Mutual Diffusion and Phase Equilibrium in Copolymers of Nonyl Acrylate and Acrylic Acid–Diglycidyl Ether of Bisphenol A Systems

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ABSTRACT: The influence of the composition of statistical copolymers of nonyl acrylate with acrylic acid on the rate of mass transfer and phase equilibrium in solutions with diglycidyl ether of bisphenol A was studied. For these systems, the data on concentration dependencies of mutual diffusion coefficients and phase diagrams were obtained. The results were interpreted on the basis of the assumption about the effect of the effective concentration of nodes of the network of hydrogen bonds on the mutual diffusion and phase equilibrium. The dependencies of the mutual diffusion coefficients on the content of acrylic acid in the copolymers are described in terms of the free volume theory. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2353–2356, 1999

Key words: phase equilibrium; copolymers of nonyl acrylate with acrylic acid; diglycidyl ether of bisphenol; network of hydrogen bonds; free volume theory

INTRODUCTION

Despite comprehensive published data[1,2] on the influence of the nature of polymers, including chemically linked objects, on the rate of mass transfer, systematic studies of the effect of specific interactions of macromolecules and density of the physical network on mass transfer of low-molecular substances are almost lacking. The data on the influence of the concentration of nodes of the physical network in binary polymer, solvent systems with a weak level of thermodynamic affinity on the phase-boundary concentrations, are also poorly known, although there are some theoretical attempts in this direction.[3]

In this work, we attempted to establish the influence of the effective concentration of nodes of the network of intermolecular bonds on the rate of mass transfer and phase equilibrium in the systems based on copolymers of nonyl acrylate with acrylic acid (CNAAA) taken in different concentrations.

EXPERIMENTAL

Statistical polynonyl acrylate (PNA) and CNAAA ($\bar{M}_w \cong 10^5$, $\bar{M}_w/\bar{M}_n = 3 \div 5$) and the content of acrylic acid (AA) of 10, 20, 30, and 40% were used as the objects for the study. The copolymers were synthesized by radical polymerization method in sealed tube at 60°C for 80 h, which corresponds to five half-life times of initiator (dinitryl of azoisooleic acid).[4,5] The content of the tube were blown with inert gas to remove the dissolved air oxygen. Diglycidyl ether of bisphenol A (DGEBA) with the epoxide number 180 served as the diffusant. The process of mutual dissolution of the components was studied by optical microinterferometry.[6−8]
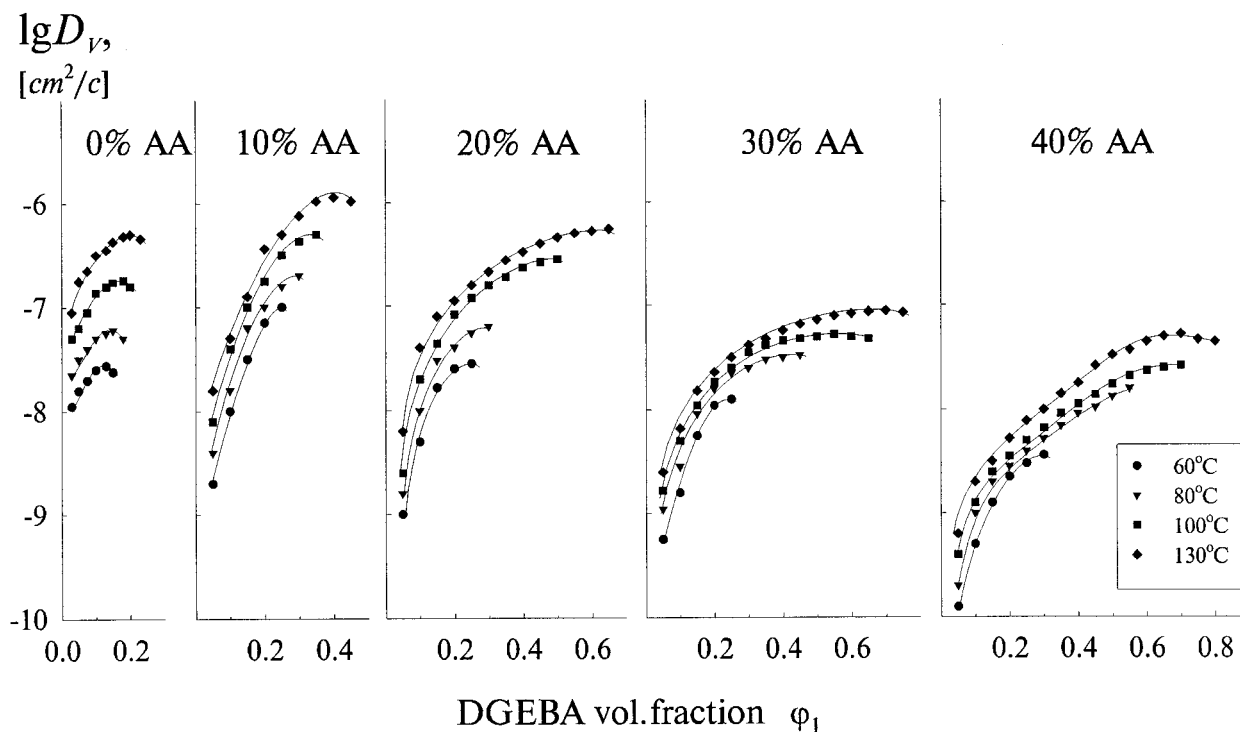
$$\lg D_V,$$
$$[cm^2/c]$$

Figure 1 Concentration dependencies for the systems NA copolymers with AA–DGEBA.

The mutual diffusion coefficients (D_V) in solutions of different composition have been calculated by the Matano–Boltzmann method[9] using curves of the diffusant concentration distribution versus distance $\varphi_1(x)$, where φ_1 is a volume fraction of the diffusant at fixed time t. In brief, the essence of this method consists in the solution of the second Fick law equation, as follows:

$$\frac{\partial \varphi_1(x,\, t)}{\partial t} = \frac{\partial}{\partial x}\left[D(\varphi)\, \frac{\partial \varphi_1(x,\, t)}{\partial x} \right] \qquad (1)$$

using the Boltzmann substitution, which comprises the introduction of new variable $y = x \cdot t^{-1/2}$. The initial and boundary conditions for chosen scheme of the diffusion experiment can be written as

$$\varphi_1(x,\, 0) = \begin{cases} \varphi_{1.0}, & \text{for } -\infty < x < 0 \\ 0, & \text{for } 0 < x < +\infty \end{cases} \qquad (2)$$

The diffusion coefficients are calculated relative to the coordinate plane determined by the following relationship:

$$X_M = \frac{1}{\varphi_{1.0}} \int_0^{\varphi_{1.0}} x\, d\, \varphi_1$$

and called the Matano plane.

The extension of diffusion zone during experiment process was reached 1.5–2.0 mm. The time of the diffusion process was 2–3 h.

RESULTS AND DISCUSSION

Analyzing the obtained results, one can conclude that the movement of isoconcentration planes and diffusion zone broadening in time obey the parabolic law $x \sim t^{1/2}$. This fact is obvious for the diffusion kinetics of the mutual dissolving and the absence of any appreciable influence of the attendant processes. In this connection, dependencies of the mutual diffusion coefficients (D_V) on time are not observed.

The concentration dependencies of the mutual diffusion coefficients (D_V) for all systems under consideration are presented in Figure 1. They are characterized by the general tendency for chang-
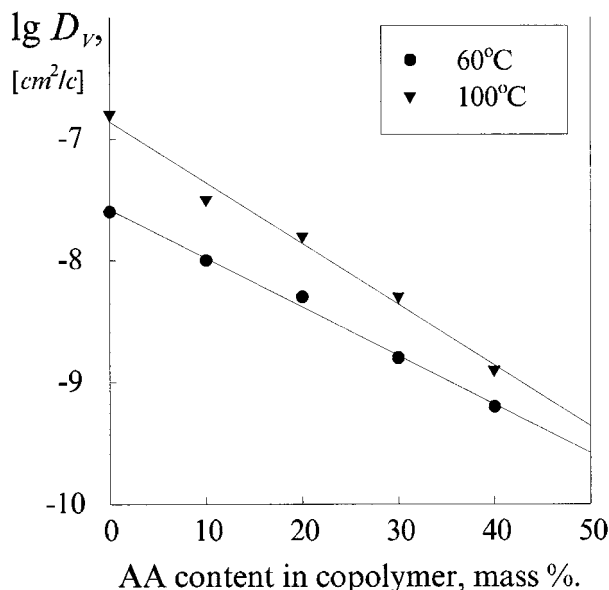
Figure 2 Dependence of $\lg D_{V,\varphi_1=0.1}$ on the content of acrylic acid in copolymer.

ing the diffusion coefficients as the composition and temperature change.[1] In the limitedly compatible systems, the dependencies of D_V on the content of a diffusant (φ_1) change along smooth vortex curves and descend sharply near the binodal.[7] In the systems studied, D_V undergo the maximum changes in the region of compositions close to the pure copolymer. The D_V values in this region of compositions are rather remote from the binodal and are not subjected to the effect of the thermodynamic factor; therefore, they were used for the estimation of the effect of the density of the network of physical bonds on the rate of mass transfer of DGEBA. This effect is indirectly manifested in the linear dependencies $\lg D_{V,\varphi_1=0.1}$ on the content of acrylic acid in the copolymers presented in Figure 2. It is characteristic that at high temperatures, a decrease in D_V with an increase in the content of acrylic acid is more pronounced.

It is known that any factor decreasing the molecular mobility results in a decrease in the relative fraction of the free volume of low and high molecular bodies. For example, the local free volume of the ends of a macromolecule is always somewhat higher than those of other units of macromolecules.[1] Hydrogen bonds form the physical network to decrease the dynamics of fragments of macromolecular chains of copolymers. It can be assumed that the concentration of hydrogen bonds increases and the fraction of the relative free volume decreases as the content of acrylic acid in the copolymers increases.

In terms of the free volume theory,[10]

$$\lg \frac{D_i^*}{D_0^*} = \frac{B}{2.3}\left(\frac{1}{f_0} - \frac{1}{f_i^*}\right) \tag{3}$$

one can relate the diffusion coefficients of DGEBA in pure polynonyl acrylate (D_0^*) and in the copolymer with the ith composition (D_i^*) to the corresponding fractions of free volume f_0 and f_i^*. This assumption is based on the fact that in the region of limiting low concentrations of a diffusing substance, the D_V values almost coincide with self-diffusion coefficients.

By analogy with the effect of the density of chemical linkages,[1] the contribution of hydrogen bonds, whose concentration increases as the content of acrylic acid increases, to a change in the fraction of free volume of the copolymer can be taken into account as follows:

$$f_i^* \approx f_0 - f_1^* \tag{4}$$

where f_1^* is a decrease in the fraction of free volume of the copolymer at the expense of formation of the network of hydrogen bonds.

Evidently, the copolymers studied can contain both intra- and intermolecular hydrogen bonds formed between the carbonyl units of nonylacrylate and acrylic acid with the mobile hydrogen atom of carboxyl, including dimers of hydrogen bonds between the carboxylic groups. In the first approximation, it can be assumed that the effects of the corresponding units of the network of hydrogen bonds on the change in the fraction of the free volume are approximately equal. In this connection, correlation (4) can be presented in the following form:

$$f_i^* \approx f_0 - k[\text{COOH}] \tag{5}$$

where k is the proportionality coefficient.

After insertion of correlation (5) into (3), we obtain

$$\lg D^* = \lg D_0 - \frac{B}{2.3}\frac{k[\text{COOH}]}{f_0(f_0 - k[\text{COOH}])}$$

$$\approx \lg D_0 - \frac{B}{2.3f_0^2}k[\text{COOH}]$$

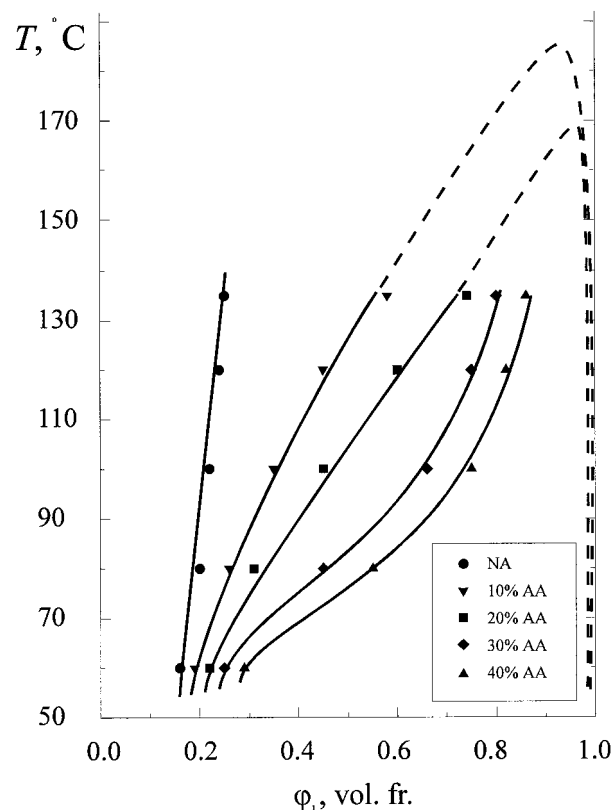$$\approx \lg D_0 - A[\text{COOH}] \tag{6}$$

Figure 3 Phase diagrams in binary systems copolymers of NA with AA–DGEBA.

It can be seen that correlation (6) in the first approximation predicts the run of the dependencies of the rate of mass transfer on the concentration of the network nodes of hydrogen bonds directly related to the content of acrylic acid in the copolymer.

Based on the data on the temperature dependencies of D_V, we calculated the activation energies (E_V) in the region of concentrated solutions at $\varphi_1 = 0.1$ since the systems studied have a rather low compatibility of the components, especially at temperatures below 80°C. For the polymers studied, regardless of the content of acrylic acid in CNAAA, the E_V values are at the level of 20 kJ/mol.

The studies of the thermodynamic affinity in the copolymer CNAAA–DGEBA systems show that the components are limitedly compatible. The phase diagrams (PD) obtained are presented in Figure 3. It can be seen that the diagrams should have the upper critical solution temperature (UCST) because the region of dissolution increases in all systems as the temperature increases. UCST are not achieved because they lie in the range of temperatures at which the copolymers and DGEBA begin to decompose. As the content of acrylic acid increases, the thermodynamic compatibility of the components in-

creases noticeably, and the region of biphase state of solutions is reduced. There was an attempt to process the results obtained from the positions of the Flory–Huggins theory.[11] This made it possible to estimate the value of the interaction parameter and UCST, as described in Mikhailov et al.[12] PD for copolymers with NA content 30 and 40% are not described by this theory. The estimated UCST values are 186 and 150°C, respectively, for copolymers with 10 and 20% NA.

As a whole, it should be mentioned that the solubility of CNAA in DGEBA is insignificant and equal to several percent. It is of interest that the solubility of DGEBA in the copolymer begins to increase noticeably at the content of acrylic acid in CNAA higher than 20% and temperatures higher than 100°C. It can be assumed that this is explained by the decomposition of hydrogen bonds in the copolymer since their strength decreases intensively in this temperature range.[13] Thus, the data obtained indicate the pronounced effect of hydrogen bonds on the diffusion and phase equilibrium in the systems studied.

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