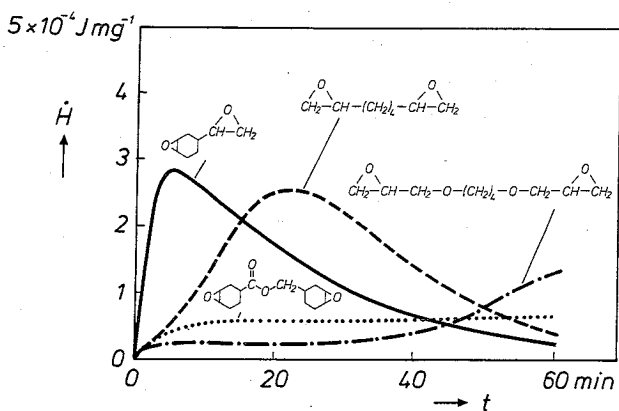


Fig. 10. Result of microcalorimetric (DSC) measurements on the photopolymerization of four bisepoxides at room temperature. The heat flux  $\dot{H}$  is plotted as a function of the reaction time  $t$ .

[9] A. C. Somersall, E. Dan and J. E. Guillet, Photochemistry of ketone polymers XI, *Macromolecules* 7, 233-244, 1974; K. J. Smit, R. Sakurovs and K. P. Chigginio, Temperature dependence of fluorescence and phosphorescence from probe molecules in polymer substrates, *Eur. Polym. J.* 19, 49-53, 1983.  
 [10] E. W. Meijer, D. M. de Leeuw, F. J. A. M. Greidanus and R. J. M. Zwiers, Molecular mobility studies in polyepoxides obtained by photoinitiated cationic polymerization, *Polym. Commun.* 26, 45-47, 1985.  
 [11] J. G. Kloosterboer, Network formation by chain crosslinking photopolymerization and its applications in electronics, *Adv. Polym. Sci.* 84, 1-61, 1988.  
 [12] E. W. Meijer and R. J. M. Zwiers, Molecular mobility of polyepoxide networks as revealed by emission spectroscopy and mechanical analysis, *Macromolecules* 20, 332-338, 1987.

pects of the three-dimensional network ultimately formed. To obtain this information we measure the intensity of the phosphorescence and the lifetime of the triplet state as a function of temperature. This is illustrated by the results of measurements on the relatively flexible network of 1,4-butanediol-diglycidyl ether. At room temperature it will not normally be possible to produce phosphorescence from such a network, but by reducing the temperature the molecular mobility of the network can be reduced sufficiently for phosphorescence to occur (fig. 11).

The increase in the intensity of the phosphorescence and the lifetime of the associated triplet state when the temperature is reduced can most easily be investigated by plotting the measured values as Arrhenius curves (fig. 12). Both curves in the figure consist of

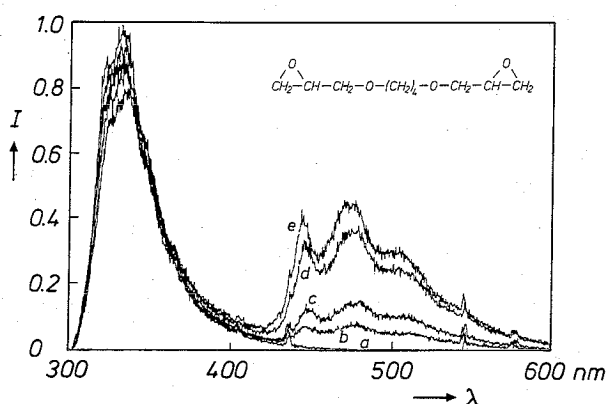


Fig. 11. Emission spectra of a network of 1,4-butanedioldiglycidyl ether (fig. 3d) for different temperatures at an excitation wavelength of 254 nm: a) 296 K, b) 279 K, c) 273 K, d) 233 K, e) 193 K.

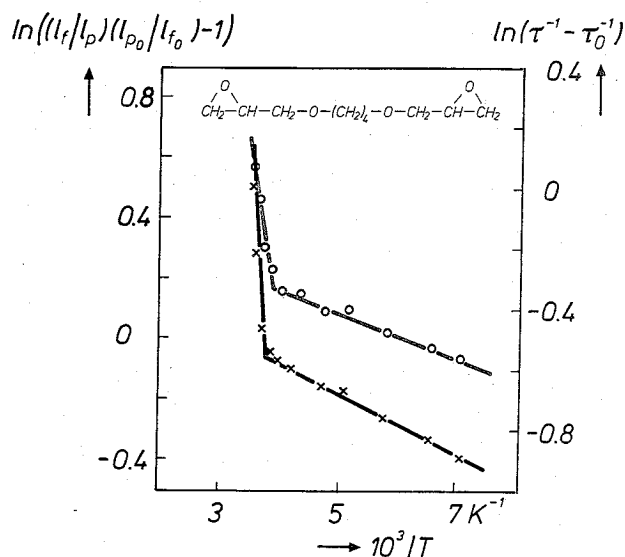


Fig. 12. Temperature dependence of the (relative) phosphorescence intensity (left) and of the (relative) half-life of the excited triplet state for a network of 1,4-butanedioldiglycidyl ether (fig. 3d).

two linear sections with a sharp transition at a temperature of about 260 K. The slope of a straight section is a measure of the activation energy of the mobility (or microviscosity) in the network. The low-temperature section (with  $E_a = 6$  to  $8$  kJ/mol) corresponds to a state of low mobility and therefore little non-radiative decay from the triplet state. The changes are mainly attributable to molecular vibrations and to local degrees of freedom in conformation. The high-temperature section corresponds to a state of greater mobility ( $E_a \geq 150$  kJ/mol) and the radiative decay and the non-radiative decay of the triplet state take place at a comparable rate. Here parts of the macromolecule are able to move, culminating eventually in the macroscopic glass-rubber transition.

These Arrhenius curves are similar for all the polyepoxide networks that we have studied (Table I). The slopes of all the low-temperature sections are the same, and the transition to the high-temperature section is at about 260 K on all the curves; only the slopes of the high-temperature sections differ. It is only in these slopes that the considerable differences between the molecular structures of the initial monomers become apparent. And indeed they show that the mobilities of the networks built up from flexible molecules like 1,4-butanediol-diglycidyl ether have a higher activation energy than those of the networks built up from rigid molecules like 1-epoxyethyl-3,4-epoxycyclohexane.

When the polyepoxides mentioned above are subjected to DMTA measurements (dynamic mechanical thermal analysis) it is found that the polymers built up from flexible monomers have a narrow transition region at low temperatures, and that the polymers built up from rigid molecules have a broad transition region at higher temperatures.

A comparison of the phosphorescence measurements and the mechanical measurements reveals the following picture of the dynamic structure of polyepoxide networks. In all the polyepoxides that we have studied the molecular mobility at very low temperatures is the same below the threshold value. In all the polyepoxides the molecular mobility starts to change at the same temperature, about 260 K. The movements that then occur are related to the molecular mobility of the individual groups. In this part of the curve above 260 K we therefore see a premonition of the macroscopic glass-rubber transition state, which will appear for the most mobile network at the lowest temperature when the temperature is increased again.

This — non-destructive — method of phosphorescence spectroscopy therefore gives us valuable supplementary information about the microscopic structure of polymer networks and the complicated way in which they are formed.



**Table I.** Experimentally obtained values for the activation energies, determined from Arrhenius curves as shown in fig. 12. The columns  $E_{a1}$  give the values in kJ/mol as determined for the low temperatures, and columns  $E_{a2}$  give the values for the higher temperatures. The columns  $T$  give the transition temperature in K.

Polymer networks of the epoxides in fig. 3	Intensity			Half-life		
	$E_{a1}$	$T$	$E_{a2}$	$E_{a1}$	$T$	$E_{a2}$
<i>c</i>	8	259	14	3	240-250	9
<i>d</i>	8	262	170	6	263	115
<i>c:d</i> = 4:6	8	266	22	5	263	17
<i>b</i>	6	225-257	23	5	245-250	10
<i>b:e</i> = 1:1	4	259	42	3	259	14

Sometimes it will also be desirable to find out more about the particular local reaction mechanism for each polymerization step during the formation of a network. An investigation of this type that we performed with the aid of NMR spectroscopy is described in the next section.

### A mechanism for epoxide polymerization

An investigation in which the mechanism of a promising new catalyst-initiator system for epoxide polymerization was studied<sup>[13]</sup> will now be described as our second example.

The high thermal and chemical stability of polyepoxide networks, combined with good electrical insulation, makes polyepoxides eminently suitable as encapsulating materials for electrical components. If these networks are to be produced by an ionic reaction mechanism, generally a very effective method, then it is particularly important that no ionogenic impurities such as catalysts should be left behind in the network. A likely material investigated for this purpose was tris(acetylacetonato) aluminium — referred to from now on as  $Al(acac)_3$  — in combination with phenolic compounds. Nothing was previously known about the mechanism of the polymerization produced with this system.

### NMR spectroscopy as an investigative method

The theoretical background of the nuclear-magnetic-resonance spectroscopy we used for this investigation has been dealt with several times in this journal<sup>[14]</sup>, but with no particular attention to the opportunities offered by NMR spectroscopy for a better understanding of the structure of complicated organic compounds (including polymers). This form of spectroscopy can be used with particular advantage for studying the hydrogen atoms (with spin quantum number 1/2) in these compounds.

An external magnetic field causes the energy associated with a nuclear spin to 'degenerate' into two

energy levels, one by aligning the nuclear spin with the field, and the other by aligning it in the opposite sense to the field. A resonance between these two levels gives rise to NMR signals. Because there are differences in the local magnetic field around a nuclear spin, due to the electron distribution in the molecule, the energy required for the resonance of each physically non-identical hydrogen atom does not have exactly the same value. These differences in resonance energy can be observed via the 'chemical shift' in the NMR spectrum, which is characteristic of the various substitution patterns in the molecule.

The spin-spin couplings that frequently occur have the effect of splitting the resonances, and are therefore an additional source of information. Spin-spin couplings in NMR spectroscopy arise from the splitting of energy levels of nuclear spins caused by the presence of adjacent spins (at a distance of up to about three covalent bonds). The parallel and antiparallel combinations cause the splitting. Identical spins do not split one another.

NMR spectroscopy can also identify other nuclei in much the same way as those of the hydrogen atoms. In organic chemistry NMR spectroscopy is very useful for studying  $^{13}C$  atoms. The use of powerful magnetic fields (up to 13.8 Tesla), with high-resolution equipment and the application of various complicated pulse techniques, have meant that NMR spectroscopy has now become one of the most powerful spectroscopic methods for analysing organic molecules. The impressive results reported have included the explanation of the structure of extremely complex proteins and parts of DNA<sup>[15]</sup>. Polymers have also been the subject of extensive investigations with NMR<sup>[16]</sup>.

Most information is now obtained from liquid systems, although solid-state NMR is in full development. We have investigated the mechanism of chain polymerization with the aid of a model compound, a monoepoxide. This forms soluble polymers, making high-resolution NMR possible.

<sup>[13]</sup> Contributions to this part of the investigation were made by F. W. v.d. Wey, J. P. H. Heynen, H. Draayer, A. W. de Bruyn, A. Schokker and C. Kruk.

<sup>[14]</sup> P. R. Locher, Proton NMR tomography, Philips Tech. Rev. 41, 73-88, 1983/84.  
D. J. Kroon, Nuclear magnetic resonance, Philips Tech. Rev. 21, 286-299, 1959/60.

<sup>[15]</sup> R. Kaptein, S. Stob, R. M. Scheek, K. Dijkstra and T. W. Schleich, High-field and photo-CIDNP studies of biological molecules, Bull. Magn. Reson. 2, 28-31, 1981;  
G. Wagner and K. Wüthrich, Observation of internal mobility of proteins by nuclear magnetic resonance in solution, Methods Enzymol. 131, 307-328, 1986.

<sup>[16]</sup> J. R. Havens and J. L. Koenig, Applications of high-resolution carbon-13 nuclear magnetic resonance spectroscopy to solid polymers, Appl. Spectrosc. 37, 226-249, 1983;  
F. A. Bovey, New directions in the nuclear magnetic resonance spectroscopy of polymers, Polym. Eng. & Sci. 26, 1419-1428, 1986.

### The initiator-catalyst system<sup>[17]</sup>

As demonstrated elsewhere, many metal-acetyl acetonates, in combination with very different phenolic compounds, can be used to bring about the polymerization of epoxides, but the most effective one is the combination of  $\text{Al}(\text{acac})_3$  with catechol (*ortho*-dihydroxybenzene)<sup>[18]</sup>. When this combination reacts with cyclohexene oxide (as a 'model monomer'; see fig. 3), a polymer is formed as shown in fig. 13. As can be seen, catechol acts as the initiator, while  $\text{Al}(\text{acac})_3$  is the catalyst.

During the polymerization an intermediate can be observed by <sup>1</sup>H-NMR spectroscopy. This same intermediate also arises when  $\text{Al}(\text{acac})_3$  and catechol react with each other *in the absence of epoxides*. Closer study of the reaction product reveals that a dimer structure is formed. This is preceded by a 'ligand' exchange, in which an acetyl-acetone group makes way for a catechol group<sup>[17]</sup> (fig. 14).

Because of this dimerization an intramolecular hydrogen bridge can form between the two phenolic groups present in the dimer, resulting in a strongly 'acidic' proton. As we have seen earlier, an acid can catalyze the polymerization of epoxides.

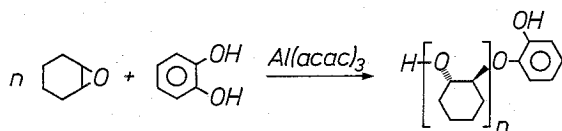


Fig. 13. The polymerization of cyclohexene oxide (fig. 3e) using the combination of  $\text{Al}(\text{acac})_3$  and catechol.

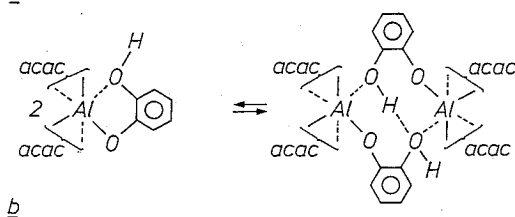
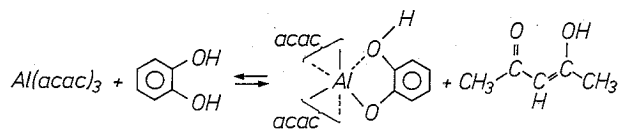
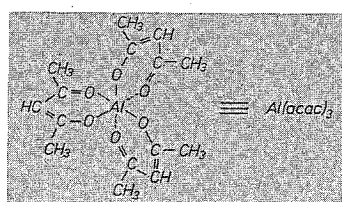


Fig. 14. Reactions for ligand exchange between  $\text{Al}(\text{acac})_3$  and catechol (a) and for dimerization (b). See also fig. 15.

The dimer consists of a complex combination of three geometrical isomers. In solution these isomers are in equilibrium with each other, and there is also a monomer-dimer equilibrium (see fig. 15). Both equilibria have been investigated in detail by NMR spectroscopy<sup>[17]</sup>.

### The mechanism of linear-chain polymerization

As we have seen, dimer formation is essential for effective catalysis and initiation. Two important reaction steps are evidently necessary for polymerization. In the first place the catechol must be activated to open the first epoxide ring; this is done by the ligand exchange with  $\text{Al}(\text{acac})_3$ . In the second step this ligand exchange results in the formation of the dimer; this is the 'acid' dimer that acts as the actual catalyst in the polymerization. Since the re-formed catalyst  $\text{Al}(\text{acac})_3$  is normally an electrically neutral non-ionic compound, it does indeed seem possible to obtain polymerization in this way without a residue of ionic 'contamination'.

By using chromatography and titration we were able to demonstrate that the formation of the dimer is very rapid, in appropriate conditions, and that the propagation step of the polymerization is the rate-determining step (fig. 16). It can also be deduced from the figure that the polymerization is just as fast with the combination of  $\text{Al}(\text{acac})_3$  and catechol as it is with a dimer obtained by separate synthesis. The figure also shows that the polymerization stops when the initiator 'catechol is used up. This is because the absence of the initiator makes further dimer formation impossible, so that both initiation and propagation of the polymerization come to a stop.

The need for the presence of an acid catalytic dimer suggests that the polymerization takes place via a cationic mechanism (and not for example via a coordinative mechanism, in which an epoxide is repeatedly inserted between the aluminium atom and the growing chain).

In an attempt to obtain further evidence of a cationic mechanism in the epoxide polymerization that we were studying, we investigated a special epoxide monomer, *exo*-2,3-epoxy-norbornane (structure *a* in fig. 17), which served as a model. In a series of experiments we tried to polymerize this compound by using a number of different catalysts. We found that polymerization was not produced by anionic or coordinative catalysis, but only when the catalysis contained a cationic mechanism. The observation that *exo*-2,3-epoxy-norbornane also polymerizes with a combination of  $\text{Al}(\text{acac})_3$  and catechol, or with the dimer, is therefore another indication of the cationic nature of this system.

Characterization of the polymer obtained from the acid-catalysed polymerization of *exo*-2,3-epoxy-norbornane revealed that a Wagner-Meerwein rearrangement takes place during this polymerization. In such a rearrangement the normal 2,3-substitution (structure *b* in fig. 17) does not occur in the polymer produced, but a 2,7 substituted product is obtained instead (structure *c* in fig. 17).

To prove that such an abnormal substitution took place, we subjected the polymer formed to a number of two-dimensional spin-spin decoupling correlated-spectroscopy (COSY) experiments [19] (fig. 18), in which we compared the spectrum of the polymer with that of low-molecular compounds like 2,7-dihydroxy-norbornane.

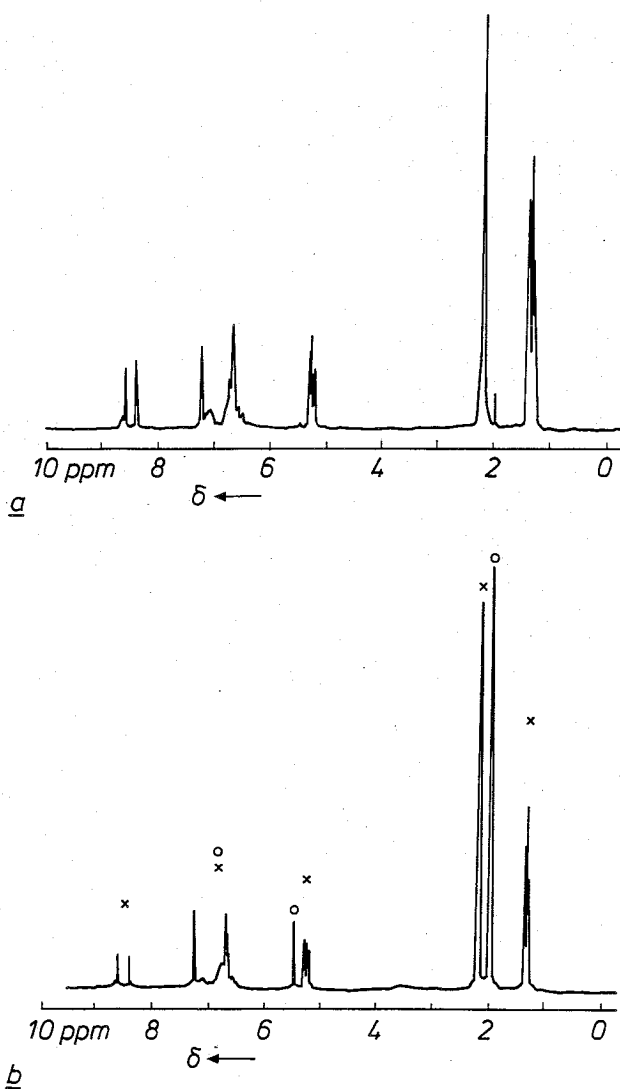


Fig. 15. a) <sup>1</sup>H-NMR spectrum of a freshly made solution of the dimer in CDCl<sub>3</sub>. Note the appearance of different resonances for the acetyl-acetate groups at δ = 1.2 and 5.2 ppm (parts per million) and the three 'acid' protons at δ = 8-9 ppm. b) <sup>1</sup>H-NMR spectrum of a solution of the dimer in CDCl<sub>3</sub> after 2 hours at room temperature. The resonances indicated by an asterisk \* correspond to the dimer, and those indicated by o to the monomer.

*Polyepoxide network formation*

In further investigation of the network formation of bisepoxides initiated and catalysed by the combination of catechol and Al(acac)<sub>3</sub>, we encountered an

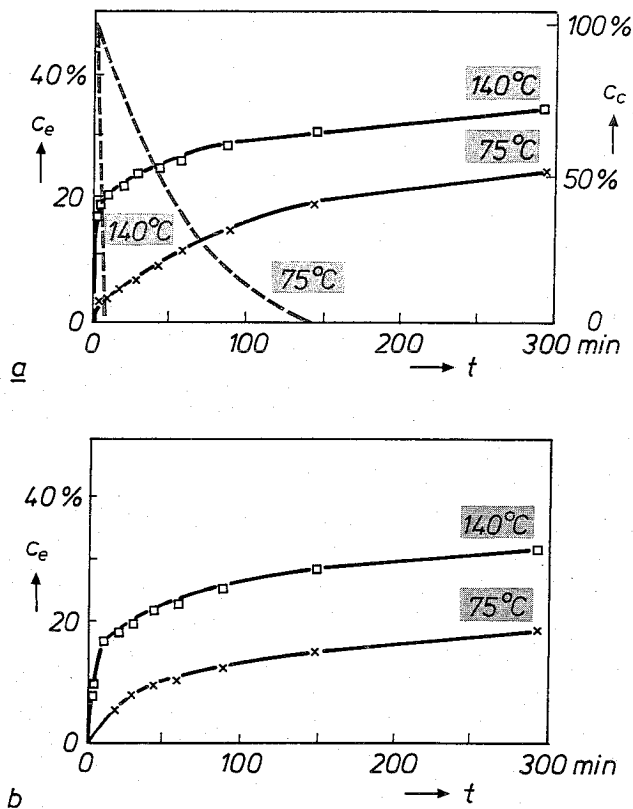


Fig. 16. The percentage *c<sub>e</sub>* of the epoxide conversion for cyclohexene oxide with the combination of Al(acac)<sub>3</sub> and catechol (a) and with dimer (b) plotted as a function of the reaction time *t* of polymerization at *T* = 140 °C and 75 °C. The concentration of catechol *c<sub>c</sub>* as a function of the reaction time is also shown in 16a.

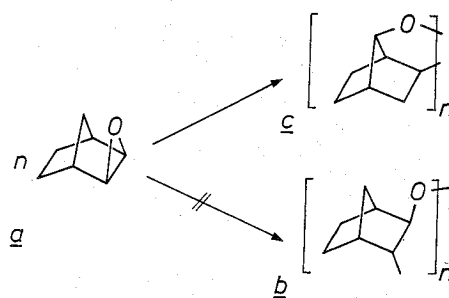


Fig. 17. Structure of *exo*-2,3-epoxy norbornane (a; see also fig. 3f), a 2,3-substituted norbornane (b) and a 2,7-substituted norbornane (c).

[17] E. W. Meijer, The synthesis and structure of bis(acetylacetonato) (2-hydroxyphenolato) aluminium: a stable dimer, *Polyhedron* 6, 525-529, 1987.

[18] M. Markovitz, Controllable reactivity epoxy resin hardeners, in: *Chemistry and Properties of Crosslinked Polymers*, S. S. Labana (ed.), Academic Press, New York 1977, pp. 49-58.

[19] R. Benn and H. Günther, Moderne Pulsfolgen in der hochauflösenden NMR-Spektroskopie, *Angew. Chem.* 95, 381-411, 1983.

additional complicating factor: the dimeric initiator-catalyst was not always soluble in the bisepoxides selected. We found, however, that this complication could also be turned to good use.

One of the bisepoxides that we studied was (3,4-epoxycyclohexyl)methyl-3',4'-epoxycyclohexane carboxylate (see fig. 3). We polymerized this compound under various reaction conditions. The reactions were monitored by titration and by determining the gel point.

From this investigation we drew the following conclusions:

- The dimer in the dissolved form is the best initiator-catalyst.
- If the dimer is added in the solid form, the polymerization does not take place or only very slowly at low temperatures, because the dimer dissolves only slightly.
- At higher temperatures fast polymerization and cross-linking do take place with a solid dimer, though

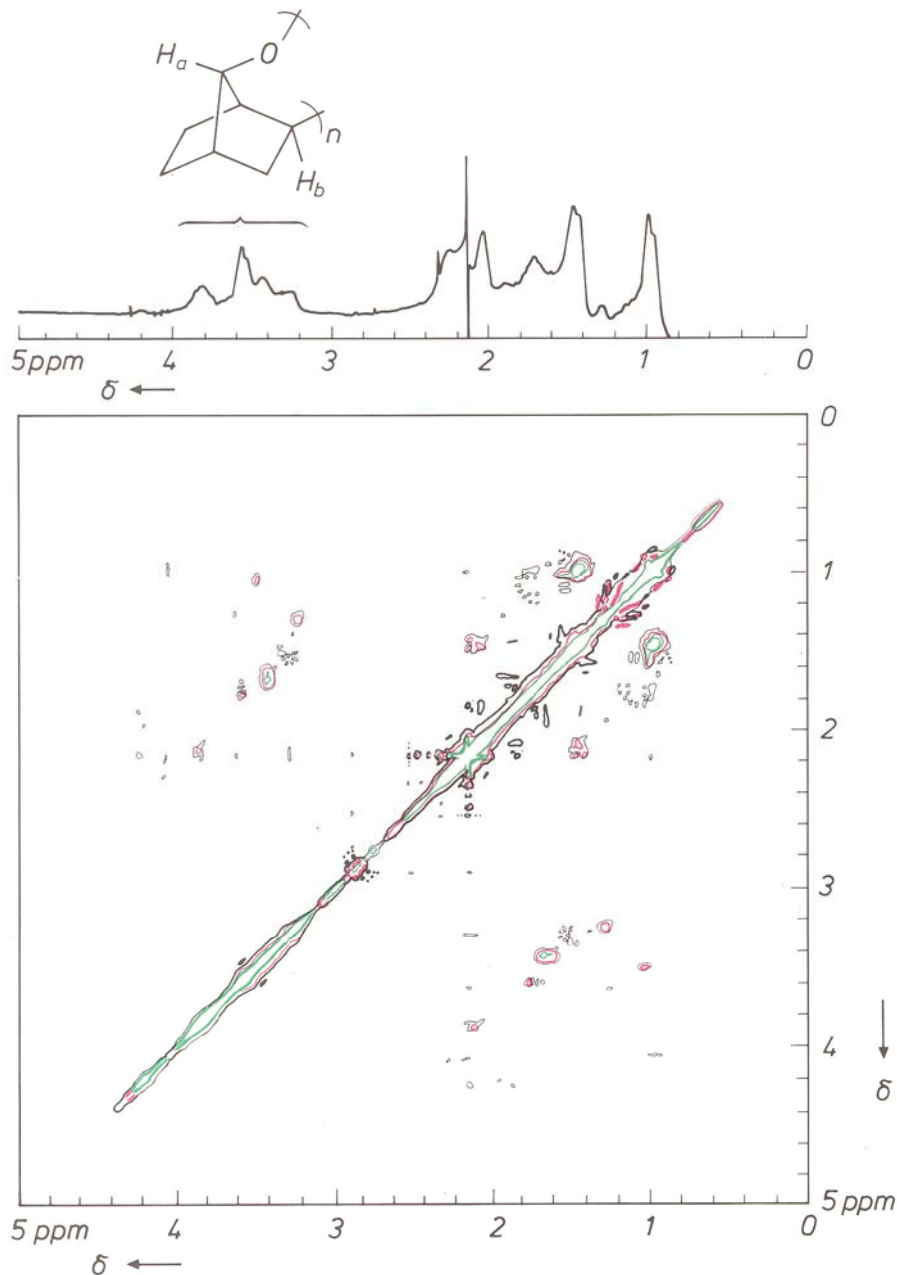


Fig. 18.  $^1\text{H-NMR}$  and COSY spectra of the polymer of exo-2,3-epoxy-norbornane. COSY experiments (COrelated SpectroscopY) indicate whether there is a spin-spin coupling between two hydrogen atoms. This coupling appears as a cross peak in the two-dimensional spectrum, where the normal  $^1\text{H-NMR}$  spectrum appears as a diagonal in the contour picture. The absence of spin-spin coupling between the hydrogen atoms  $H_a$  and  $H_b$  in the polymer (between  $\delta = 3.1$  and 4.0 ppm) is a strong indication that these atoms are in a 2,7 and not in a 2,3 relationship.

only after some delay. Initially, a reaction is only possible at the interface between the solid dimer and the liquid bisepoxide. The dimer is more soluble in polymerized bisepoxide, so that the rate of polymerization increases during the reaction.

- The temperature dependence of the rate of polymerization is not described by a simple Arrhenius equation, because of an irreversible change in the solid dimer<sup>[17]</sup>.
- In the case of the catechol/ $\text{Al}(\text{acac})_3$  combination we have a situation intermediate between the two cases mentioned above (fig. 19).

The above conclusions show that the addition of the dimer in solid form produces a latent initiator-catalyst system.

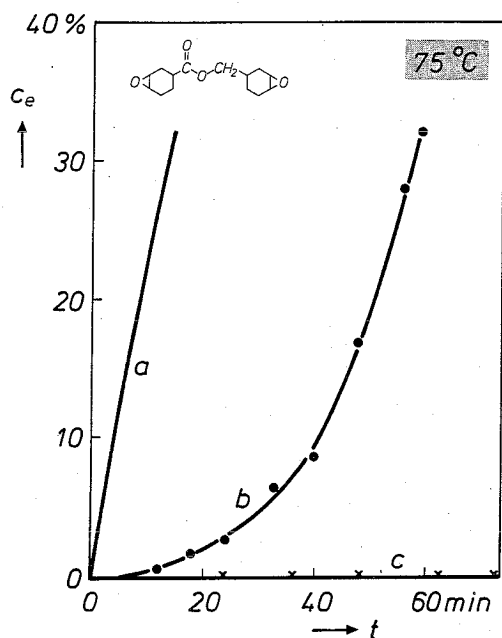


Fig. 19. The epoxide conversion ( $c_e$ ) as a function of polymerization time  $t$ , as measured by means of titration. It is found to make a great difference whether the dimer is added ( $a$ ) in a solution (of  $\text{CHCl}_3$ ) or ( $c$ ) as a solid.  $b$ ) Progress of the epoxide conversion with the combination of  $\text{Al}(\text{acac})_3$  and catechol.

A polymer network that can be built up from such a two-phase situation has the advantage of remaining stable for a long time at low temperatures; fast polymerization and cross-linking can only take place at high temperatures, because a homogeneous reaction mixture is then formed.

Good use can be made of this form of latent catalysis in the production of polymer networks, if at least the perfectly homogeneous phase is reached. If the solid phase is excessively reactive and insufficiently soluble in the reaction mixture, the inevitable result will be an inhomogeneous polymer network. The associated problems are still the subject of investigation.

The two investigations described have been chosen to give some idea of the approach now possible in this sector of chemistry. One shows how phosphorescence spectroscopy can be used to find the relationship between the molecular mobility and the physical properties, and the other how nuclear-magnetic-resonance spectroscopy can help in sorting out the highly complex reaction mechanisms. Both have given a better understanding of the relation between the structure and properties of polyepoxides.

**Summary.** The polymerization of epoxide monomers with catalysts or initiators results in polyepoxides. Special attention is given to chain polymerization from bisepoxides; the three-dimensional networks formed permit a wide variety of applications. Methods of gaining a fundamental understanding of the formation of these networks and their structure are illustrated by two examples. In the first example it is shown how phosphorescence spectroscopy can be used to monitor changes in the molecular mobility of polymer segments, both during the formation of the network and as a function of temperature. In the second example it is shown how nuclear-magnetic-resonance spectroscopy can be used to study the mechanism of network formation with the aid of model compounds. Emphasis is placed here on the part played by the  $\text{Al}(\text{acac})_3$ /catechol initiator-catalyst system.