

Photoinitiated cationic polymerization; a study to the polymerization and molecular mobility of polyepoxide networks using phosphorescence spectroscopy

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PHOTOINITIATED CATIONIC POLYMERIZATION; A STUDY TO THE POLYMERIZATION AND MOLECULAR MOBILITY OF POLYEPOXIDE NETWORKS USING PHOSPHORESCENCE SPECTROSCOPY

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SYNOPSIS

The paper presents the use of phosphorescence spectroscopy to reveal the structure of polyepoxide networks. The polyepoxide networks are prepared by a photoinitiated cationic polymerization and cross-linking of (cyclo)-aliphatic bisepoxides. These networks emit fluorescence ($\lambda_{\max} = 340$ nm) and phosphorescence ($\lambda_{\max} = 480$ nm) originating from intermediates in the photolysis of the latent catalyst di(4-*tert*-butylphenyl)iodonium hexafluoroarsenate. The emission properties have been studied as a function of the degree of polymerization. The increase in intensity of emission during polymerization and cross-linking is characteristic for the rate of network formation. This new method for measuring the rate of network formation is compared with DSC measurements. The half-life τ of the triplet excited state appeared to be constant during conversion. This result strongly suggests that the increase in cross-link density proceeds via an inhomogeneous pathway. This statement is confirmed by ESR spectroscopy.

The phosphorescence intensity and half-life of the triplet excited state have been measured as a function of temperature. For several polyepoxide networks polymerized at room temperature to maximum conversion, both phosphorescence intensity and half-life show a discontinuity in their Arrhenius plots. For all networks this discontinuity is situated around 260 K and is due to the onset of quenching of the triplet excited state. The activation energy above this transition temperature is characteristic of the individual network and is an indication of the increase in motion as the temperature is raised, ultimately leading to a simultaneous motion of large parts of the network. From these emission data, being informative for the preamble of the glass transition temperature, it is possible to estimate the glass transition temperature and the width of that transition region.

The mechanical properties of the polyepoxide networks are established with DMTA. A striking correlation between the mechanical properties, E-modulus and $\tan \delta$, and the molecular mobility (from the emission data) is observed.

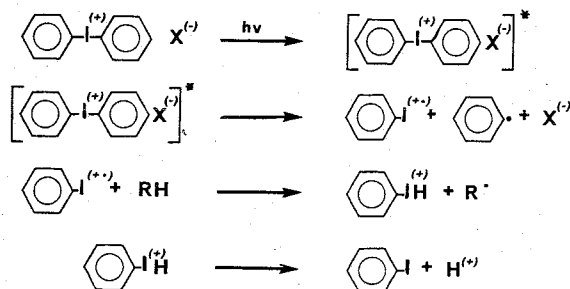
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INTRODUCTION

In recent years the application of emission spectroscopy to the study of a variety of phenomena in linear polymers has become widespread (1,2). The luminescence of a chromophore incorporated in a polymer is in many cases very sensitive to properties of the local environment. Important parameters are emission intensity, half-life data, and degree of depolarization of both fluorescence and phosphorescence. Using the appropriate luminescent probe and monitoring the parameters to match, one sensitively can measure properties such as polymer compatibility, ordering of polymer chains, viscosity, glass transition temperature, micromobility, sub-group motion, or micropolarity (3-7).

Our interest is focused on three-dimensional polymer networks, densely cross-linked materials with a complicated structure and to which, to the best of our knowledge, phosphorescence spectroscopy has never been performed to gain insight in problems related to micromobility (8). Recently a few studies for monitoring polymerization and cross-linking in epoxy-amine networks have been presented using fluorescence techniques (9,10) and in polyacrylate networks using the depolarization of fluorescence (11). We have investigated polyepoxide networks, obtained by photoinitiated cationic polymerization. Several factors governing the photoinitiated homopolymerization of epoxides have been investigated intensively (12-15). The proposed mechanism for the photolysis of diaryliodonium salts is depicted in scheme 1 (12). This simplified scheme does not account for the difference in quantum yields of iodobenzene and the Brønsted acid, to wit 0.39 and 0.65, respectively (15). Several other intermediates are proposed (15).



scheme 1

However, information about the structure and properties of the polymer networks produced is scarce. We have studied the molecular mobility of polyepoxide networks using phosphorescence spectroscopy. The networks are obtained by the photopolymerization of bisepoxides with diaryliodonium salts. The molecular mobility is investigated during the formation of the networks and as a function of temperature for polyepoxides at complete conversion.

BACKGROUND

Since most organic molecules possess an S_0 groundstate, the absorption and emission of light by these molecules can be visualised by the simplified Jablonski diagram shown below (16):

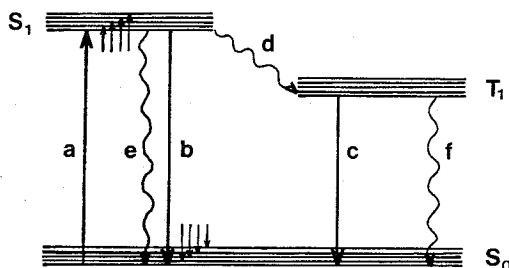


Fig. 1. *a* = absorption
b = fluorescence
c = phosphorescence
d = intersystem-crossing
e and *f* = non-radiative transitions

The rate constants for fluorescence, phosphorescence, and intersystem crossing are about $10^9 > k_f > 10^5$, $10^3 > k_p > 10^{-1}$, and $10^{11} > k_{st} > 10^5$, respectively (16). All three transitions are in competition with non-radiative processes. Phosphorescence is most sensitive to this type of deactivation. Thus, in order to observe a complete electronic emission spectrum it is usually necessary to minimize the non-radiative decay. This is routinely accomplished by cooling the sample to very low temperatures, thereby bringing the emitting species in a rigid environment. The rigidity of the sample eliminates bimolecular quenching processes, since the diffusion is eliminated in solid solutions. In addition, a rigid solvent matrix may restrict certain molecular motion, and this is particularly effective for promoting radiationless transitions. However, even at 77 K, where all solid solutions are glasses, the sum of quantum yields of fluorescence and phosphorescence is generally less than 1.00 indicative for some remaining non-radiative transitions.

Several polymers and most highly cross-linked polymer networks are glasses at room temperature. Hence in these polymer matrices the non-radiative transitions at room temperature are minimized. The degree of quenching of the excited states is often used in the molecular mobility studies of polymers.

Since no marked differences in the mechanism of absorption, intersystem-crossing, and emission are to be expected between linear polymers and networks, we use in our study the assumptions that are generally accepted for linear polymers (1). The half-life of the triplet excited state is given by $\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$, where τ_r and τ_{nr} are the radiative and non-radiative half-life of the triplet excited state, respectively. The following

expressions for the measurements as a function of temperature, for both phosphorescence intensity and decay half-life are well established (1,3,4):

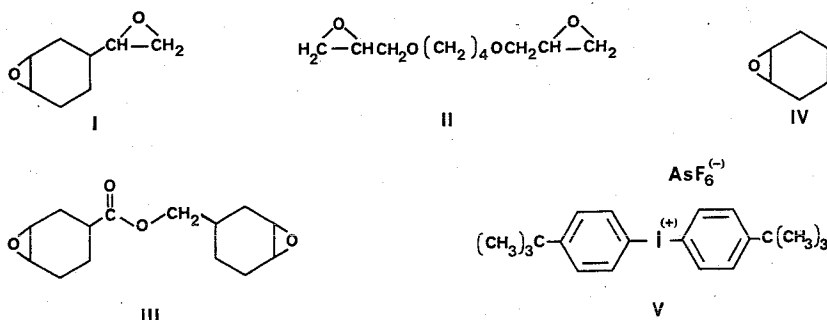
$$(I_f/I_p) \cdot (I_{p0}/I_{f0}) - 1 = A \exp(-E'/RT)$$

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

where I_f , I_p , I_{f0} , I_{p0} are the fluorescence and phosphorescence intensities at temperature T and the low temperature limit (in this study $T_0 = 100$ K), respectively, τ and τ_0 are the half-life of the triplet excited state at temperature T and the low temperature limit, A and B are constants, and E' and E'' are the energy terms governing the temperature dependence of the phosphorescence. Arrhenius plots of $\ln(\tau^{-1} - \tau_0^{-1})$ and $\ln((I_f/I_p) \cdot (I_{p0}/I_{f0}) - 1)$ versus $1/T$ should give straight lines of slope $-E/RT$.

EXPERIMENTAL

The bisepoxides studied comprise 1-epoxyethyl-3,4-epoxycyclohexane (I) (Union Carbide), 1,4-butanediol diglycidyl ether (II) (Ciba Geigy), and 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (III) (Ciba Geigy). 1,2-Epoxycyclohexane (IV) (Janssen Chemicals) was used as monoepoxide. The bisepoxide monomers were used as purchased. The purity of the samples proved to be ($^1\text{H-NMR}$) spectroscopically pure for I, II, and IV. For one set of experiments bisepoxide III was purified by column chromatography ($\text{Al}_2\text{O}_3 - \text{CH}_2\text{Cl}_2$) in order to remove polar impurities. The photoinitiator, di(4-*tert*-butylphenyl)iodonium hexafluoroarsenate (V), was synthesized following a well-known procedure (12), apart from some minor modifications.



The emission spectra of the networks were measured from freshly prepared films of the monomers on optical grade aluminium. In all cases the amount of initiator in the bisepoxide was 2 mol%. The samples were polymerized by irradiation at $\lambda = 254$ nm at ambient temperature using a Camag lamp with an intensity at the film of about

1 mW/cm². In order to determine the irradiation time necessary for maximum conversion at ambient temperature a specially equipped Perkin Elmer DSC 2 apparatus was used.

The instrumentation for recording the emission spectra and the mechanical properties of the samples was published recently (17,18).

EMISSION CHARACTERISTICS

The photolysis of di(4-*tert*-butylphenyl)iodonium hexafluoroarsenate by UV light affords a Brønsted acid which in turn is the catalyst for epoxide polymerization (12-15). We observed a long-lasting bright blue emission after exposure of cross-linked polyepoxides to UV light. It was found that intermediates in the photolysis of the iodonium salt exhibit this remarkable luminescent properties in a polymer matrix (17). The emission of a network from 1-epoxyethyl-3,4-epoxycyclohexane and V is depicted in fig. 2.

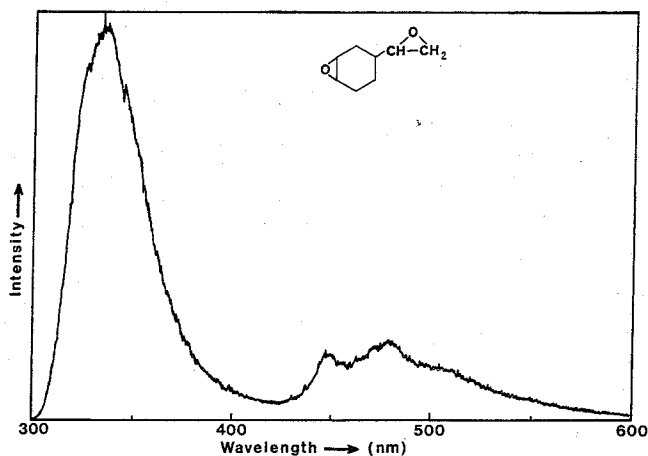


Fig. 2. The emission spectrum of a network of 1-epoxyethyl-3,4-epoxycyclohexane (I) and V upon excitation at $\lambda = 254$ nm.

Both fluorescence and phosphorescence are observed at $\lambda_{\text{max}} = 340$ nm and $\lambda_{\text{max}} = 480$ nm, respectively. The latter shows a nearly exponential decay with a half-life of 1.6 sec at ambient temperature (fig. 3).

Excitation spectra reveal that the maximum intensity for both fluorescence and phosphorescence is obtained by irradiation at 290 nm.

In order to gain insight in the structure of the emitting species, we have investigated also the unsubstituted diaryliodonium salt. Using diphenyliodonium hexafluoroarsenate the fluorescence and phosphorescence intensity at room temperature are decreased by a factor of 10 with respect to the initiator with the two *tert*-butyl groups. Furthermore, a small blue

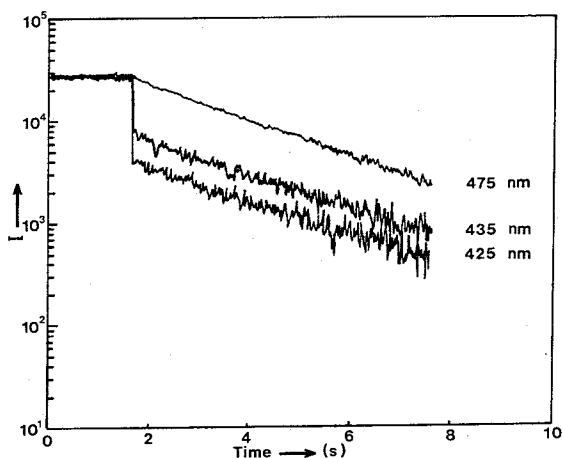


Fig. 3. The decay curve of the triplet excited state for network I, detected at $\lambda = 475$ nm, 435 nm, and 425 nm.

shift of the phosphorescence is observed. Several other iodonium salts are currently under investigation. Preliminary results show that only V possesses strong luminescence. When an acetyl group is attached to one of the phenyl rings a large red shift of the (at room temperature) low intensity phosphorescence is observed. Despite the current study the exact nature of the emitting species is still unknown.

LUMINESCENCE DURING POLYMERIZATION AND CROSS-LINKING

In order to investigate the photopolymerization of several bisepoxides with di(4-*tert*-butylphenyl)iodonium hexafluoroarsenate, we monitored the intensity of fluorescence and phosphorescence, as well as the half-life τ of the triplet excited state of the emitting species for the epoxides throughout conversion (17). Right from the start of the photopolymerization a rapid increase in fluorescence intensity was observed, in many cases followed by a build-up of the phosphorescence after variable periods of time (dependent on the structure of the bisepoxide). Both fluorescence and phosphorescence intensity increase exponentially. In figure 4 the results are presented for the photopolymerization and cross-linking of bisepoxide I, II, and mixtures thereof. The ratio $I_p (\lambda = 480 \text{ nm}) / I_f (\lambda = 340 \text{ nm})$ is plotted against the photopolymerization time. Three parameters, the onset of phosphorescence, the slope of the curve, and the I_p/I_f end-value emerge from these measurements. The onset of phosphorescence and the slope of the curve are very sensitive to the fraction of 1,4-butanediol diglycidyl ether in the mixture (fig. 4). When the luminescence is measured on-line during the polymerization, even differences in composition up to a few percent give rise to a detectable change in onset time. Furthermore, this onset of phosphorescence is related to the rate to which the phosphorescence intensity is

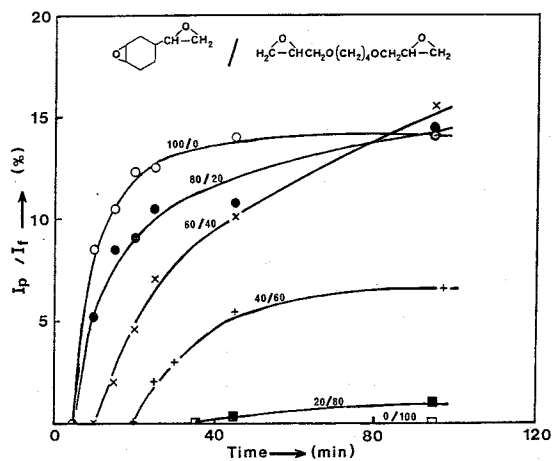


Fig. 4. The relative increase in phosphorescence intensity as a function of polymerization time for the mixtures 1-epoxyethyl-3,4-epoxycyclohexane/1,4-butanediol diglycidyl ether (ww%). (\circ) = 100/0; (\bullet) = 80/20; (\times) = 60/40; ($+$) = 40/60; (\blacksquare) = 20/80; (\square) = 0/100.

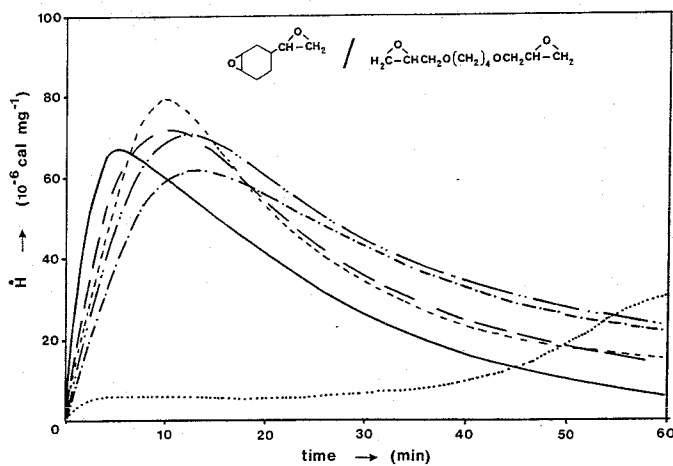


Fig. 5. Differential Scanning Calorimetry measurements of the polymerization and cross-linking of the mixtures of 1-epoxyethyl-3,4-epoxycyclohexane/1,4-butanediol diglycidyl ether (ww%). (—) = 100/0; (---) = 80/20; (- - -) = 60/40; (- · -) = 40/60; (- · ·) = 20/80; (·····) = 0/100.

increased (the slope of the curve). Since the increase in phosphorescence intensity is closely related to the decrease in matrix mobility and thus to the extent of the polymerization and cross-linking reaction, it is possible to determine the cure of polyepoxide networks using emission spectroscopy. In order to show the validity of this method we performed kinetic DSC measurements with the same epoxides. The results are given in figure 5. Upon addition of 1,4-butanediol-diglycidyl ether to 1-epoxyethyl-3,4-epoxycyclohexane the reactivity decreases. The same phenomenon was observed with the emission measurements. Remarkable is the great sensitivity of the emission data for the composition of the mixture compared to the DSC measurements. It should be noted that the differences in light intensity for both measurements hampers a direct comparison of the reaction rates. In figure 6 and 7 results of some other bisepoxides are given, showing the versatility of using emission spectroscopy to monitor polymerization and cross-linking of polyepoxides. Practically, a sensitive measurement is limited to polyepoxides polymerized by using photoinitiator V, since up to now only V furnishes a high luminescence intensity.

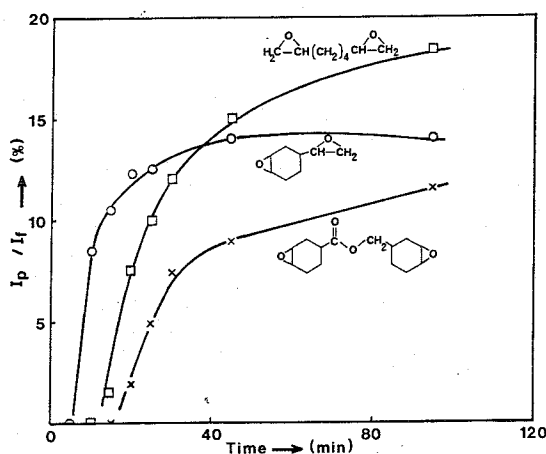


Fig. 6. The relative increase in phosphorescence intensity as a function of polymerization time for I (\circ), III (\times), and 1,2,7,8-diepoxyoctane (\square).

The half-life of the triplet excited state for a particular polyepoxide network is another parameter to measure. We monitored this half-life throughout conversion and it appears to be independent of the degree of polymerization for a particular network, when cross-linked at ambient temperature. At first glance this observation is remarkable. Since the observed lifetime is the result of radiative and non-radiative transitions, it is expected that at a gradual increase in cross-link density and hence in immobility, the observed lifetime will also increase gradually. However, the observation of a constant lifetime leads to the following interpretation. The network is thought to be composed of domains with low internal mobility (in which radiative phosphorescence predominates τ) and domains with higher internal mobility (in which radiationless deactivation of the triplet excited state predominates τ).

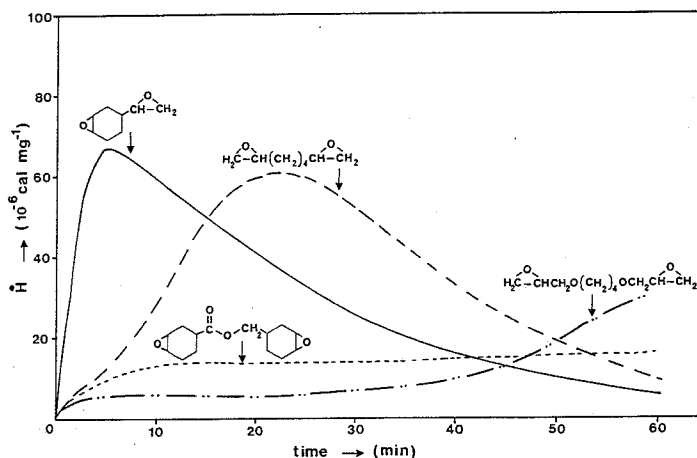


Fig. 7. Differential Scanning Calorimetry measurements of the polymerization and cross-linking of I (—), II (---), III (-·-·-), and 1,2,7,8-diepoxyoctane (— —).

The volume fraction of domains with low internal mobility will increase as polymerization and cross-linking proceed. This volume fraction is expressed by the ratio I_p/I_f (as depicted in figs. 4 and 6).

The "two-domain hypothesis" outlined above is supported by data obtained with ESR spectroscopy. Since most intermediates of the photolysis of the iodonium salts are radicals, we performed ESR to detect trapped intermediates with unpaired electrons. The ESR spectra of the trapped radicals in two different networks are shown in figure 8. Evaluation of the ESR signal intensity in time shows that the concentration of trapped radicals increases

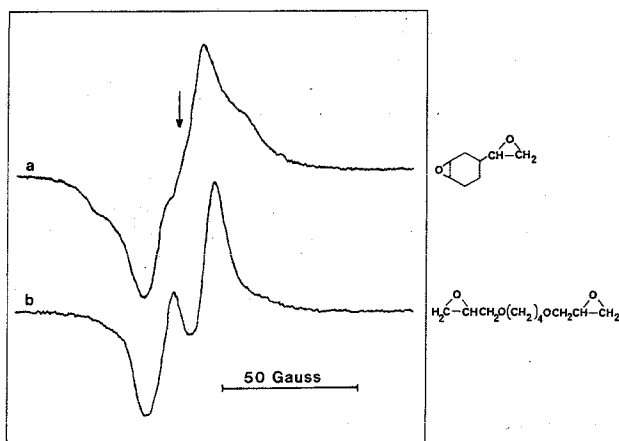


Fig. 8. The ESR spectra of trapped radicals in networks of I and II.

during polymerization, while the shape of the signal is unaffected. Moreover, the stability of the radicals is only slightly dependent on degree of polymerization. Again no gradual increase in decay time and hence in stability and immobility has been observed. On the basis of these mobility studies we conclude that the photoinitiated cationic polymerization of bisepoxides is inhomogeneous in nature, leading to networks with domains with lower and higher internal mobility at room temperature.

MOLECULAR MOBILITY AS A FUNCTION OF TEMPERATURE

Detailed information about the molecular mobility of polyepoxide networks at maximum conversion was obtained by measurements as a function of temperature (18). With decreasing temperature the molecular rigidity of the network is increased, furnishing a decrease in quenching rate of the triplet excited state and hence an increase in phosphorescence intensity is expected. Several polyepoxide networks were investigated as a function of temperature. In figure 9 the effect of temperature on the luminescence intensity of the polymer network of 1,4-butanediol diglycidyl ether (II) is given when it is irradiated with light of 254 nm. When the temperature is decreased, we observe that the fluorescence intensity is increased slightly, while the change in phosphorescence intensity is dramatic. The half-life of the triplet excited state was determined at all temperatures at the wavelength of 480 nm. At all temperatures the decay curve proves to be nearly exponential.

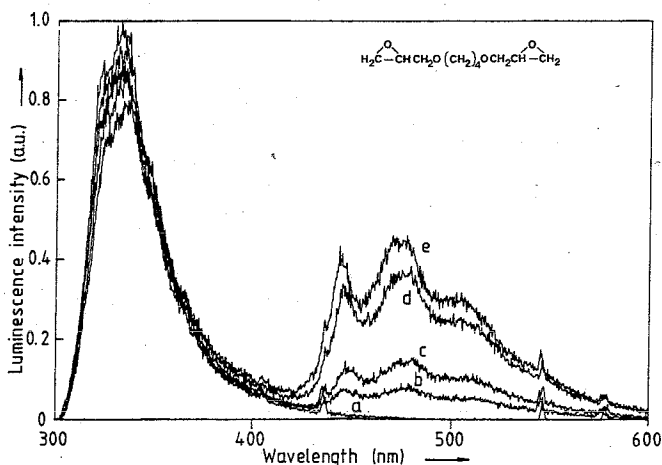


Fig. 9. The emission behaviour (excitation wavelength: 254 nm) of a network of 1,4-butanediol-diglycidyl ether (II) as a function of temperature.

a) = 296 K; b) = 279 K; c) = 273 K; d) = 233 K and e) = 193 K.

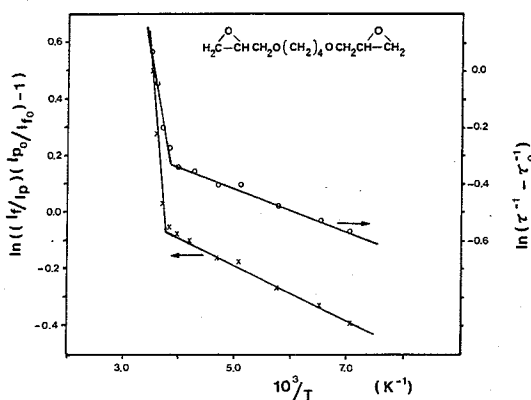


Fig. 10. Arrhenius plot showing the temperature dependence of the phosphorescence intensity and the triplet excited state half-life of the network of 1,4-butanediol diglycidyl ether (II).

As outlined in the section background, the intensity and half-life data can be plotted using Arrhenius equations. Figure 10 shows such Arrhenius plots for 1,4-butanediol diglycidyl ether (II). Both curves show two distinct linear parts with a discontinuity in the slope within a narrow temperature region around $T = 260$ K. The estimated activation energies from these data are given in Table 1. Several other individual bisepoxides and mixtures thereof are subjected to these Arrhenius equations, showing comparable behaviour.

Table 1

Polymer network	Intensity			Half-life		
	Ea1 ^{a)}	T ^{b)}	Ea2 ^{c)}	Ea1 ^{a)}	T ^{b)}	Ea2 ^{c)}
I	8	259	14	3	240–250	9
II	8	262	170	6	263	115
I+II (40:60 w/w)	8	266	22	5	263	17
III	6	225–257	23	5	245–250	10
III+IV (50:50 w/w)	4	259	42	3	259	14

a) = activation energy in kJ/mol as determined at the temperature region below the transition temperature T .

b) = transition temperature in K.

c) = activation energy in kJ/mol as determined at the temperature region above the transition temperature T .

In the densely cross-linked polyepoxides networks studied so far the transition point in the Arrhenius plots of phosphorescence intensity and half-life of their triplet excited state is always situated around 260 K and is hardly dependent of the structure of the network. This indicates that the onset of quenching of the emitting species in its triplet excited state is due to the onset of motion of a structural element that all networks have in common. Below the transition temperature the radiationless deactivations are more or less excluded. The observed activation energies for both intensity and half-life data are very low (< 10 kJ/mol) and hardly dependent of the molecular structure of the monomer and hence of the polyepoxide network. These E_a values are comparable with those found for linear polymers in the low temperature region (1,3). This indicates that, with respect to the frequency scale, the difference in molecular motion of polymers with physical cross-links and of polymers with chemical cross-links is only marginal in the glassy state (far) below T_g .

Above the transition temperature the differences in activation energies for the various epoxides are substantial. In polyepoxide I the increase in molecular mobility by raising the temperature is very small, indicating the remaining rigidity of the network above 260 K. This rigidity is related to restricted motion at the molecular level. Therefore, a simultaneous motion of large parts of polymer network I is only expected at high temperatures, which in turn will lead to a high glass transition temperature. The low activation energy also implies a broad temperature range in which this glass transition occurs.

In sharp contrast with the data of I are the results for the network II prepared from 1,4-butanediol diglycidyl ether. In this case the increase in molecular mobility is considerable when the temperature is raised above the transition temperature at 262 K. The very flexible $-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-$ unit connecting the two epoxide groups in II causes a fast increase in quenching rate of the triplet excited state at relative low temperatures, resulting in an activation energy well above 100 kJ/mol. From this high E_a value a low glass transition temperature as well as a short temperature range in which this transition takes place is expected. Similar considerations have been applied to the other bisepoxides and mixtures thereof (18).

In order to relate the local molecular mobility of the individual polyepoxides with the mechanical properties we performed Dynamic Mechanical Thermal Analysis on these polyepoxide networks. When the DMTA data for the different networks are compared, there is only one low temperature transition around 210 K that is observed in all networks. This is probably the β -relaxation, due to mobile hydroxyethyl oxide end groups (19-22). A variety of transition temperatures and widths in transition range are observed at the main transition (fig. 11). A low glass transition temperature is found for the flexible bisepoxide II, together with the short temperature range in which this transition occurs. In contrast to II, the main transition of I is situated at high temperatures and it is a rather broad transition. The results of a few other polyepoxides are included in figure 11. All these mechanical properties are in agreement with the extrapolations deduced from the emission measurements. The latter is indicative for the preamble of the glass transition which is observed with DMTA.

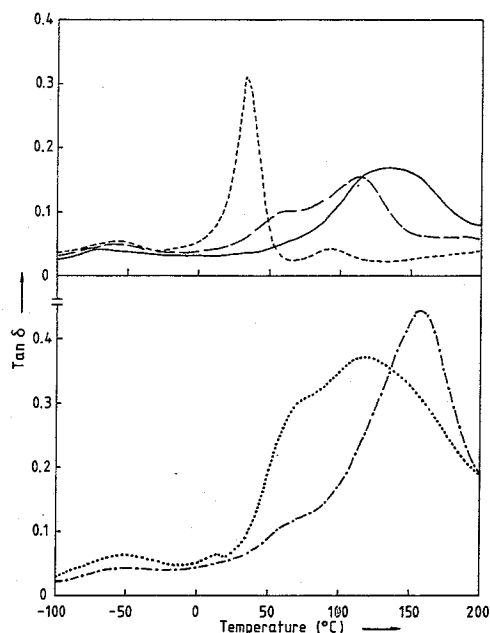


Fig. 11. $\tan \delta$ as a function of temperature for several polyepoxide networks, measured at a frequency of 1 Hz. Upper part: (—) = I; (---) = II; (-·-) = mixture of I and II (4:6 ww%). Lower part: (·····) = III (technical batch); (-·-·) = III (purified material).

CONCLUSIONS

Throughout the years the use of luminescence from aromatic species incorporated in linear polymers has proved to be very useful in the study of molecular mobility (1,2). The study presented in this paper shows that polymer networks with a much more complicated structure can also be subjected to this technique (17,18). In the photoinitiated cationic polymerization of bisepoxides the probe molecule originates from the photoinitiator. When the luminescence is measured during polymerization and cross-linking the rate of network formation is monitored. This new technique is very sensitive to the composition of the bisepoxides. Furthermore, the results can only be explained when we assume the polymerization being inhomogeneous in nature. A "two-domain hypothesis" is proposed. Activation energies for the local internal mobility can be estimated from the temperature dependence of the luminescence. These results are indicative for the preamble of the glass transition state and appears to be supplementary with data obtained from dynamic mechanical thermal analysis.

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