

Phase Equilibria of Modified Ethylene Glycol–Maleic Anhydride–Phtalic Anhydride Polyester Resins

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SYNOPSIS

This paper describes the influence of a termination of ended carboxyl groups of ethylene glycol–maleic anhydride–phtalic anhydride polyesters with cyclohexanole on a position of phase interface of the unsaturated polyester–styrene system. At given temperatures, optimal molecular weights were determined for the achievement of maximal miscibility of this polymer with styrene. Simultaneously, a model implicit equation was proposed, which is based on the assumption that the dependence of the interaction parameter χ on number-average molecular weights is similar to the dependence of the interaction parameter χ on temperature. Solution of these implicit equations are isotherms in the phase diagram $\bar{M}_n - \phi_2 - T_{\text{cloud point}}$.

INTRODUCTION

Unsaturated polyester (UP) resins are solutions of unsaturated polyesters in reactive solvents, mainly styrene. Except for the method of initiation and cure, which has influence on the network density of the UP–styrene system, criteria of physical and chemical properties of cross-linked resins are, above all, the composition of synthesized polyesters, their molecular weight averages and distributions, and, further, generally known effects caused by the method of synthesis. A very important factor is also the content of the reactive solvents and remainder monomers. The choice of the polymerization degree at preparation of UPs and the contents of the reactive solvent is, however, also influenced by the required processing properties of UP before cross-linking. This is, above all, a question of requirements on optimal viscosity, reactivity, and emission of reactive solvents. Then, it is necessary to find UP behavior in the solution with styrene in connection with molecular weight and polydispersity. Phase equilibria and miscibility boundary conditions of the polyester–solvent system may be a limiting criterion of optimalization of UP properties.

THEORY

According to the generally known Flory–Huggins theory, the χ parameter is considered to be independent of temperature, concentration of polymer in the solution, and its molecular weight.^{1–3} In modifying the Flory–Huggins theories, this χ parameter is considered mostly as function of temperature and concentration. In this paper, we assume that the χ parameter is also a function of molecular weight.

Flory assumed simplifying presumptions in his theory, such as, for example, identical size of polymer molecules, undisturbed interactions of polymer segments with solvent molecules, and accidental mixing of solvent molecules with polymer. Real systems are obviously different in these aspects connected to a change of energy at elementary contacts of solvent molecules (1) and polymer segments (2). The change of energy at elementary mixing is

$$\Delta w_{12} = w_{12} - (w_{11} + w_{22}/2) = w_H + w_S \quad (1)$$

where w_{11} is an energy of contact type 1-1; w_{22} is an energy of contact type 2-2; w_{12} is an energy of contact type 1-2, which contributes to production of solution; w_H is the enthalpic term of change of an interaction energy; w_S is an entropic term of change of an interaction energy dependencies on temperature; and Δw_{12} is a change of energy at mixing and it has the

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character of free enthalpy. Considered energies are referred to the state of an ideal gas, when force influencing is zero. Then, these energies w_{11} , w_{22} , and w_{12} are negative.

Real polydisperse UPs usually contain a certain amount of low molecular weight oligoesters and, on the other hand, fractions with molecular weights running into five or even six figures. The solubility in styrene and the interaction parameter χ will be, consequently, influenced by the relative fraction of strongly polar end groups —COOH and —OH in the oligomers. The contribution of w_{12} is very small in the area of low molecular weights in regard to the preference of contact types 2-2 (hydrogen and association bonds) and 1-1 (solvent contact). Part of energy w_{12} is consumed, in addition, on necessary entropic changes.

Δw_{12} , therefore, reaches to maximum positive value and χ has the maximal value:

$$\chi = (\Delta w_{12}/RT)N_A(z/2) \quad (2)$$

where z is a lattice coordination number; N_A is Avogadro's constant; $N_A(z/2)$ is the total number of solvent molecules and lattice segment contacts in 1 mol of the system; R is the gas constant; and T is the absolute temperature. Δw_{12} and χ refer to a single place of lattice and, therefore, to a single segment of the polymer. This Δw_{12} in the original Flory conception is the same for all segments. But in real polyesters with different values of Δw_{12} for each segment due to different polarity, we assume that real Δw_{12A} , and, therefore, χ_A , will be the average value of all energy changes of elementary mixing of Δw_{12i} of single segments with solvent molecules:

$$\Delta w_{12A} = \left(\sum_i w_{12i} y_i \right) / \sum_i y_i \quad (3)$$

where Δw_{12A} is the average energy by mixing of all polymer segments with solvent molecules; Δw_{12i} is the energy by mixing of polymer i segment with solvent; and y_i is the number of single-type polarity segments.

The result of these considerations is that the χ_A parameter is large at a high fraction of polar groups and can be bigger than the critical interaction parameter χ_C and that the polyester-styrene system does not form a homogeneous solution. This system is shown by $\Delta H_M \gg 0$, $\Delta G_M > 0$, where

$$\begin{aligned} \Delta H_M &= RT\chi_A n \phi_1 \phi_2 \\ &= RTn\phi_1\phi_2 N_A(z/2) \left(\sum_i w_{12i} y_i \right) / \sum_i y_i \quad (4) \end{aligned}$$

ΔH_M is the enthalpy of the average polymer segment mixing with the solvent molecule; ΔG_M is the Gibbs energy of mixing; χ_A is the average interaction parameter of all polymer segments with the solvent; $n = n_1 + n_2 r$, $r = V_1/V_2$; $n_{1,2}$ is the number of mol solvent (1) and polymer (2); and $\phi_{1,2}$ is the volume fraction 1, 2.

With growing \bar{M} , the relative fraction of strongly polar end groups on the segment decreases. Because of the number of contacts of the 1-2 type, the negative value of Δw_{12A} increases. Interaction parameter χ_A , therefore, decreases. However, the fraction of branched molecules also increases with growing \bar{M} . These branched molecules originate because of adjacent reactions during polycondensation. In this manner, the number of segments accessible for accidental contacts with solvent is reduced repeatedly, and the negative value of Δw_{12A} decreases and χ_A increases.

It is a question of what kind of influence a physical network has here, because in concentrated solutions, coils of macromolecules are in the theta state and, therefore, will some fraction of physical junctions. For these reasons, the function $\Delta w_{12A} = f(\bar{M})$ has a minimum and therefore χ_A also has a minimum. Then, the interaction parameter χ_A will be the function \bar{M} in real polyester-styrene systems. Polyester will be thus most compatible with styrene in the polymerization degree corresponding to a minimal parameter χ_A . This is a question of the function extreme:

$$\chi_A(\bar{M}) = f(\bar{M})_{T,p,\phi_2} \quad (5)$$

formally analogous to an interaction parameter temperature dependence^{2,4,5}:

$$\chi = a/T + b + cT = \chi_H + \chi_S \quad (6)$$

where $\chi_H = a/T - cT$ and $\chi_S = b + 2cT$ and where a , b , and c are constants, χ_H is an enthalpic term of the interaction parameter, and χ_S is an entropic term of the interaction parameter.

The interaction parameter $\chi_A(\bar{M}) = f(\bar{M})_{T,p,\phi_2}$ thus can be similar, such as $\chi(T) = f_1(T)_{M,p,\phi_2}$ being considered as contributing sums of chemical and structural effects or correction on a combinatory entropy. At a constant temperature, pressure, and concentration, under the influence of molecule polarity and hydrogen-bond formation, the frequency of microstates, which molecules can occupy, is reduced and so the entropy of dissolving is also reduced. The contribution of $\chi_S = f(\bar{M})$ is, consequently, with regard to the influence of end polar

groups —COOH and —OH, different from $\chi_S = f_1(T)$. The growing fraction of branched and cross-linking molecules with an increasing polymerization degree has a similar effect on $\chi_A(\bar{M}) = f(\bar{M})$ as does the increasing of temperature on $\chi = f(T)$.⁶ Equation (1) will then be replaced formally by the same expression:

$$\chi_A(\bar{M})_{T,p,\phi_2} = d/\bar{M} + e + g\bar{M} \quad (7)$$

where d , e , and g are constants. This function has an extreme in the point $\bar{M} = (d/g)^{1/2}$, which is a local minimum under the presumption that $c > 0$. The linear dependence $g\bar{M}$ is considered in regard to the experimental results. It is the sum of the real molecular weight dependence contribution of χ on \bar{M} and the contribution of seemingly χ dependence on \bar{M} , which ensues from the critical temperature dependence on chain length.

Applying continuous thermodynamics, when polydisperse polymer is described by continuous molar mass distribution density function $W(M)$ and when it is accepted that $W(M)dM$ is a relative segment or mass fraction of all polymer species with molar masses between M and $M + d$, we acquire a real dependence description of the interaction parameter χ_A of polydisperse polyester on molecular weight distribution. The normalization condition is accepted⁷⁻¹⁰:

$$\int_0^\infty W(M)dM = 1 \quad (8)$$

Equation (7) becomes

$$\chi(M)_{T,p,\phi_2} = d_w/W(M) + e_w + g_w W(M) \quad (9)$$

Šolc et al.,¹¹⁻¹⁴ and Koningsveld and Staverman,¹⁵ assumed dependence of χ only on ϕ_2 and T . Matsuda and Kamide also considered dependence of χ on the polymerization degree and take that¹⁶⁻²⁰

$$\chi = \chi_{00}(1 + k'/P_n) \left(1 + \sum_j p_j \phi_2^j \right) \quad (10)$$

where $\chi_{00} = a + b/T$; p_j and k' are molecular weight and the concentration independent parameters, respectively; and P_n is the number-average polymerization degree.

For unsaturated polyesters, we considered that

$$\chi_A = \chi_{00}(1 + p_1\phi_2 + p_2\phi_2^2)(d/\bar{M} + e + g\bar{M}) \quad (11)$$

and then the Gibbs energy of mixing is

$$\Delta G_M/RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \phi_1 \phi_2 \chi_{00} \times (1 + p_1\phi_2 + p_2\phi_2^2)(d/\bar{M} + e + g\bar{M}) \quad (12)$$

where n_1 , n_2 are numbers of moles; 1 is the solvent, 2 is the polymer, and p_1 , p_2 , d , e , and g are the molecular weight and the concentration independent parameters.

An analogous form uses the Flory–Huggins equation when introducing expression (9).

Unsaturated polyesters are polydisperse polymers ($i = 2, 3, 4, \dots$), where i denotes polymer molecules of the same chemical composition but of different molecular weights. In the Flory–Huggins equation, it is necessary to consider interaction parameters among diversely large oligomers:

$$\Delta G_M = \left(n_1 \ln \phi_1 + \sum_{i=2} n_i \ln \phi_i + \sum_{i=2} \chi_{1i} n_1 \phi_1 \phi_i + \sum_{i=2} \chi_{1i} n_i \phi_1 \phi_i r_{1i} + \sum_{i=2} \sum_{\substack{j=2 \\ i \neq j}} \chi_{ij} \phi_i \phi_j n_i + \sum_{i=2} \sum_{\substack{j=2 \\ i \neq j}} \chi_{ij} n_j r_{ij} \phi_i \phi_j \right) RT \quad (13)$$

Under simplifying presumptions, when contribution sums of single, differently long molecules are replaced by total contributions of the polymer part,

$$\begin{aligned} \sum_{i=2} n_i \ln \phi_i &= n_2 \ln \phi_2 \\ \sum_{i=2} r_{1i} \chi_{1i} \phi_1 \phi_i &= \chi_A r \phi_2 \\ \sum_{i=2} \chi_{1i} \phi_1 \phi_i &= \chi_A \phi_2 \\ \sum_{i=2} \sum_{\substack{j=2 \\ i \neq j}} \chi_{ij} n_i \phi_i \phi_j &= \chi_2 n_2 \phi_2^2 \\ \sum_{i=2} \sum_{\substack{j=2 \\ i \neq j}} r_{ij} n_j \chi_{ij} \phi_i \phi_j &= r n_2 \chi_2 \phi_2^2 \end{aligned}$$

For low polydispersity, we assume that χ_2 , valid for mutual dissolving of polyester oligomers, is approximately 0. Then, eq. (13) is equivalent to eq. (12) and is valid for a quasi-binary system.

For a phase liquid–liquid equilibrium in cloude points, the following is valid:

$$\begin{aligned} \Delta \mu'_1 &= \Delta \mu''_1 \\ \Delta \mu'_2 &= \Delta \mu''_2 \end{aligned}$$

where $\Delta\mu_1$ and $\Delta\mu_2$ are, respectively, the change of chemical potentials of polymer 2 and solvent 1 in polymer-lean ('') and polymer-rich ('') conjugated phases. For the phase border of nonstable and metastable area, the condition is

$$\partial\Delta\mu_1/\partial\phi_2 = -\phi_2(\partial^2\Delta G_M/\partial\phi_2^2) = 0 \quad (13)$$

and the chemical potential $\Delta\mu_1$ is

$$(1/RT)d\Delta G_M/dn_1 = \ln(1 - \phi_2) + (1 - 1/r)\phi_2 + \phi_2^2\chi_A - C(1 - \phi_2)\phi_2^2 \quad (14)$$

where $C = \chi_{00}(p_1 + 2p_2\phi_2)[d_w/W(M) + e_w + g_w W(M)]$.

Assuming that cloude points are influenced only the concentration of polymer ϕ_2 and distribution function $W(M)$, for T and pressure p are constants, then condition (13) is valid and

$$\begin{aligned} \partial\Delta\mu_1/\partial\phi_2 = RT[-1/(1 - \phi_{2,Z}) + (1 - 1/r) \\ + 2X_{00}(d_w/W(M) + e_w + g_w W(M)) \\ \times [6p_2\phi_{2,Z}^2 + 3\phi_{2,Z}(p_1 - p_2) - p_1 + 1]\phi_{2,Z}] \\ = 0 \quad (15) \end{aligned}$$

and $\phi_{2,Z}$ is the volume fraction of the polymer in cloude point. This way we obtain the implicit function that describes the dependence of polyester solubility in styrene on the molecular weight of this polyester. Graphic descriptions of the function in explicit form, for T and p constants,

$$\phi_{2,Z} = f[W(M)_{T,p}]$$

are isotherms in the ternary phase liquid-liquid diagram $\phi_2 - \bar{M} - T_{cp}$ (cloude point temperature).

Under the known relationship between the concentration expressed by volume fraction ϕ_2 and weight percentage of polyester in solution w_2 ,

$$w_2 = \{\phi_2/[\phi_2(1 - \sigma_1/\sigma_2) + \sigma_1/\sigma_2]\} \cdot 100$$

where σ_1 and σ_2 are, respectively, the density of the solvent and the polymer and it is accepted that

$$w_Z = f_1[W(M)_{T,p}]$$

where w_Z is weight percentage of polymer in solution at cloude points.

Isotherms in Figures 1-4, obtained from experimental data, are graphic solutions of these functions for different temperatures.

EXPERIMENTAL

Materials

Cyclohexanole was obtained from s.p. Lachema, ČSFR; maleic anhydride, from Dunai Kőolajipari, Hungary; phtalic anhydride, from s.p. VCHZ Synthesis Semtín, ČSFR; and ethylene glycol, from s.p. Slovnaft Bratislava, ČSFR, and were used as received. Styrene was obtained from s.p. Kaučuk Kralupy nad Vltavou, ČSFR, and dried over anhydrous calcium chloride for 1 day and then distilled under reduced pressure (20 mmHg, 44.6°C) with 1% wt hydroquinone and 1% wt anhydrous calcium chloride. After distillation, styrene was inhibited by 30 ppm *tert*-butylpyrocatechol.

Polymerization

Polycondensation was done under a temperature of 200°C without using any catalysts or azeotropic agents, which would influence the interaction pa-

Table I Analytical Data of the Prepared Polyesters of the First Type: Polyester 1, 0% Wt of Cyclohexanole

Sample	From End Groups (\bar{M}_n)	From GPC			Contents Unreacted EG ^a (% wt)
		\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	
1	730	690	1130	1.6	1.6
2	1174	970	2130	2.2	0.4
3	1600	1290	3840	3.0	0.2
4	1930	1530	6450	4.2	0.1

^a EG = ethylene glycol.

Table II Analytical Data of the Prepared Polyesters of the Second Type: Polyester 2, 5% Wt of Cyclohexanole

Sample	From End Groups (\bar{M}_n)	From GPC			Contents Unreacted (% Wt)	
		\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	EG ^a	Cyclohexanole
1	550	470	690	1.5	2.1	0.6
2	770	600	950	1.6	1.3	0.3
3	980	730	1290	1.8	0.7	0.25
4	1260	870	1750	2.0	0.4	0.2
5	1650	1390	4060	2.9	0.2	0.1

^a EG = ethylene glycol.

rameters of the polyesters. During the reaction, carbon dioxide was introduced as an inert gas and reaction water was carried away. At required conversions, samples were taken from which various concentrated solutions in styrene were prepared. A final sample was put to 20 min evacuation.

Determination of Molecular Weights

Average values of molecular weight and molecular weight distribution of a polyester sample were determined by gel permeation chromatography (GPC). Problems of GPC of UP are described in Ref. 21.

A Spectra-Physics equipment was used, consisting of an SP 8100 liquid chromatograph, an SP 8440 UV-visible detector operating at 254 nm, and an SP 4200 computing integrator. Two systems of GPC columns were used: (a) four Microgel (Chrompack) columns 250 × 7.7 mm connected in series with pore sizes of 50, 100, 500, and 1000 Å for the analyses of low molecular weight samples; and (b) an Ultrastragel Linear (Waters Assoc.) column 300 × 7.8

mm for the analyses of high molecular weight samples. The two systems gave approximately the same results. Tetrahydrofuran (THF) served as a mobile phase at 40°C, and the flow rate was 1 mL/min. The concentration of polyester samples was 0.25% (0.15% in the case of column b) and the volume injected was 100 μL (50 μL in the case of column b). The columns were calibrated by polystyrene standards that were supplied by Polymer Laboratories.

\bar{M}_n were also determined from end carboxyl and hydroxyl groups. A well-known equation was used:

$$\bar{M}_n = \frac{56.11 \cdot 1000 \cdot 2}{AV + HV}$$

where AV is the acid value/the amount (mg) of KOH needed for neutralization of carboxyl groups and anhydrides in 1 g of polyester and HV is the hydroxyl value/the amount (mg) of KOH needed for neutralization of acetic acid bounded by acetylation in 1 g of polyester.

Table III Analytical Data of the Prepared Polyester of the Third Type: Polyester 3, 10% Wt of Cyclohexanole

Sample	From End Groups (\bar{M}_n)	From GPC			Contents Unreacted (% Wt)	
		\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	EG ^a	Cyclohexanole
1	630	450	690	1.5	1.6	1.2
2	850	530	850	1.6	0.7	1.0
3	1190	650	1110	1.7	0.4	0.5
4	1780	810	1590	2.0	0.2	0.2
5	2130	1330	3780	2.8	0.1	0.1
6	2420	1490	6370	4.3	0.1	0.1

^a EG = ethylene glycol.

Determination of Unreacted Monomers

The contents of unreacted monomers were determined by a gas chromatography Hewlett-Packard 5890 II with a flame-ionization detector (FID) and identification was verified by a low-resolution quadrupole mass spectrometer Finnigan MAT 44S.

Preparation of Samples and Cloud Point Temperature Determination

Melts of single modified polyesters of different polymer degrees were mixed at 150°C with 0.1% wt hydroquinone as the polymerization inhibitor, homogenized, cooled, and weighed out into 30 ccm test tubes equipped with a ground-glass joint. Test tubes had ground-glass joint guiding ways for the glass stirrers. The calculated amount of distilled styrene, inhibited by 30 ppm *tert*-butylpyrocatechol, was added. Mixtures were heated up to 80°C, homogenized, and cooled. Then, test tubes were placed into a thermostat and heated at the rate of 1°C/2 min under intensive stirring. The temperature corresponding to forming of a homogeneous single-phase system (extinct cloud) is the cloud point.

RESULTS AND DISCUSSION

Three series of ethylene glycol-maleic anhydride-phtalic anhydride polyester with cyclohexanole as termination agent in quantities of 0, 5, and 10% wt on polyester were synthesized. Characterizations of these polyesters are described in Tables I-III.

Cloud point temperatures of single types of UP and corresponding concentrations of unsaturated polyesters in UP and their molecular masses were processed by computer. Results are presented in Figures 1-3. The area multiphase system is below the saddle surface corresponding to the cloud points. A homogeneous single-phase region is then above the saddle surface. Isotherms from 0 to 140°C define experimentally obtained values. Temperatures below 0°C and over 140°C are computer extrapolations of dependencies. An area of average molecular weights exists that is optimum for miscibility of UPs and styrene (Figs. 1-3). The upper critical solution temperature of polydisperse polyesters in this range reaches a minimum, and at the same time, isohypses according to eq. (9) have extremes in surface $\bar{M}_n - w$ [Figs. 1(a)-3(a)]. These extremes correspond to \bar{M}_n for maximal miscibility at different temperatures for concentrations of polyesters higher than those corresponding to the

cloud point. These isohypses (isotherms) are the graphic solution of explicit functions (9) derived previously in implicit form.

In Figure 4 (a) and (b), the maximum miscibility with styrene is given for the polydisperse ethylene glycol-maleic anhydride-phtalic anhydride polyesters modified with cyclohexanole to different degrees

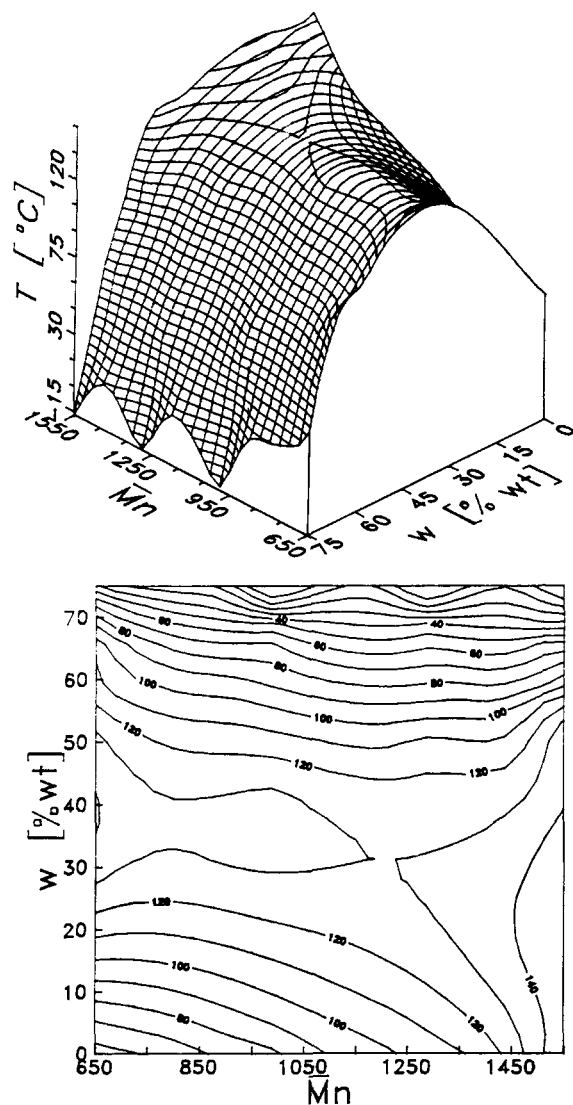


Figure 1 Three-dimensional phase equilibrium for polyester 1 in terms of temperature (T), number-average molecular weight (\bar{M}_n), and weight percentage of polymer in solution (w). The saddle surface corresponds to cloud points. The multiphase system is below the saddle surface. (a) Two-dimensional isohypse representation of phase equilibrium for polyester 1 in terms of number-average molecular weight (\bar{M}_n) and weight percentage of polymer in solution (w). Isohypes are isotherms designed in °C. They are in accordance with functions $w_2 = f_1[W(M)]_{T,p}$ for single temperatures.

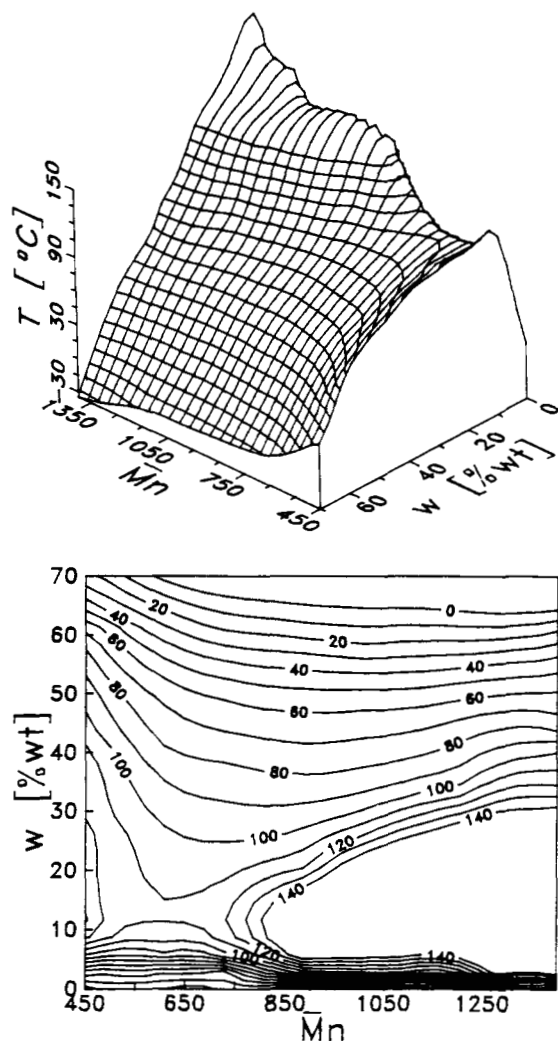


Figure 2 Three-dimensional phase equilibrium for polyester 2 in terms of temperature (T), number-average molecular weight (\bar{M}_n), and weight percentage of polymer in solution (w). The saddle surface corresponds to cloud points. (a) Two-dimensional isohypse representation of phase equilibrium for polyester 2 in terms of number-average molecular weight (\bar{M}_n) and weight percentage of polymer in solution (w). Isohypses are isotherms designed in $^{\circ}\text{C}$.

and to different number-average molecular weights for the two temperatures. Only molecular weights were chosen that are within the region of maximum miscibility [Fig. 1(a)–3(a)]. The miscibility with styrene grows accordingly as the termination of oligomer end carboxyl groups increases. The optimum of number-average molecular weights for maximum miscibility moves with increasing termination of end groups. It is from $\bar{M}_n \approx 1200$ at contents of cyclohexanole 0% wt to $\bar{M}_n \approx 900$ at

contents of cyclohexanole 10% wt. The miscibility in the range of molecular weights $\bar{M}_n \approx 900$ –1200 is almost identical at cyclohexanole contents of ca. $6 \pm 1\%$ wt in polyester. The dependence of miscibility on the amount of cyclohexanole is more sensitive with increasing temperature [Fig. 4(a) and (b)].

CONCLUSION

It was found that miscibility of ethylene glycol–maleic anhydride–phthalic anhydride polyesters with

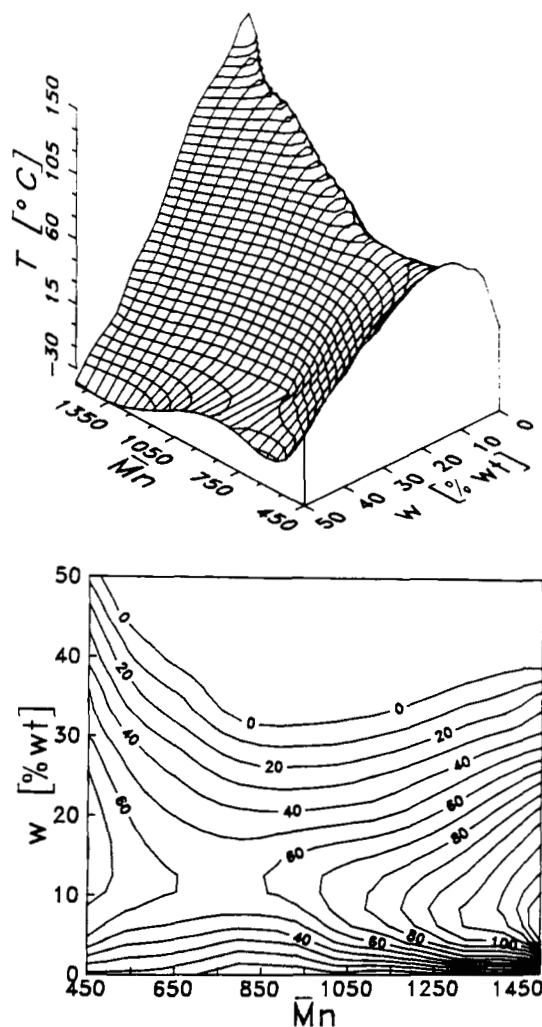


Figure 3 Three-dimensional phase equilibrium for polyester 3 in terms of temperature (T), number-average molecular weight (\bar{M}_n), and weight percentage of polymer in solution (w). The saddle surface corresponds to cloud points. (a) Two-dimensional isohypse representation of phase equilibrium for polyester 3 in terms of number-average molecular weight (\bar{M}_n) and weight percentage of polymer in solution (w). Isohypses are isotherms designed in $^{\circ}\text{C}$.

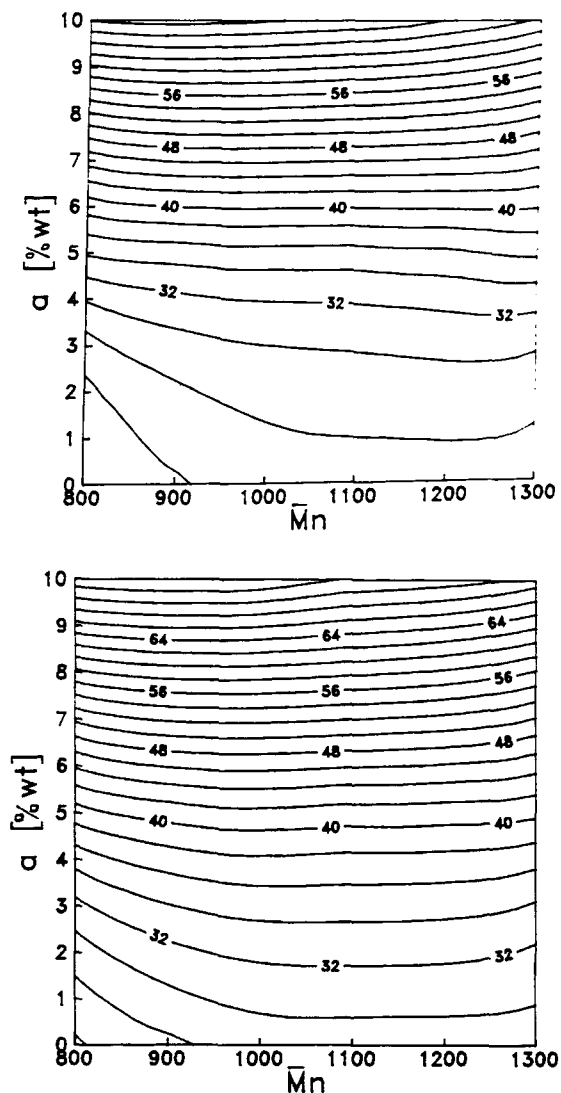


Figure 4 (a) Two-dimensional isohypse representation of miscibility dependence of ethylene glycol–maleic anhydride–phthalic anhydride polyesters with styrene on amount of cyclohexanole as termination agent (a) in polyesters and number-average molecular weight (\bar{M}_n) for 0°C. (b) Two-dimensional isohypse representation of miscibility dependence of ethylene glycol–maleic anhydride–phthalic anhydride polyesters with styrene on amount of cyclohexanole as termination agent (a) in polyesters and number-average molecular weight (\bar{M}_n) for 20°C.

styrene reaches its maximum due to the decreasing fraction of polar end groups and increasing molecular weights of polyesters. With an increased degree of end carboxyl groups, termination optimum molecular weight \bar{M}_n for maximum miscibility decreases from 1200 to 900. The phase interface, due to the termination of polyesters with cyclohexanole, moves

to lower temperatures and polyester concentrations and, thus, the region of homogeneous solution increases. The surface corresponding to phase interface has a saddlelike character, and an apparent upper critical dissolving temperature shows its minimum at optimal molecular mass.

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REFERENCES

1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
2. A. F. M. Barton, *Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, FL, 1985.
3. L. Mandík and F. Kašpar, *The Selection of Solvents for Film-Forming Materials*, Research Institute for Synthetic Resins and Lacquers, Pardubice, Czechoslovakia, 1972.
4. R. Koningsveld, *Br. Polym. J.*, **7**, 435 (1975).
5. S. P. Papkov, *Ravnovesie Faz v Sisteme Polymer-Rastvoritel*, Chimija, Moscow, 1981.
6. D. Patterson, *Rubber Chem. Technol.*, **40**, 1 (1967).
7. R. Koningsveld and A. J. Staverman, *J. Polym. Sci. A2*, **6**, 367, 383 (1968).
8. H. Kehlen and M. T. Rätzch, in *Proceedings of the 6th International Conference on Thermodynamics*, Merseburg, 1980, p. 41.
9. R. L. Cottermann, R. Binder, and J. M. Prausnitz, *Ind. Eng. Chem. Process. Des. Dev.*, **24**, 194 (1985).
10. A. H. Wu and J. M. Prausnitz, *J. Appl. Polym. Sci.*, **39**, 629 (1990).
11. K. Šolc, *Macromolecules*, **3**, 665 (1970).
12. K. Šolc, *Macromolecules*, **10**, 1101 (1977).
13. K. Šolc, L. A. Kleinjens, and R. Koningsveld, *Macromolecules*, **17**, 573 (1984).
14. K. Šolc and K. Battjes, *Macromolecules*, **18**, 220 (1985).
15. R. Koningsveld and A. J. Staverman, *J. Polym. Sci. A-2*, **6**, 325 (1968).
16. K. Kamide, S. Matsuda, T. Dobashi, and M. Kaneko, *Polym. J.*, **16**, 839 (1984).
17. S. Matsuda, *Polym. J.*, **18**, 981 (1986).
18. K. Kamide and S. Matsuda, *Polym. J.*, **16**, 807 (1984).
19. K. Kamide, S. Matsuda, and H. Shirataki, *Eur. Polym. J.*, **26**, 379 (1990).
20. K. Kamide and Y. Miyazaki, *Polym. J.*, **13**, 325 (1981).
21. Š. Podzimek, J. Hanuš, J. Klaban, and J. Kitzler, *J. Liq. Chromatogr.*, **13**(9), 1809 (1990).

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