# Phase Equilibrium in the Diglycidyl Ether of Bisphenol A– Hydroxyl-Terminated Oligobutadiene Derivatives Systems

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ABSTRACT: The phase equilibrium in the binary systems based on hydroxyl-terminated butadienes and diglycidyl ether of bisphenol A has been studied in wide ranges of temperature and compositions of the solution. The analysis of the obtained experimental and calculated data shows that the molecular weight, content of hydroxyl groups, functionality of the oligomer, and the presence of bromine in the oligomer affect the level of the thermodynamic compatibility. An increase in the content of hydroxyl groups and bromine results in an increase in the compatibility of the components. The results obtained are interpreted in terms of the Flory–Huggins theory. The correlation between the phase boundary concentrations and an upper critical solution temperature and solubility parameters of the oligobutadienes has been established. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 953–957, 1999

**Key words:** phase equilibrium; hydroxyl-terminated oligobutadienes; diglycidyl ether of bisphenol A; thermodynamic compatibility; Flory–Huggins interaction parameter

## INTRODUCTION

One of the promising approaches to the development of complex multicomponent polymer materials with specified properties is based on controlling the process of phase separation in the initial oligomeric systems. This process is purposefully named either solidification or change in external conditions.<sup>1</sup> Detailed studies of the phase equilibrium in the initial and solidifying oligomeric systems are necessary to develop theoretical grounds of this approach. There are published data on phase diagrams in the region of amorphous phase separation for several oligomeric systems.<sup>2-6</sup>

The binary oligomeric systems, one of the components of which contains epoxy groups, are described by Estrin et al.<sup>7,8</sup> These works contain the data on phase diagrams of some systems based on diglycidyl ether of bisphenol A (DGEBA) and hydroxyl-terminated oligobutadienes. However, these data are not systematized and do not allow one to form the complete picture of the effects of the concentration, functionality of hydroxyl groups, and additional polar centers in oligomers on the phase equilibrium. In addition, oligobutadienes with the broad molecular mass distribution (MMD) and noncharacterized distribution of terminal hydroxyl groups over chains were used in these publications.

In this work, we studied the phase equilibrium in the systems of DGEBA–oligobutadienes,  $\alpha$ -oligobutadienemonools, and  $\alpha, \omega$ -oligobutadienediols with different molecular mass and the narrow MMD. The series of oligomers with the known functionality were studied for the first time.

### **EXPERIMENTAL**

Oligobutadienes and monofunctional oligobutadienes were obtained by the polymerization of

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No.	Oligomer	Abbreviation	$ar{M}_w$	$ar{M}_{w}/ar{M}_{n}$	OH Group Content (%)	$n_D^{20}$
1	Oligobutadiene	OB-1	1960	1.13	_	1.5124
2	Oligobutadiene	OB-2	3460	1.10	_	1.5160
3	Oligobutadiene	OB-3	10500	1.13	_	1.5158
4	Oligobutadienemonool	OBM-1	1830	1.15	0.74	1.5124
5	Oligobutadienemonool	OBM-2	3520	1.09	0.45	1.5160
6	Oligobutadienemonool	OBM-3	10100	1.17	0.18	1.5158
7	Oligobutadienediol	OBD-1	3300	1.10	0.91	1.5140
8	Oligobutadienediol	OBD-2	5560	1.15	0.51	1.5162
9	Oligobutadienediol	OBD-3	9200	1.34	0.32	1.5174

Table I Molecular Mass Properties of Oligomeres

butadiene under the action of sec-butillithium in heptane. The molecular weight was controlled by the ratio of the concentrations of the monomer and initiator. The formation of terminal hydroxyl groups was performed by the treatment of oligomer with ethylene oxide. Oligobutadienes were prepared by the treatment of "living" oligomer with water. Bifunctional hydroxyl-terminated oligobutadienes were obtained in an analogous way to monofunctional oligobutadienes using 2,5-dilithiumhexane as the initiator.<sup>7</sup> Molecular mass parameters of the oligomers were determined according to a procedure described by Estrin.<sup>8</sup> The data on the composition, functionality, and molecular mass parameters of the oligomers studied are presented in Table I.

Bromine-containing oligomers obtained from  $\alpha, \omega$ -oligobutadienediol OBD-1 with the mean numerical molecular mass of 3300 (sample no. 7 in Table I) were studied along with the oligomers presented in Table I. Oligobutadienediol was brominated in a 4% solution in carbon tetrachloride by the addition of a calculated quantity of bromine. The data on the brominated oligomers are presented in Table II.

The method based on the determination of compositions of saturated solutions, which are

 Table II
 Bromine Content, Refraction Indices

 of Brominated Oligomeres

No.	Abbreviation	Bromine Content, Mass (%)	$n_{D}^{20}$
1	OBD-Br-1	3	1.5238
2	OBD-Br-2	12	1.5268
3	OBD-Br-3	40	1.5280
4	OBD-Br-4	50	1.5310

established at the phase boundary in the mutual solubility zone of the components, was used for developing phase diagrams. The concentration structure of the diffusion zones was determined by the interference micromethod.<sup>9-11</sup> The method used by Duda, Sigelko, and Vrentas<sup>11</sup> is the closest to our method.

The measurements were carried out in the 80–130°C temperature range.

#### **RESULTS AND DISCUSSION**

The phase diagrams for all systems studied are presented in Figures 1–4. As a whole, a fairly low thermodynamic compatibility of the components can be stated for all of them. Phase diagrams are characterized by the presence of an upper critical solution temperature (UCST), since the mutual solubility of the components increases as the temperature increases. However, UCST was achieved in none of the systems studied. The phase diagrams are asymmetrical, which is manifested by the greater solubility of DGEBA in oligomers and the shift of UCST to the DGEBA region.

The processing of the results obtained using the Flory–Huggins theory<sup>12</sup> made it possible to estimate the value of the interaction parameter and UCST. Equation (1) was used, and the linear dependences of  $\chi_{12}$  on the inverse temperature were extrapolated to the  $\chi_{cr}$  value determined from equation (2).

$$\begin{split} & \left[ \ln \varphi_1' + \left( 1 - \frac{\bar{V}_1}{\bar{V}_2} \right) \varphi_2' \right] \\ & \chi_{1,2} = \frac{-\left[ \ln \varphi_1'' + \left( 1 - \frac{\bar{V}_1}{\bar{V}_2} \right) \varphi_2'' \right]}{\left[ (\varphi_2'')^2 - (\varphi_2')^2 \right]} \end{split} \tag{1}$$



**Figure 1** Phase diagrams in systems diglycidyl ether of bisphenol A–oligobutadienes without hydroxyl groups: (1) OB-1; (2) OB-2; (3) OB-3.

$$\chi_{cr} = \frac{1}{2} + \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{1/2} + \frac{\bar{V}_1}{2\bar{V}_2} \tag{2}$$

In equations (1) and (2),  $\varphi_1$  and  $\varphi_2$  are the volume fractions of components;  $\bar{V}_1$  and  $\bar{V}_2$  are their molar volumes;  $\chi$  is the Flory–Huggins interaction parameter; and strokes designate the symbols corresponding to the phases in equilibrium.

The analysis of the experimental and calculated data obtained made it possible to establish the following regularities. First, the molecular mass of oligomer, the content of hydroxyl groups, and the functionality have an effect on the level of thermodynamic compatibility. This is confirmed by the comparison of phase diagrams for oligomers with approximately equal molecular mass, but with a different content of hydroxyl groups (Figs. 1-3) and the dependence of the solubility of DGEBA in oligomers with different functionality on  $M_n$  at constant T (Fig. 5). Since for hydroxyl-terminated oligomers, the molecular mass correlates with the hydroxyl concentration, a decrease in  $\overline{M}_n$  results in an increase in the content of hydroxyl groups. Thus, both factors



**Figure 2** Phase diagrams in diglycidyl ether of bisphenol A-oligobutadienemonool systems: (1) OBM-1; (2) OBM-2; (3) OBM-3.



**Figure 3** Phase diagrams in diglycidyl ether of bisphenol A-oligobutadienediol systems: (1) OBD-1; (2) OBD-2; (3) OBD-3.



**Figure 4** Phase diagrams in diglycidyl ether of bisphenol A-bromated oligobutadienediol systems: (1) OBD-1; (2) OBD-Br-1; (3) OBD-Br-2, OBD-Br-3, OBD-Br-4.

favor an increase in the thermodynamic affinity. It follows from the data in Figure 5 that for hydroxyl-terminated oligomers with the same functionality, the effect of  $\bar{M}_n$  is more pronounced than for nonfunctional oligomers. At the same time, the solubility is almost the same for monoand bifunctional oligomers, which differ almost twofold in the  $\bar{M}_n$  value and contain the close number of hydroxyl groups (samples nos. 5, 6, 7, and 8 in Table I). For example, the solubility of DGEBA in the oligomers is 13.1 and 12.5 wt %, respectively, at T equal to 95°C.

When the phase boundary concentrations at a constant T are presented as a function of the concentration of hydroxyl groups (Fig. 6), the data for mono- and bifunctional oligomers form a single dependence. This is evidence for the determining effect of hydroxyl groups in the systems considered.

As follows from Figure 4, bromination of the oligomers favors an increase in the thermodynamic compatibility of the components. The increase in the bromine content from 0 to 50 wt % decreases UCST approximately by 40°C and results in an increase in the solubility of DGEBA in the oligomers from 15 to 22% at T equal to 95°C



**Figure 5** Dependences of the phase boundary concentration of DGEBA on the oligomer molecular mass. (1) oligobutadienes; (2) oligobutadienemonools; (3) oligobutadienediols.

(Fig. 4). As the bromine content increases, the solubility first increases rather sharply and then depends linearly on the molar content of bromine in the oligomer.

The solubility parameters  $(\delta)$  were calculated to obtain the general dependence of the parameter of the level of thermodynamic affinity for all oligomers studied. The solubility parameters of



**Figure 6** Dependences of the phase boundary concentration of DGEBA on the content of oligomer OH groups: (1) 80; (2) 95; (3) 110; and (4) 130°C.



**Figure 7** Dependences of the estimated UCST and experimental phase boundary concentration of DGEBA on the oligomer solubility parameter.

the oligomers were calculated by the procedure of group contributions described by Van Krevelen.<sup>13</sup>

The dependences of UCST and solubility of DGEBA in oligomers on the solubility parameter at T equal to 95°C (Fig. 7), as well as the dependences in Figures 5 and 6, form single dependences for the hydroxyl-terminated and brominated oligomers. For OB without polar groups, the values discussed do not obey these dependences.

Thus, the analysis of the obtained experimental and calculated data shows that the molecular mass and related content of hydroxyl groups have the determining effect on the phase equilibrium in the studied systems based on DGEBA with oligobutadiene derivatives containing terminal hydroxyl groups. The modification of the hydroxyl-terminated oligomers by bromine results in the regular increase in the thermodynamic compatibility of components.

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