

## **On the Problem of Structural Microinhomogeneity of Epoxy Network Polymers**

**L. M. Bogdanova, I. M. Belgovskii, V. I. Irzhak and B. A. Rosenberg**

Institute of Chemical Physics, USSR Academy of Sciences, Moscow, USSR

*Presented at the 7th IUPAC Discussion Conference "Polymer Networks",  
Karlovy Vary, CSSR, September 15-19, 1980*

### Summary

An increase in light scattering intensity was observed throughout the curing of diepoxides with amines. The value of such an increase depends on the chemical structure of the reagents and on the curing temperature. This phenomenon was explained by polycondensation reaction peculiarities and the glass state transition nature.

### Introduction

The purpose of the research described here is to investigate how peculiarities of the mode of formation of network polymers are seen in the glass state structure of the latter. To understand this, it is necessary to study both the topological structure that is formed throughout the ideal polycondensation process yielding network polymers and the supermolecular structure that is realized in a topologically simple system, for example in linear polymers.

As far as the topology of polycondensation network polymers is concerned it is characterized by many defects even if it was formed under the most favourable conditions. The underestimation of this fact leads to the appearance of a front-factor different from unity in the equation for the equilibrium moduli in the viscoelastic state. However, these inhomogeneities are too small to affect the supermolecular structure of network polymers (TOPOLKARAEV et al. 1979, 1980). On the other hand, linear polymers in the glassy state are characterized by definite degrees of inhomogeneities detected by small-angle X-ray scattering and electron microscopy and seen as globular structure in the second case (LEBEDEV 1978).

### Experimental

The systems studied were epoxides obtained by curing of resorcin and diethylene glycol diglycidyl ethers (RDGE and DDGE, respectively) with stoichiometric amounts of diamines. The purity of the initial

oligomers determined by epoxy group titration was 99.5% and 98%, respectively. Epoxy oligomers were purified by vacuum distillation, m-phenylenediamine (m-PhDA) by sublimation and 4,4'-diaminodiphenylsulfone (DPhSDA) by crystallization from alcohol.

The method used was as follows: To remove dust the reaction mixture was filtrated through a dense filter into a cylindrical cell of 10 mm in diameter and placed in the light scattering instrument; then, the mixture was freed from air bubbles with the help of a vacuum pump. The temperature in the cell was kept constant. The light scattering intensity was measured during the curing process of diepoxides with amines under isothermal reaction conditions at scattering angles of 30-150°,  $\lambda = 546$  nm. The corresponding reaction kinetics was measured either calorimetrically or by epoxy group titration.

The Debye and Bueche theory was applied to experimental data treatment (DEBYE and BUECHE 1949). According to this theory, if  $\gamma(r) = e^{-r/a}$ , then

$$R_{\theta} = 4\pi^3 \bar{\eta}^2 a^3 / \lambda_0^4 (1 + k^2 s^2 a^2)^2 \quad (1)$$

where  $\gamma(r)$  is a correlation function for fluctuation,  $r$  the scalar distance between volume elements 1 and 2,  $a$  the distance over which inhomogeneities extend,  $R_{\theta}$  the Rayleigh ratio for unit scattering volume,  $\bar{\eta}^2$  the mean-square average dielectric constant fluctuation,  $\lambda_0$  the wavelength in vacuo,  $\theta$  the scattering angle,  $k = 2\pi/\lambda$  and  $s = 2 \sin \theta/2$ . The values  $a$  and  $\bar{\eta}^2$  can be obtained graphically from equation (1) or from dissymmetry calculations as made by GALLACHER et al. (1962)

$$\Delta = R_{\theta_2} / R_{\theta_1}; \quad a = (1/k) [(1 - \Delta^{1/2}) / (\Delta^{1/2} s_2^2 - s_1^2)]^{1/2};$$

$$\bar{\eta}^2 \text{ from eq. (1).}$$

The internal structure of cured epoxy resins was derived by surface etching in high frequency plasma in argon. Samples for the transmission electron microscopy were prepared by preshadowing with Pt alloy and by perpendicular deposition of the carrier carbon film. The replicas were peeled off by means of gelatine.

### Results and discussion

It is known that scattering is the result of density fluctuations or, in other words, of dielectric constant fluctuations. The extent of these fluctuations is a measure of the inhomogeneity of the solid. The investigation showed that in the curing of epoxy oligomers with amines there occurred, even far from the

gel point, an increase in the light scattering intensity whose limiting value depended on the chemical structure of the initial oligomers and the curing temperature (Fig.1).

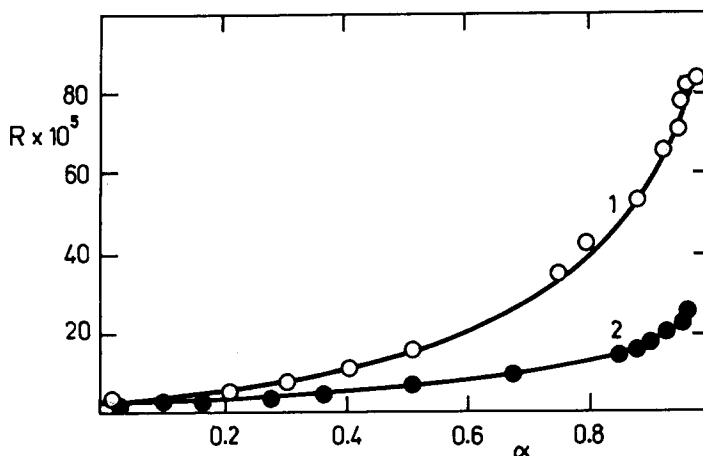


Fig.1. Light scattering intensity change  $R$  ( $\text{cm}^{-1}$ ) in the curing of epoxy oligomers with amines. 1 RDGE with DPhSDA,  $140^\circ\text{C}$ ; 2 DDGE with DPhSDA,  $138^\circ\text{C}$ ;  $\alpha$  is the conversion,  $\theta = 90^\circ$ .

A graphical treatment of the experimental results showed that the correlation function is defined by the equation  $\gamma(r) = e^{-r/a}$  at the final stages of the reaction. Consequently, the parameters of structural inhomogeneities can be calculated from equation (1) (Fig.2).

To explain the light scattering increase in the curing of epoxy resins with amines it is necessary to consider the chemical peculiarities of the polycondensation reaction of these two components. It is known now that this reaction is a complex one accompanied by increasing concentration of hydroxy groups which are responsible for autocatalysis and the formation of intra- and intermolecular bonds. This effect leads to aggregate formation in the reaction media (ARUTUNYAN et al. 1974, BLYACHMAN et al. 1974). The light scattering intensity increase in the initial reaction stages was shown by two methods - rapid variation of temperature or addition of polar solvents to the reaction mixture of RDGE and m-PhDA - to be due to aggregation. An abrupt temperature increase in the experimental cell (3 mm in diameter) in the curing of RDGE with m-PhDA leads to a sharp decrease of the light scattering intensity and vice versa (Fig.3a).

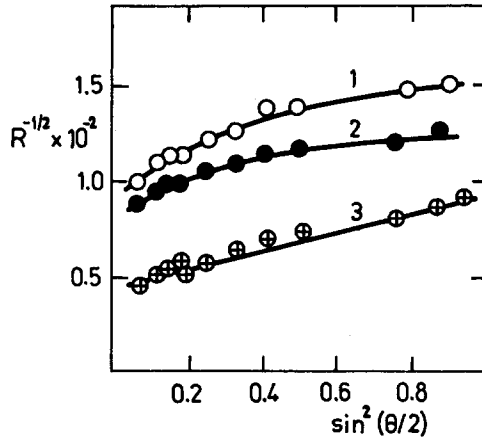


Fig.2. The evidence of the correlation function  $\gamma(r) = e^{-r/a}$ , DDGE - DPhSDA, 138°C; 1  $\alpha = 0.35$ ; 2  $\alpha = 0.80$ ; 3  $\alpha = 0.93$ ;  $\theta = 90^\circ$ .

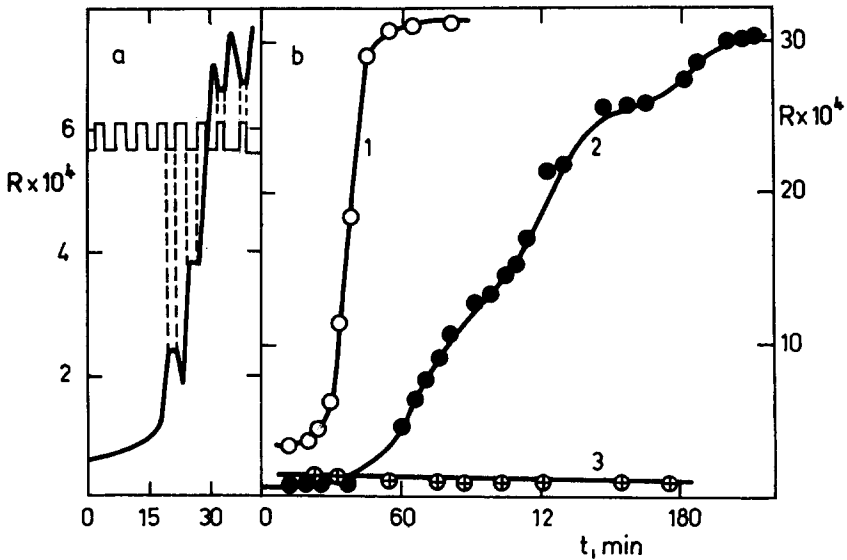


Fig.3. The dependence of the light scattering intensity  $R(\text{cm}^{-1})$  on the pulsing curing temperature (a) and on the addition of polar solvents (b). 1 RDGE - m-PhDA, 70°C, 2 the same as with the addition of 3.5% DMPPhA; 3 the same as with the addition of 54% DMPPhA,  $\alpha = 0.75$ ;  $\theta = 45^\circ$ .

The addition of polar solvents (for example, 1.5% of butanol or 3.5% of dimethylformamide (DMPhA)) which destroys the hydrogen bonds in the initial reaction mixture leads to a decrease in the intensity of light scattering and the addition of DMPhA in a concentration of 54% by weight eliminates the light scattering completely (Fig.3b).

The role of intramolecular interactions in the formation of inhomogeneous structures of network polyacrylates and polyurethanes was shown by infrared spectroscopy, light scattering and spectroturbidity methods (LIPATOVA et al. 1974, BERLIN 1969). Aggregates formed in the reaction mixture and observed first as density fluctuations are fixed by the curing reaction and then appear as the centres of inhomogeneous polymer structures. If the aggregation, caused by hydroxy groups the contents of which increase in the polycondensation process of epoxides with amines, really contributes to the formation of polymer structure inhomogeneities, then the values of  $R_0$  and  $\alpha$  will be dependent upon the curing temperature. In fact, the lower the curing temperature, the greater are the size of aggregates and the viscosity of the reaction mixture. Because of that, the diffusion effects are greater and so the polycondensation process becomes more local. If the curing temperature is low the transition into the glassy state occurs at lower conversions and also gives rise to a local process. Due to these two factors (aggregation and glass state transition) the network polymer structure formed is soft and the extent of inhomogeneities is higher at a low curing temperature than at a high temperature. The higher the temperature, the more rapidly appear the reaction centres whereas the reaction centre propagation is much slower. Consequently, the extent of inhomogeneities decreases. This phenomenon was shown experimentally in isothermic curing of RDGE with m-PhDA at 48, 70, 90°C (Fig.4).

Throughout polymer structure formation provided the above-mentioned fixed aggregates do not contact each other, contraction occurs without hindrances and the polymer chains are packed in the equilibrium state. But when the associates come into contact the system becomes hard and then regions of network polymer with a non-equilibrium structure are formed. As a result, polymer regions of different densities and consequently light scattering are observed. Some of the polymer structure regions will be etched much more easily than others so that globular structures are detected under the electron microscope. Perhaps exactly this fact explains that the extent of inhomogeneities determined by the light scattering method is the same as the globular dimensions ascertained by

electron microscopy. The results are represented in Table 1. For comparison, data on model network investigations are given.

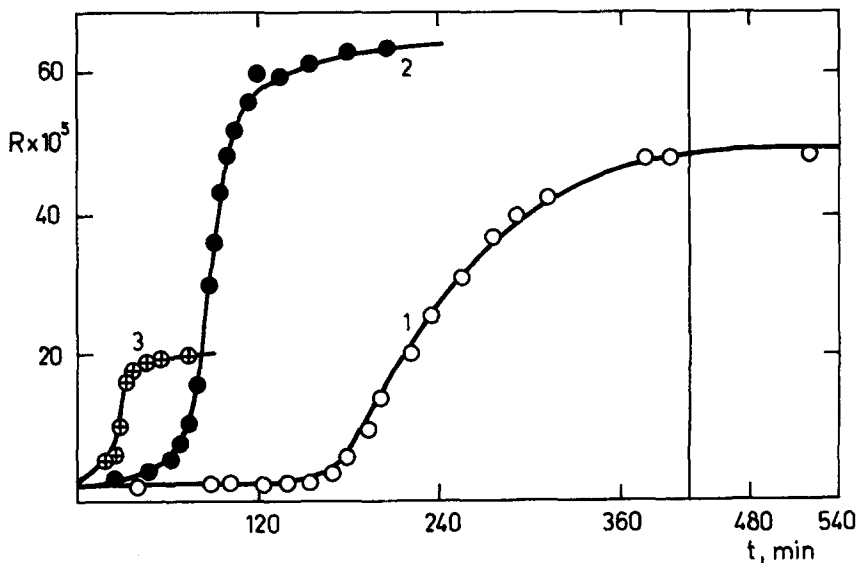


Fig.4. The dependence of the light scattering intensity  $R(\text{cm}^{-1})$  on the curing temperature RDGE - mPhDA: 1 48, 2 70, 3 90°C;  $\theta = 90^\circ$ .

TABLE 1  
The structure characteristics of cured epoxy resins

	$T_c, ^\circ\text{C}$	$R_{90} \times 10^5$	$a, \text{nm}$	$\text{g.d., nm}$	$\bar{\eta}^2 \times 10^7$	$T_g, ^\circ\text{C}$
FGE-aniline	70	1.3	-	-	-	
FGE-m-PhDA	70	5.0	-	-	-	
RDGE-aniline	70	2.0	-	-	-	70
RDGE-m-PhDA	48	41.0	95	70-80	3.3	
	70	65.0	60	50-60	4.6	120
	90	18.0	40	40	1.6	
RDGE-DPhSDA	140	82	100	140	6.2	156
DDGE-DPhSDA	140	16.0	50	80	0.8	47

$T_c$  is the curing temperature, g.d. are globular dimensions,  $T_g$  is the glass temperature, FGE is phenylglycidyl ether,  $R$  ( $\text{cm}^{-1}$ ).

The evaluation of density fluctuations in cured epoxy resins by light scattering data gives a value of  $\Delta d \approx 1 \times 10^{-3} \text{g/cm}^3$  that is ten times less than that for addition polymers. However, in the latter case, the polymerization process from the very beginning proceeds as a local one and is accompanied by considerable structural and physical transformations up to micro-syneresis (ROSHCHUPKIN et al. 1977). In the polycondensation process there are no reasons to expect a highly nonideal polymer structure though our experimental data allow us to anticipate a more nonideal polymer structure than was reported by other authors before (DUŠEK et al. 1975, TOPOLKARAEV et al. 1979). However, the correlation between synthetic conditions, glass state-transition features and topological structure is quite evident. It is not quite clear, however, what is the amount of nonideality of polycondensation epoxy polymers and whether it is sufficient to affect such properties as viscoelastic modulus, sol fraction yield etc. measured inaccurately.

#### References

- ARUTUNYAN Ch.A., TONoyAN A.O., DAVTYAN S.P., ROZENBERG B.A., and ENIKOLOPYAN N.S.: Dokl.Akad.Nauk SSSR, 214, 832 (1974).  
 BERLIN A.A.: Europ.Polym.Symp. 15-41 (1969).  
 BLYACHMAN E.M., NIKITINA A.A., ZELENINA N.L., and SHEBCHENKO Z.A.: Vysokomol.Soed. A16, 1031 (1974).  
 DEBYE P. and BUECHE A.: J.Appl.Phys. 20, 518 (1949).  
 DUŠEK K., ILAVSKÝ M., and LUŇÁK S.: J.Polym.Sci., Symp. 53, 29-44 (1975).  
 GALLACHER L. and BETTELHEIM F.A.: J.Polym.Sci. 58, 697 (1962).  
 LEBEDEV V.P.: Uspechi Chim. 47, 127 (1978).  
 LIPATOVA T.E., MOYSA E.G., ZUBKOV S.A., and SEMENOVICH G.M.: Vysokomol.Soed. A14, 287 (1972).  
 ROSHCHUPKIN V.P., OSERKOVSKII B.V., KALMYKOV Yu.B., and KOROLEV G.V.: Vysokomol.Soed. A19, 699 (1977).  
 TOPOLKARAEV V.A., OSHMYAN V.G., NISITSHENKO V.P., ZELENETSKII A.N., PRUT E.V., BERLIN A.A., and ENIKOLOPYAN N.S.: Vysokomol.Soed. A21, 1515 (1979).  
 TOPOLKARAEV V.A., RUDNEV S.N., OSMYAN V.G., BERLIN A.A., OLEINIK E.F., and PRUT E.V.: Vysokomol.Soed. A22, 1013 (1980).

*Received September 25/Revised October 20/December 12, 1980*  
*Accepted December 12, 1980*