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Citation for published version (APA):

Meijer, E. W., Leeuw, de, D. M., Greidanus, F. J. A. M., & Zwiers, R. J. M. (1985). Molecular mobility studies in polyepoxides obtained by photoinitiated cationic polymerization. *Polymer Communications*, 26(2), 45-47.

Document status and date:

Published: 01/01/1985

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Molecular mobility studies in polyepoxides obtained by photoinitiated cationic polymerization

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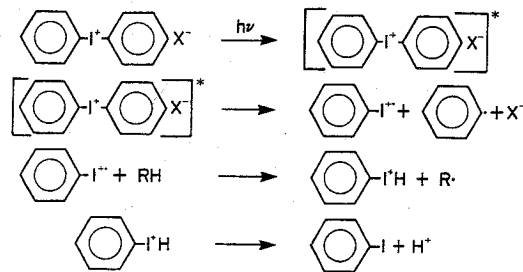
(Received 14 August 1984; revised 26 October 1984)

Using fluorescence, phosphorescence, and e.s.r. spectroscopy the molecular mobility in crosslinked polyepoxides was studied. The networks were obtained by photoinitiated cationic polymerization. Initiator and photoproducts were used as intrinsic probes. A mechanism of inhomogeneous polymerization is proposed to explain the experimental results.

(Keywords: molecular mobility; photoinitiation; phosphorescence; electron spin resonance)

Introduction

In studying the properties of polymers for optical components, we observed a long-lasting bright blue emission after exposure of crosslinked polyepoxides to u.v. light. Three dimensional networks of polyepoxides as coating material recently became available by the introduction of very effective photoinitiators for the cationic polymerization of 1,2-epoxides^{1,2}. This polymerization is initiated by Brønstedt acids, which are obtained by the photodegradation of iodonium or sulphonium salts upon irradiation with u.v. light. The proposed mechanism for the photolysis of diaryliodonium salts is depicted in *Scheme 1*¹. This simplified scheme does not account for the difference in quantum yields of iodobenzene and the Brønstedt acid, 0.39 and 0.65 respectively^{3,4}. Several other intermediates are proposed.



Propagation in the cationic polymerization of cyclic ethers is considered to proceed via a tertiary oxonium ion⁵. The formation of cyclic oligomers due to termination by chain-transfer is a well-known side reaction⁶. Homopolymerization of bisepoxides leads to highly

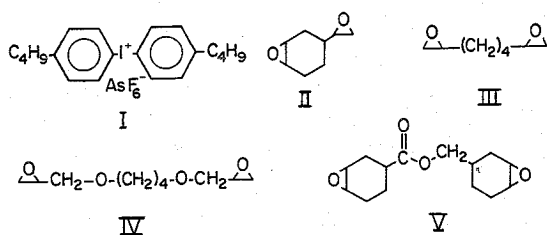
crosslinked networks. The structure of polymer networks obtained by addition polymerization has been the subject of intensive studies⁷⁻⁹. Intramolecular cyclization is commonly referred to as the main reason for the occurrence of inhomogeneous polymerization⁷.

At present there are several techniques available for determining molecular mobility. Emission spectroscopy using fluorescent and/or phosphorescent probe molecules has been performed to gain insight into the viscosity behaviour of linear polymers at the molecular level¹⁰⁻¹². Lifetimes of excited states have been determined as a function of temperature, indicating abrupt changes in internal mobility¹³⁻¹⁵. The fluorescence depolarization method is successfully applied to linear polymers and polymer networks^{16,17}. Another important technique is e.s.r. spectroscopy, which can be used to study radicals trapped in a polymer matrix¹⁸. Most of these microstructure-sensitive methods make use of added probe molecules.

In this communication we describe investigations into the structure of networks obtained from bisepoxides using emission spectroscopy and e.s.r. The photoinitiator system supplies the intrinsic probes. Inhomogeneous polymerization is proposed to explain the experimental results.

Results and Discussion

The polymerization of bisepoxides described here is initiated by the photolysis of di(4-tert-butylphenyl) iodonium hexafluoroarsenate (I) by irradiation at $\lambda = 254$ nm. The bisepoxides comprise 1,2-epoxyethyl-3,4-epoxycyclohexane (II), 1,2,7,8-diepoxyoctane (III), butanediol-diglycidylether (IV), and 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (V). The irradiation time necessary for maximum conversion was established with isothermal d.s.c. measurements. The polymerizations were carried out in air atmosphere.



A typical emission spectrum of a freshly prepared network at ambient temperature is shown in Figure 1. All samples exhibited fluorescence at $\lambda = 340$ nm while polymers of II, III and V showed additional phosphorescence emission with vibrational fine structure around $\lambda = 480$ nm. The lifetime τ obtained from the exponential decay curve of the emission at $\lambda = 480$ nm was calculated to be 1.6 s. The lifetime of the emission at $\lambda = 340$ nm was shorter than the resolution of the apparatus. Maximum intensity of both fluorescence and phosphorescence was obtained by irradiation at $\lambda = 290$ nm. All the experiments were performed at $\lambda = 254$ nm. The lifetimes of the short and long wavelength bands are characteristic of $S_1 \rightarrow S_0$ (fluorescence) and $T_1 \rightarrow S_0$ (phosphorescence) transitions¹⁹.

The polymerization of bisepoxides was investigated by monitoring the luminescence throughout the conversion (to full cure). Right from the start a rapid increase in

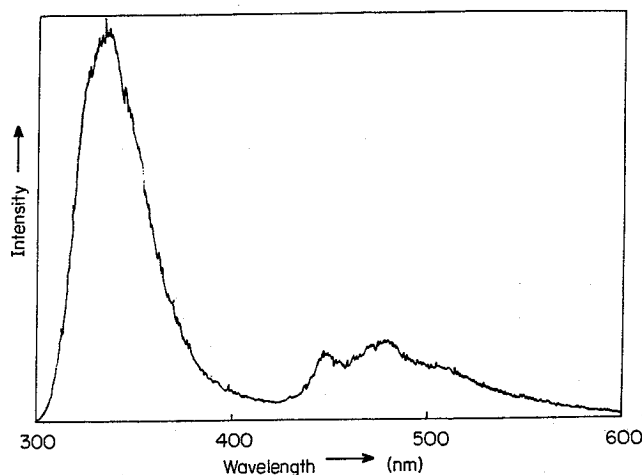


Figure 1 Emission spectrum of a network of bisepoxide II at ambient temperature by irradiation at $\lambda = 254$ nm

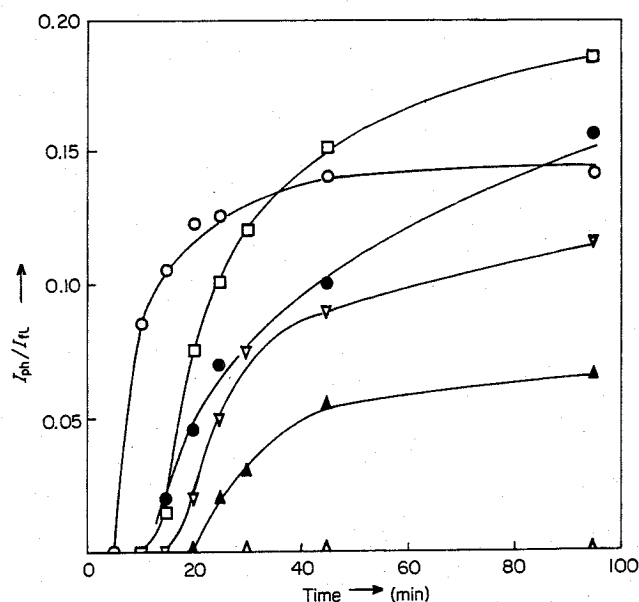


Figure 2 Ratio $I_{ph}(480 \text{ nm})/I_f(340 \text{ nm})$ versus irradiation time for several bisepoxides: (○) II; (□) III; (△) IV; (▽) V; (●) mixture of II and IV; 60:40 ww%; (▲) mixture of II and IV; 40:60 ww%

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). When samples were stored in the dark the fluorescence intensity decreased slightly (10%) after about 20 h, while the phosphorescence vanished. A fast complete regeneration of the latter was accomplished within a few minutes by irradiation. Extended irradiation resulted in an irreversible disappearance of both fluorescence and phosphorescence. In order to compare the individual bisepoxides and mixtures thereof we measured the ratio $I_{ph}(\lambda = 480 \text{ nm})/I_f(\lambda = 340 \text{ nm})$ as a function of irradiation time. Examples are given in Figure 2.

The decay time of the phosphorescence at ambient temperature appeared to be independent of both bisepoxide structure and degree of polymerization.

Although the structure of the emitting species is still unknown, the experimental results indicate that intermediates in the photolysis of the diaryliodonium salt

are responsible for the observed emission phenomena. Most probably, electron transfer processes have to be taken into account since most intermediates contain unpaired electrons and no transitions of the type $Q_1 \rightarrow D_0$ (long lifetime) and $D_1 \rightarrow D_0$ (short lifetime) at short and long wavelengths, respectively, have been observed.

The observation that the decay time of phosphorescence proved to be constant during polymerization is at first sight a remarkable result. The decay time, τ , is given by $\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$, where τ_r and τ_{nr} are the radiative and nonradiative lifetimes of the triplet state, respectively. The nonradiative lifetime is determined by inter- and intramolecular deactivation processes¹⁹. Intermolecular quenching can be attributed to a high local mobility of the luminescent centre or to chemical reactions. For homogeneous polymerization leading to highly crosslinked networks one would expect a gradual increase in crosslink density and hence a gradual decrease of the local mobility. A gradual increase in total lifetime of the triplet state, as polymerization proceeds, is then expected. The constant lifetime leads to the following interpretation. The polymer 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 state predominates τ). The volume fraction of domains with a low internal mobility will increase with conversion.

Networks of II, III and V possess domains with low internal mobility. The volume fraction of these domains is expressed by the ratio I_{ph}/I_n . The ratio I_{ph}/I_n versus time and the onset of the phosphorescence is dependent on the structure and reactivity of the monomers used. Domains in the network formed from IV are apparently too flexible to exhibit phosphorescence at room temperature, which is reasonable on a structural basis. Lowering the temperature will lead to a decreased internal mobility and hence to an increase of the total lifetime. Indeed cooling a sample of IV gives the expected bright blue emission.

Since most intermediates from the photolysis of the iodonium salt are radicals, we performed e.s.r. spectroscopy to detect trapped intermediates with unpaired electrons. All freshly prepared polyepoxides using initiator I contain trapped radicals. The shape of the e.s.r. signals is dependent of the bisepoxide used, as shown in Figure 3. No hyperfine structure could be obtained.

Since the shape of the e.s.r. signal is determined by time-dependent interactions in a complex way, it is premature to correlate differences in the observed spectra with differences in molecular mobility and/or structure of the polyepoxide.

Evaluation of the e.s.r. signal intensity in time showed that the concentration of trapped radicals increases during polymerization, while the shape of the signal is unaffected. The stability of the trapped radicals in the dark was studied at several stages of the polymerization. The decay was only slightly dependent on bisepoxide structure and degree of polymerization. Apparently, the stability (decay) and mobility (shape of signal) of the radical is independent of the stage of the polymerization at which it is trapped. No gradual increase in decay time is observed. Since the e.s.r. signal intensity is increased with time, the volume of domains in which radical are trapped, increases. These e.s.r. results support the 'two-domain hypothesis' outlined above for the emission phenomena.

On the basis of mobility studies we conclude that the

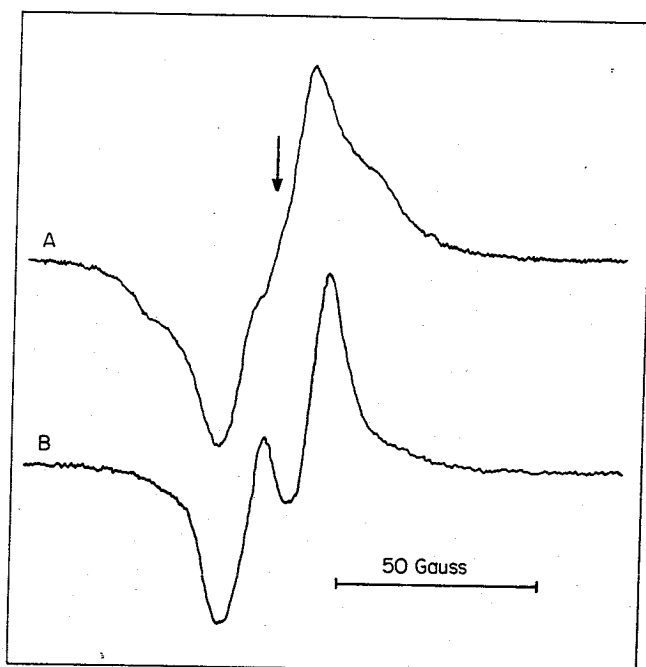


Figure 3 E.s.r. spectrum of (A) polyepoxide II and (B) polyepoxide IV

photoinitiated cationic polymerization of bisepoxides leads to polymer networks with domains of lower and higher internal mobility at room temperature. This heterogeneous structure is the result of a polymerization in which an inhomogeneous increase in crosslink density takes place. Further research concerning the nature of the emitting species and trapped radicals in combination with the temperature dependence of fluorescence and phosphorescence of polyepoxides is in progress.

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