

Change of molecular mobility during formation of epoxy allylic interpenetrating polymer networks

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Abstract

The results of investigation of a change of molecular mobility in sequential and simultaneous curing of the compositions based on epoxy and allylic oligomers are given, using the pulse NMR spectroscopy method. It was established that by simultaneous formation of epoxy and allylic networks the mutual hindrances to the full conversion of reactive groups occur resulting in the increase of defects in the interpenetrating polymer network (IPN) structure and an increasing molecular mobility of all its fragments. In the case of polymerization of allylic component of the IPN, when the formation of epoxy network is basically fully completed, the increase of molecular mobility in the system is due to a decrease of the limit conversion degree of polymerizable groups in the allylic monomer. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The concepts of phase separation of constituent networks during the formation of interpenetrating polymer networks (IPNs) are the basis of the modern theory of IPNs [1]. The relationships between kinetics of the network formation and microphase separation [2–5] allow to explain and predict practically all the features of the structure formation of IPN and their properties. Depending on the reaction rates of the network formation and their ratios, the formation of: (i) thermodynamically non-equilibrium systems with quasi-one-phase structure that is similar to the initial reaction mixture; and (ii) systems with high degree of phase segregation [6–11] become possible. Inhibition and acceleration effects of polymerization and polycondensation reactions [2,3], a change of rheokinetics of IPN formation [12], the peculiarities of viscoelastic and magnetic properties and microphase structure of polymers [13–15] are due to the structure formation of dissimilar networks through the phase separation process. In a series of cases the change of kinetics of independent networks formation is accompanied by a change of the limiting degree of reactive groups

conversion [2,4,16], that may lead to the formation of topological defects in the IPN structure and to the change of relaxation properties and molecular mobility of fragments of network intersites.

The distinct influence of kinetics conditions of independent networks formation on the structure and relaxation properties of binary IPN is yet to be shown in systems where both of components are dense networks. Evidently, in this case owing to the sterical limitations, even partial networks penetration will result in the formation of topological defects (sites of lower functionality, intramolecular cycles, ends of chains with non-reacted functional groups etc.). From this point of view, great interest has been shown in the investigations of peculiarities of IPN structure formation based on epoxy and allylic oligomers under conditions of simultaneous and sequential polymerization. However, during polymerization of epoxy and allylic oligomers, polymers with very close viscoelastic, relaxation and thermo-physical properties are formed and after completion of IPN synthesis they become difficult to distinguish. In the present paper the influence of conditions of epoxy–allylic IPN formation on their structure and properties is considered by an analysis of the molecular mobility change during the process of multistage polymerization. The estimation of molecular mobility was carried out through the change of

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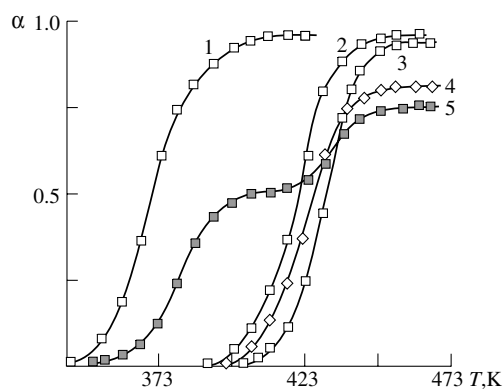
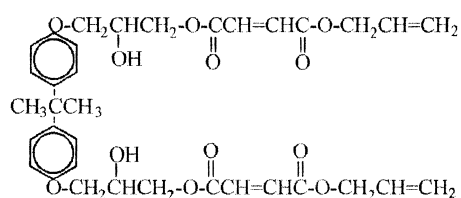


Fig. 1. Change of the conversion degree (α) of reactive groups upon non-isothermal curing of ED-22 (1,2); EAM (3); and mixtures thereof in the ratio of 30:70 (4) and 50:50 (5) mass% in the presence of $C_6H_5CH_2NH_2:BF_3$ (2,4); $C_6H_5NH_2:BF_3$ (1,5); and DCP (3–5).

magnetic characteristics of the system (spin–spin relaxation time and population of proton groups with different relaxation times) [17].

2. Experimental

Epoxy oligomer based on bisphenol A (ED-22) of molecular mass 380 g mol^{-1} , weight fraction of epoxy groups 23.5%, $n_D^{20} = 1.5694$ has been used. A condensation product of the epoxy oligomer ED-22 with monoallylmalenate (allylic iodine number 590 mg g^{-1} , maleinate iodine number 570 mg g^{-1} , acid number 10 mg g^{-1} KOH) with the following idealized structural formula (without calculation of oligomerization) was used as the oligomeric diallyl compound (EAM):



Polymerization of allylic oligomer via allylic and maleinate groups was carried out by free-radical mechanism [18] in the presence of dicumyl peroxide (DCP, $T_m = 312 \text{ K}$, density $d_4^{20} = 1.085 \times 10^6 \text{ g m}^{-3}$). Trifluoride complexes with aniline $C_6H_5NH_2:BF_3$ (21.5 wt% BF_3 , 4.3 wt% nitrogen, $d_4^{20} = 1.230 \times 10^6 \text{ g m}^{-3}$) and benzylamine $C_6H_5CH_2NH_2:BF_3$ (20.3 wt% BF_3 , 4.2 wt% nitrogen, $d_4^{20} = 1.238 \times 10^6 \text{ g m}^{-3}$) dissolved in diethylene glycol were used as catalysts for the cationic polymerization of the epoxy oligomer [19]. The amount of dicumyl peroxide and boron trifluoride complexes introduced into the compositions were 3 and 5 wt% (with respect to the oligomer), respectively.

The total degree of conversion of all reactive groups (epoxy, allylic and maleinate) was determined by differential scanning calorimetry (DSC) from the ratio of the heat of reaction at time t , ΔQ_t , to its limiting value, ΔQ_∞ , which was estimated under a linear heating rate of 6.67 K s^{-1} ($\alpha = \Delta Q_t/\Delta Q_\infty$). Additionally, the conversion of epoxy groups was determined by IR-spectroscopy from the change of the intensity of the absorption band at 915 cm^{-1} . The degree of epoxy group conversion (or the relative fraction of the reacted group) was determined by the ratio of the change in the optical density D of the bands at 915 cm^{-1} at a given time to the initial optical density D_0 (5 min after component mixing): $\alpha = (D_0 - D)/D_0$. The effective concentration of crosslink sites was calculated from the elasticity modulus for high-crosslinked polymer networks [20]. The elasticity modulus was determined at temperatures higher than T_g using thermomechanical analysis during stationary operative compressible load 0.78 MPa on the cylindrical samples with diameter 0.01 m and height 0.01 m . Glass transition temperature was measured from a beginning step in the α -relaxation transition region from the temperature dependence of heat capacity which was estimated by DSC. Microcalorimetric investigations were conducted using DCM-2M calorimeter with heating rate of $6.7 \times 10^{-2} \text{ K s}^{-1}$. The transmission spectra were taken using two-ray prismatic spectrometer UR-20 at a scanning rate of 32 cm m^{-1} , recording scale 20 mm cm^{-1} . The spin–spin relaxation times T_2 were measured under isothermal conditions (during the process of IPN formation) using proton NMR relaxometer at a frequency of 17 MHz . The curves of the fading of the transverse magnetization were recorded using the Carr–Purcell–Meiboom–Gill impulse sequence [16]. The form of fading curves were analysed in the range of magnetization reducing to 5–7% of the initial value.

3. Results and discussion

To estimate the temperature range of simultaneous and sequential curing of epoxy and allylic networks formation, the microcalorimetry investigations of individual oligomers and their mixtures were carried out under isothermal conditions. Dicumyl peroxide which has a high temperature of homolytic decay (half-life period of DCP: 1 h at 408 K) was used for the initiation of polymerization of allylic oligomers. It was taken into account that with increasing temperature of the curing process there occurs a growth in the rate constant of reinitiating polymerization reaction by low-active allylic radicals. This results in a decrease of negative effect of the degradation chain transfer to the monomer. As a result, the total rate and conversion degree increase [18]. In the presence of such an initiator, the curing of allylic oligomer proceeds in the temperature range from 398 to 448 K . The total heat effect of the curing process of EAM reaches 355 J g^{-1} , of which all the unsaturated bonds of the oligomer (allylic and maleinate) accounted for

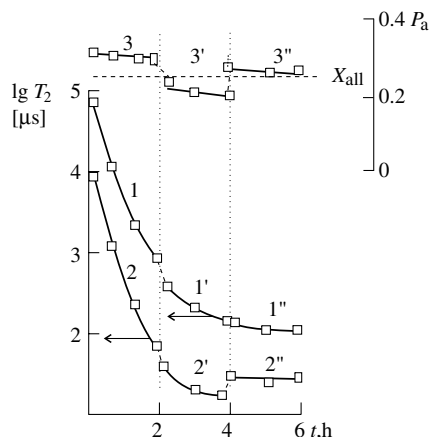


Fig. 2. Change of spin–spin relaxation times T_{2a} (1, 1', 1''), T_{2b} (2, 2', 2'') and the share of protons corresponding to the long component of FTM P_a (3, 3', 3'') by curing of IPN with 30 mass% of EAM in the presence of $C_6H_5NH_2:BF_3$ and DCP at temperatures 333 K (1–3), 373 K (1'–3'), and 413 K (1''–3''). Change of the curing temperature is marked by vertical dotted lines.

81 kJ mol⁻¹. This testifies in favour of high degree of polymerization ($\alpha > 90\%$) for both, allylic and maleinate groups of the oligomer. In this temperature range (398–448 K) complete polymerization of the epoxy oligomer ED-22 takes place in the presence of boron trifluoride complex with the highly basic aromatic amine — benzylamine ($K_A = 2.35 \times 10^{-5}$) as catalyst: the degree of epoxy groups conversion (α) reaches the topological limit for network polymers (Fig. 1). For the mixture of ED-22 with EAM in the presence of $C_6H_5CH_2NH_2:BF_3$ and DCP during the increase of temperature from 388 to 448 K, fast polymerization involving all reactive groups (epoxy, allylic, maleinate) was observed. There was also a distinct decrease in their total limiting conversion (Fig. 1).

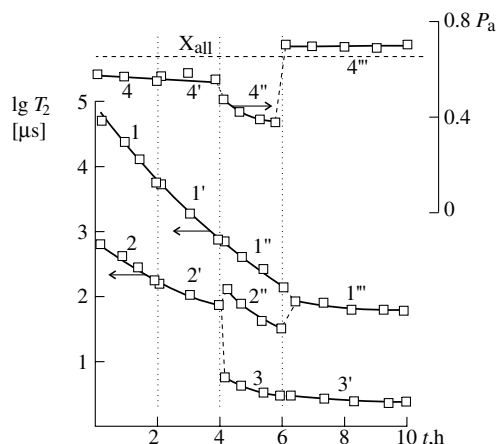


Fig. 3. Change of the spin–spin relaxation times T_{2a} (1, 1', 1'', 1'''), T_{2b} (2, 2', 2''), T_{2c} (3, 3') and the share of protons corresponding to the long component of FTM P_a (4, 4', 4'') upon curing of IPN with 70 mass% of EAM in the presence of $C_6H_5NH_2:BF_3$ and DCP at temperatures 333 K (1, 2, 4), 373 K (1', 2', 4'), 413 K (1''–4''), and 443 K (1''', 3', 4''). Change of the curing temperature is marked by vertical dotted lines.

Upon using boron trifluoride complex with a less-basic aromatic amine — aniline ($K_A = 5.2 \times 10^{-10}$) — for curing the epoxy oligomer, the full polymerization of ED-22 is completed at temperatures up to 393 K. This change in the temperature of synthesis of an IPN allows the separation of the curing processes of epoxy and allylic constituents of the reaction mixture (Fig. 1). Thus, in the case of curing of the mixture ED-22 and EAM in the presence of $C_6H_5NH_2:BF_3$ and DCP at temperatures from 370 to 390 K, only polymerization of the epoxy oligomer occurs. It is only upon further increase of temperature that the polymerization of the allylic oligomer begins. The curve of the temperature dependence of total degree of conversion degree of oligomers is S-shaped.

Thus, the change of the curing temperature and the basicity of the complex-forming amine in the epoxy oligomer catalyst and the curing temperature gives a possibility to obtain systems in which the formation of networks proceeds simultaneously (as in the presence of $C_6H_5CH_2NH_2:BF_3$ and DCP) or sequentially (as with $C_6H_5NH_2:BF_3$ and DCP). Undoubtedly, this should be reflected in the structure of the IPN and in the features of the changes in molecular mobility upon curing of the compositions.

The investigations of changes in the magnetic properties of the reaction systems during the formation of epoxy and allylic networks have been carried out using the NMR relaxation method. This was done by multistage increasing of isothermal polymerization temperature of the oligomer mixture (with the ratio ED-22/EAM = 70:30 mass%) in the presence of $C_6H_5NH_2:BF_3$ and DCP. It was established that from the very onset of reaction, the system becomes non-homogeneous in the sense of molecular mobility and contains two groups of protons with spin–spin relaxation times T_{2a} and T_{2b} , which are different by one order of magnitude (Fig. 2). During 2 h the short spin relaxation time T_{2b} decreases rapidly and acquires the values that are inherent to polymers with dense networks in elastic state [17]. The long relaxation time T_{2a} also decreases upon curing but after the first stage of curing is completed, T_{2a} maintains the high values. While this takes place, the fraction of protons involved in the group (P_a), corresponding to the long component of the fading of the transverse magnetization (FTM), coincides with the fraction of proton introduced into the composition with EAM ($X_{all} = 0.23$, Fig. 2). By taking into account the fact that in the given system an epoxy network is formed at 333 K, where the allylic oligomer is not polymerized, the group of protons with relaxation times T_{2a} may be uniquely assigned to the EAM molecules. The group of protons with spin–spin relaxation times T_{2b} corresponds, on the other hand, to the epoxy network protons. Then, the decrease in the relaxation times T_{2a} by two orders of magnitude testifies that the epoxy network formed restricts the molecular mobilities in the allylic oligomer.

Uncured oligomer also has an influence on the molecular mobility of an epoxy network. From the data for the system

Table 1

The influence of the composition of epoxy allylic IPNs on the conversion degree of reactive groups, effective concentration of crosslink sites (v_c) and glass transition temperature (T_g)

Oligomers and mixtures thereof	Degree of conversion of reactive groups		v (mol m ⁻³)	T_g (K)
	Total (DSC)	Epoxy groups (IR spectrosc.)		
Epoxy oligomer hardener C ₆ H ₅ NH ₂ :BF ₃ (5%)				
ED-22	0.95	0.95	2000	403
ED-22:EAM (70:30)	0.85	0.97	1500	363
ED-22:EAM (50:50)	0.75	0.93	730	343
ED-22:EAM (30:70)	0.70	0.96	1300	355
EAM	0.95	–	1400	405
Epoxy oligomer hardener C ₆ H ₅ CH ₂ NH ₂ :BF ₃ (5%)				
ED-22	0.95	0.95	1900	395
ED-22:EAM (70:30)	0.84	0.89	1400	370
ED-22:EAM (50:50)	0.60	0.78	860	340
ED-22:EAM (30:70)	0.67	0.74	970	360
EAM	0.87	–	1400	400

with high EAM content (70 mass%) it is seen that after completing the first stage of IPN synthesis (333 K, 2 h) fragments of the epoxy network formed have high molecular mobility and T_{2b} values are characteristic of plasticized polymers having low concentrations of tri- and tetra-functional sites (Fig. 3). This strongly expressed mutual influence of fragments of epoxy network and allylic (uncured) oligomer on each other's molecular mobility forms the basis of the suggestion that the system is formed with incomplete phase segregation of the components (epoxy polymer and allylic oligomer).

For the system with EAM content 70 mass%, the high molecular mobility of epoxy network (high values of T_{2b}) is also retained at the second stage of curing (373 K, 2 h). Only at 413 K when the polymerization of allylic monomer proceeds (Fig. 1), a group of protons with short relaxation times T_{2c} is evolved (Fig. 3). The fraction of protons in this group is close to that introduced into the composition with ED-22. Here, the fading of the transverse magnetization has three components with appropriate spin–spin relaxation times, while T_{2c} values are characteristic of polymers with

dense network (30 ms). At a given stage of the curing, the group of protons relaxing with time T_{2c} corresponds to the epoxy network, while the groups of protons with relaxation times T_{2a} and T_{2b} correspond to uncured oligomer EAM and to the network based on it. Upon further curing of allylic oligomer (443 K, 4 h) the allylic network formed becomes more homogeneous in the sense of molecular mobility and protons with relaxation times T_{2a} and T_{2b} unite into a single group (Fig. 3).

As a result of the polymerization of allylic oligomer, the post-cure of the system considered (443 K, 4 h) leads to a decrease of its molecular mobility and the values of T_{2a} decrease (Figs. 2 and 3). However after the structure formation is completed (i.e. the values T_2 reach their limit) the slowly relaxing group of protons is still retained, and in all the cases its “population” coincides with the fraction of protons introduced into the composition with EAM. The T_{2a} values reached up to the moment of completeness of the structure formation increase with the concentration of EAM and are characteristic of structurally plasticized networks (the networks with lower concentration

Table 2

The influence of the composition of epoxy allylic compounds on the parameters of relaxation processes during different stages of IPN curing

EAM concentration (mass%)	Curing conditions (temp. K/time h)	Relaxation times		Share of protons	
		log T_{2a} (μs)	log T_{2b} (μs)	P_a	X_{all}
30	393/4	2.1	2.7	0.55	0.23
	420/2	1.5	2.3	0.45	
	440/2	1.5	2.4	0.35	
50	393/4	2.3	3.1	0.62	0.45
	420/2	1.8	2.7	0.50	
	440/2	1.8	2.7	0.35	
70	393/4	2.6	3.4	0.65	0.68
	420/2	2.0	2.7	0.55	
	440/2	2.0	2.8	0.45	

of tri- and tetra-functional sites). A decrease in the effective concentration of crosslink sites is particularly marked in the system enriched with allylic component (Table 1), and it may be because the epoxy network formed at first makes the allylic network formation difficult (probably sterically). As a consequence, a general plasticization of IPN is observed, which shows up in non-additive decrease of its glass transition temperature (Table 1). Besides the NMR-relaxation data, the explanation suggested is also confirmed by the fact that the decrease in the total limit conversion of reactive groups takes place with no decrease in the conversion of epoxy groups (Table 1).

As in the case of the above systems, by using a complex of boron trifluoride with benzylamine ($C_6H_5CH_2NH_2 \cdot BF_3$) for curing of epoxy constituents of IPN, from the very onset of curing and up to its full completion the fading of the transverse magnetization is of non-exponential type and is characterized by two values of spin–spin relaxation times, while the kinetic dependencies of T_{2a} and T_{2b} are similar to the ones shown in Fig. 2. However, in this case, as can be seen from the data in Table 2, the relaxation properties of IPN formed have the following distinguishing features: (i) the short relaxation times of T_{2b} retain the relative high values even upon full completion of structure formation; and (ii) the P_a values, as a rule, are inconsistent with the fraction of protons introduced into the systems with EAM (X_{all}) or ED-22 (X_{ep}), and the proton groups evolved cannot be assigned either to epoxy or to the allylic constituent of the IPN. Thus, for example, if it is granted that all the protons of allylic component in the system with EAM of 30 mass% belong to the group corresponding to the long constituent of the FTM, the large increase of P_a value over X_{all} is indicative of the contribution of epoxy oligomer protons to the given group. On the other hand, the lower values of P_a in comparison with X_{all} for the system containing EAM of 70 mass% testifies that a portion of allylic component protons is included in the group corresponding to the short component of the FTM. Such peculiarities of changes of magnetic characteristics of the system indicates that on simultaneous curing of IPN components, both epoxy and allylic networks contain the structural fragments with high and low molecular mobility. The reason is that during simultaneous curing of ED-22 and EAM some mutual sterical difficulties emerge for the formation of epoxy and allylic networks and both networks contain sites with lower functionality. While this occurs, a decrease in the effective concentration of crosslink

sites is due to a reduction in both the total degree of the conversion of reactive groups and in the conversion of epoxy groups (Table 1), while non-additive decrease in glass transition temperatures is a manifestation of the mutual plasticization of polymers of different nature.

4. Conclusions

The experimental data show that by polymerization of allylic component of the IPN when the structure formation is basically fully completed, a decrease of the limiting degree of the conversion of polymerizable groups of allylic oligomer is observed. This results in an increase of defects in the allylic network and in the enhancement of the molecular mobility of its fragments. By simultaneous formation of epoxy and allylic networks the mutual hindrances for the full conversion of reactive groups of both components occur, and the molecular mobility of the all structural fragments of IPN increases.

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