Macromolecules **1997,** *30,* 885−889

Shear Effects on the Phase Diagrams of Solutions of Highly Incompatible Polymers in a Common Solvent. 1. Equilibrium Behavior and Rheological Properties

Cora Krause and B. A. Wolf*

Institut für Physikalische Chemie, Johannes Gutenberg-Universität, Jakob-Welder-Weg 13, D-55099 Mainz, Germany

Received July 3, 1996; Revised Manuscript Received October 11, 1996[⊗]

ABSTRACT: Phase diagrams (cloud points, tie lines, critical compositions) and viscosities of homogeneous solutions were determined at temperatures ranging from 20 to 100 °C for three representatives of the ternary system cyclohexanone/polystyrene/poly(*n*-butyl methacrylate) [CHO/PS/PBMA] in preparation of a study on shear influences. An only moderate increase of the two-phase region observed upon heating (LCST behavior) witnesses little heat effects upon mixing. Tie lines which are nearly parallel to the PS/PBMA edge of the Gibbs phase triangle indicate comparable solvent quality of CHO for both polymers. The quantitative mathematical description of the equilibrium behavior—required for a theoretical treatment of shear influences—was performed on the basis of the Flory−Huggins equation by means of composition and temperature dependent binary (integral) interaction parameters g_{ij}. The present approach avoids the use of chemical potentials and minimizes the Gibbs energy of mixing directly. Experimental data for $g_{\mathrm{CHO/PS}}$ and $g_{\mathrm{CHO/PBMA}}$ were available from earlier work; $g_{\mathrm{PS/PBMA}}$ was adjusted to reproduce the measured phase diagram of the ternary system. Calculated and measured phase diagrams match very well. The rheological results were used to establish a mathematical expression describing the composition and temperature dependence of the solution viscosities; such an equation is required for the theoretical treatment of shear influences on the phase diagram.

Introduction

The demixing conditions for polymer-containing liquids can change markedly as the systems flow. In contrast to the situation with low molecular weight fluids, where shear effects are on the order of typically 10^{-3} K only,[1] alterations may reach 100 K with polymer solutions, as will be demonstrated in part 2 of this series.[2] For the system studied here, it suffices to shake a cloudy mixture in an ordinary test tube to make the turbidity disappear.

The presently available experimental information concerning shear effects (recalled briefly in part 2) reveals a great diversity of phenomena, part of which is even seemingly contradictory. Some years ago we have therefore initiated a systematic experimental and theoretical study of shear-induced phase changes. Polymer solutions (binary systems) were of main interest in the past and one of the central observation of that work concerns the dominant role the rheological properties of the liquids play for shear effects.

The aim of the present paper is 2-fold: Firstly, an extension of the experimental knowledge concerning shear effects on phase separation to ternary systems made up of two highly incompatible polymers and a solvent which is thermodynamically good for both components and, secondly, the test of the usefulness of a theoretical approach that generalizes the Gibbs energy of mixing by adding the energy the liquid stores during stationary flow for these ternary systems. A solvent of favorable interaction with both types of polymers was chosen (instead of one which is good for one component of the blend but a Θ solvent for the other) to realize a situation where thermodynamic reasons for phase separation are as similar as possible to that in a binary blend of incompatible polymers. Abstaining from Θ solvents (i.e. from limited solubility of one or both polymers) increases the probability of observing the characteristic features of binary polymer mixtures with the present type of ternary systems in a clear-cut manner. Due to high viscosity, limited miscibility, and frequently required elevated temperatures, direct information is hard to obtain for blends.

The results of the current work are presented in two parts. Part one is dedicated to the equilibrium phase behavior and its theoretical modeling. Furthermore, it supplies the rheological information required for the calculation of the stored energy. Part two is devoted to the measurement and to the theoretical description of changes in the demixing conditions by shear.

Both parts use composition dependent interaction parameters (measured with a combination of a headspace sampler and a conventional gas chromatograph) and avoid derivatives of the Gibbs energy of mixing in the calculation of phase diagrams of stagnant and sheared solutions.

Experimental Section

Materials. The poly(*n*-butyl methacrylate)s (PBMA) used in this work were supplied by Röhm, Darmstadt, Germany. The polystyrene PS 196w (J 110, Vestyron) was obtained from Hüls AG, Marl, Germany, and PS 207 from Polymer Standards Service, Mainz, Germany. The characteristic data of the polymers, i.e. weight average (M_w) and number-average molecular weight (M_n) plus molecular nonuniformity $U = (M_w/M_n) - 1$, and refractive indices (n) are given in Table 1.

The solvent, cyclohexanone (CHO), obtained from Aldrich, Steinheim, Germany, was distilled before its use.

Methods. Cloud point curves were determined by turbidimetry. The construction of the apparatus used for the experiments in the quiescent state is analogous to that described in the second part of this contribution.[2] However, in contrast to the device shown there, where the laser is reflected at the rotor of the apparatus, the light passes through the liquid in the quiescent case of present interest in a straight manner.

---

* E-mail: wolf@pc-ak-wolf.chemie.uni-mainz.de.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1997.

S0024-9297(96)00974-6 CCC: $14.00

Table 1. List of Polymers Used and Sample Characteristics

	PBMA 2050	PBMA 335	PS 196w	PS 207
M_w/kg mol^{-1}	2050	335	196	207
M_n/kg mol^{-1}	1780	325	66	204
$U = M_w/M_n - 1$	0.15	0.03	1.95	0.02[a]
n_D	1.483 (20−25 °C)[b]		1.590−1.592 (20 °C)[b]	

[a] Data of supplier. [b] Brandrup, J.; Immergut, E. H. *Polymer Handbook,* 2nd ed.; John Wiley & Sons: New York, 1975.

Critical compositions were estimated in the course of turbidimetric titrations in the following manner.[3] Different solutions of PBMA in CHO (ca. 5 mL) of typical polymer contents ranging from 5 to 10 wt % were titrated at constant temperature with a solution of PS in CHO of ca. 15 wt %. After reaching the cloud point, one further droplet of the titrator was added and the mixture transferred into volumetrically calibrated tubes, where they were kept at constant temperature until macroscopic phase separation was completed. By measuring the phase volume ratio (r_Δ) for incipient demixing as a function of the composition of the polymer blend (binary subsystem), the critical point manifests itself by a phase volume ratio of unity.

For the determination of tie lines, homogeneous solutions of the blend were prepared in CHO at temperatures sufficiently below room temperature and gradually heated to 20 °C and equilibrated. Samples of the coexisting phases were then taken by means of Pasteur pipets and analyzed. After weighting, the solutions were properly diluted (to ca. 5 wt % total polymer content) with THF and the polymers precipitated by pouring the solution into a ca. 10-fold surplus of methanol. Filtering, drying, and determining the weight of the nonvolatile components yield the amount of CHO; in the next step, the composition of the blend was determined by means of GPC measurements.

The GPC apparatus consisted of three columns filled with PS gels (SDV 10^3, 10^5, 10^6 Å of Polymer Standard Service, Mainz, Germany) and an UV detector (Spectra 200 from Spectra-Physics, San Jose, CA) plus a RI detector (Shodex SE-61 from Showa Denko, Tokyo, Japan). The solvent was THF and 50 μL of the solutions was injected. Calibration has demonstrated that the areas of the RI signal (registering PBMA plus PS) and that of the UV signal (registering PS only) are proportional to the amount of the respective polymer.

Rheological measurements as a function of composition, temperature, and shear rate were performed on the shear stress controlled instrument Carri-Med CSL 500 (Dorking, Great Britain) using cone and plate geometries [radius (cm)/angle: 4/0° 30′; 4/1° 59′ and 2/1° 0′]. The temperature was kept constant within ± 0.1 K.

Results and Discussion

For experimental simplicity, most of the experiments were performed at constant composition of the blend, i.e. a constant ratio of the two polymers, and variable fraction of solvent. The results are mostly presented in terms of w_{pol}, the overall weight fraction of the polymer ($w_{pol} = w_{PS} + w_{PBMA}$) and w^*_{PBMA}, the weight fraction of PBMA in the blend ($w^*_{PBMA} = w_{PBMA}/(w_{PS} + w_{PBMA})$). Due to the fact that an investigation of the present type requires large amounts of polymers, the majority of measurements was performed with the system CHO/PS 196*w*/PBMA 2050, where polystyrene is a technical product with a relatively broad molecular weight distribution. With the above system the molecular weight of PBMA was chosen rather high to achieve large effects on the phase diagram when shear is applied. To gain some insight on possible effects of molecular nonuniformity, some measurements were also performed with the narrowly distributed PS 207 instead of PS 196w. Furthermore, the high molecular weight PBMA of the above mentioned system investigated in great detail was exchanged against the lower molecular weight PBMA 335 to obtain some quantitative information on the effects of chain length.

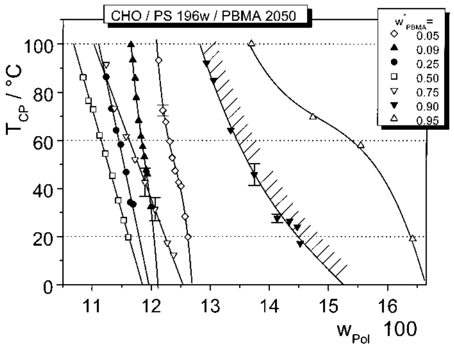

Figure 1. Cloud point temperatures (T_{cp}) for the system CHO/PS 196*w*/PBMA 2050 as a function of the weight fraction of the polymers w_{pol} ($=w_{PS} + w_{PBMA}$) for the different constant blend compositions w^*_{PBMA} ($=w_{PBMA}/(w_{PS} + w_{PBMA})$) indicated in the graph. The two-phase regime is situated on the hatched side of the curves.

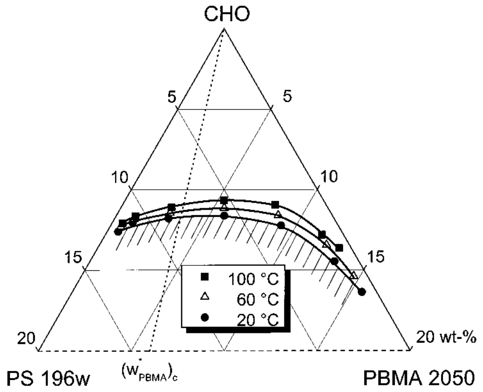

Figure 2. Cloud point curve of the system CHO/PS 196w/PBMA 2050 obtained from the data shown in Figure 1 for the indicated temperatures. The broken line indicates the critical composition of the blend resulting from the phase volume ratios measured at 20 °C.

Equilibrium Behavior. Experiments. Cloud point temperatures, T_{cp}, of the present system—which phase separates upon heating—were measured as described in the experimental section; an example for primary data and their evaluation is given in the second part of this series.[2] Figure 1 demonstrates for CHO/PS 196w/PBMA 2050, the system investigated in detail, how T_{cp} depends on w_{pol}, the sum of the weight fractions of PS and PBMA, for different constant values of w^*_{PBMA}, i.e. different composition of the blend.

Extension and shape of the miscibility gap in the Gibbs phase triangle at constant temperatures can be easily constructed from the above data by appropriate interpolation. The results for 20, 60, and 100 °C are shown in Figure 2. As expected from the pronounced incompatibility of PS and PBMA, the maximum polymer concentration at which the blend still mixes totally with CHO, irrespective of its composition, is on the order of 12 wt % only. The tiny displacement of the curves observed within an interval of 80 °C is indicative of an only slightly exothermal heat of mixing. The critical composition shown in this diagram was obtained from phase volume ratios (cf. Figure 5) as described in the Experimental Section.

The phase diagrams measured in the case in which the PS component is of similar weight average molar mass than before but of much higher molecular unifor-

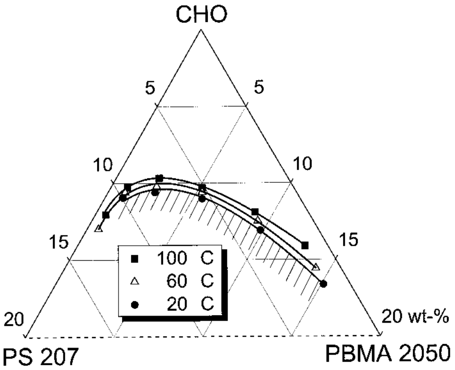

Figure 3. Cloud point curve of the system CHO/PS 207/PBMA 2050 for the indicated temperatures.

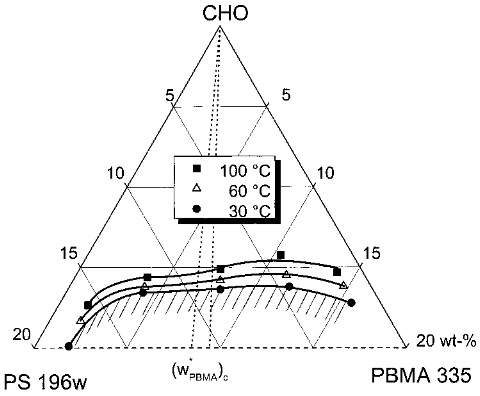

Figure 4. Cloud point curve of the system CHO/PS 196w/PBMA 335 for the indicated temperatures. The broken lines indicate the composition range within which the critical point should be located according to phase volume ratios measured at 20 °C.

mity are shown in Figure 3. In accord with theoretical calculations,[4] the two phase area, as visible in the cloud point curve, shrinks on the PBMA side of the phase triangle, whereas it expands on the PS side as the molecular nonuniformity of PS is decreased.

Figure 4 gives the cloud point curves measured as the molar mass of PBMA is reduced by a factor of approximately 6–7 as compared with the first example of the present system. Expectedly, the homogeneous region becomes larger and the critical composition shifts toward higher PBMA contents. The critical blend composition in Figure 4 cannot be determined exactly because of experimental errors, so a range for this composition is indicated in the graph. Furthermore, it can be noted that the cloud point curve exhibits a depression in the critical range, in accord with earlier observations[5] for ternary systems and calculations for quasi-binary ones.[6]

After this short discussion concerning the influences of molar mass and molecular nonuniformity on the equilibrium phase diagram, we are in the following again focusing our attention on the system CHO/PS 196w/PBMA 2050. Figure 5 demonstrates how the critical compositions were estimated by means of the new method described in the experimental part. In the present case r_Δ is plotted as a function of blend composition (free of solvent).

According to our practical experience,[3] the uncertainty in the positioning of the critical point using the condition that the ratio r_Δ (the volumes of *the first experimentally accessible coexisting phases*, i.e. overall compositions close to the cloud point) be unity is comparable[7] to that of much more laborious procedures.[8] The reliability of the method was also checked by analyzing the coexisting phases. From the Figure 6 it can be seen that the endpoints of the tie lines are—as expected—not positioned on the cloud point curve; they are in good qualitative accord with the critical point obtained from the evaluation shown in the previous diagram.

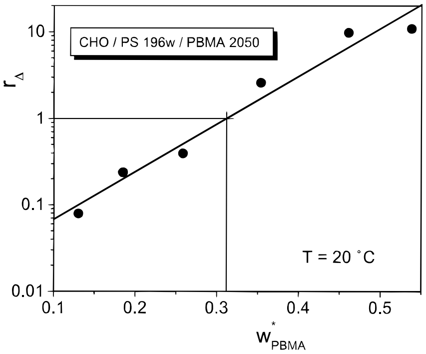

Figure 5. Dependence of the phase volume ratio (r_Δ, volume of the phase rich in PBMA divided by that rich in PS) for *the first experimentally accessible coexisting phases* as a function of blend composition $w^*_{PBMA} = w_{PBMA}/(w_{PS} + w_{PBMA})$ for the system CHO/PS 196w/PBMA 2050 at 20 °C.

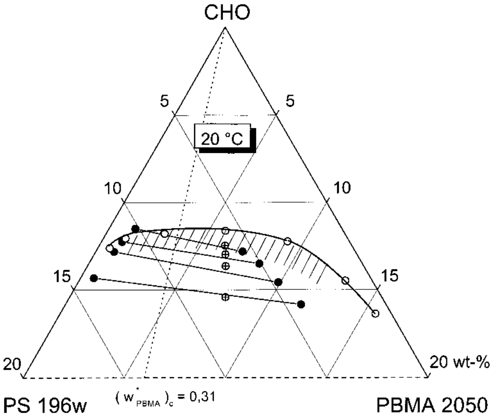

Figure 6. Phase diagram of the system CHO/PS 196w/PBMA 2050 at 20 °C. Open symbols represent cloud points, full symbols give the composition of the phases that coexist for the indicated overall compositions of the ternary mixtures. The dotted line indicates the critical weight fraction of PBMA in the blend.

Equilibrium Behavior. Theory. It is the central goal of the present section to establish equations describing the dependence of the segment molar Gibbs energy of mixing ($\overline{\Delta G}$) (of the stagnant system) on composition and temperature. Since it is irrelevant for that purpose which theoretical relation is used, we select the most wide-spread Flory–Huggins equation here formulated for ternary systems

$$\frac{\overline{\Delta G}}{RT} = \sum_{i=1}^{3}\frac{1}{N_i}\varphi_i\ln\varphi_i + \sum_{i=1}^{2}\sum_{j=i+1}^{3} g_{ij}\varphi_i\varphi_j \qquad (1)$$

N_i signifies the number of segments of component i and φ_i the corresponding volume fractions. For the present calculation the molar volume of the solvent CHO was taken as the size of the segment. To model the experimentally determined phase diagrams theoretically as precisely as possible, g_{ij}, the binary (integral) interaction parameter between the components i and j, must depend on composition and on T in a considerably more complex manner than in the original theory; all inadequacies of the Flory–Huggins expression are incorporated into $g(\varphi,T)$. For the calculation of the phase diagrams of ternary systems the concentration dependencies of the binary interaction parameters g_{ij} (as obtained from measurements with the binary subsystems) were used, replacing the φ_i values by φ_i*, the volume fraction of component i referring to the subsystem i/j, $\varphi_i{}^* = \varphi_i/(\varphi_i + \varphi_j)$, as described and justified in the literature.[9,10] In a binary system φ_i* and φ_i become identical.

The interaction parameters for the subsystems CHO/PS and CHO/PBMA are already known from earlier measurements. In terms of the Koningsveld and Kleintjens relation[11] they read for the temperature interval of interest (20−100 °C)—in good approximation independent of T—

$$g_{\mathrm{CHO,PS}} = -0.2750 + \frac{0.89}{(1 - 0.20\varphi^*{}_{\mathrm{PS}})} \tag{2}$$

for the system CHO/PS[12] and

$$g_{\mathrm{CHO,PBMA}} = 0.2536 + \frac{0.44}{(1 - 0.54\varphi^*{}_{\mathrm{PBMA}})} \tag{3}$$

for the system CHO/PBMA.[13] The latter equation differs at high polymer contents (where the experimental uncertainties are particularly high) somewhat from that published in ref 12; it was modified on the basis of additional measurements. The reason why this expression is preferred lies in the fact that the concentration dependence is similar to that of the other subsystem formulated in eq 2 and that it can account better for the position of the measured tie lines which are found to be approximately parallel to the base line of the Gibbs phase triangle. In the subsequent modeling of the ternary system, possible influences of chain length of PBMA on the interaction parameter $g_{\mathrm{CHO,PBMA}}$ were neglected.

The interaction parameters between highly incompatible polymers cannot be measured directly. For that reason $g_{\mathrm{PS,PBMA}}$ was determined as a function of composition by adjusting the calculated binodal to the experimental cloud points (neglecting the differences between cloud points and binodal curves resulting from molecular nonuniformity). These calculations were performed by means of a method[14] that minimizes the Gibbs energy of mixing in a direct manner (i.e. does not require chemical potentials). The details of the procedure for the determination of interaction parameters between highly incompatible polymers from the phase diagram of the solution in a common solvent are described in more detail elsewhere.[10] With the present computations it was also ascertained that the theoretical critical point (for the mathematical procedure cf. ref 15) matches the actually measured critical point. For a quantitative description of the phase diagram, the following relation for the concentration dependence of $g_{\mathrm{PS,PBMA}}$ turned out to be suited best

$$g_{\mathrm{PS,PBMA}} = \frac{a + b\varphi^*{}_{\mathrm{PS}}(1 - \varphi^*{}_{\mathrm{PS}})}{(1 - c\varphi^*{}_{\mathrm{PS}})} \tag{4}$$

The parameters of eq 4 formulating the concentration and temperature dependence of $g_{\mathrm{PS,PBMA}}$ obtained in the manner described above are collected in Table 2.

Similar to the blend polystyrene/polyisobutylene (PS/PIB), to which the present method has been applied first,[10] the polymer/polymer interaction parameter results are very high; furthermore $g(\varphi)$ exhibits a maximum. Both observations are in accordance with the results of inverse gas chromatography[16] (IGC) yielding an interaction parameter $g_{\mathrm{PS,PBMA}}$ with a maximum g value of approximately 0.4. In the cited investigation, however, $g_{\mathrm{PS,PBMA}}$ ranges from −0.2 to 0.4 with the composition of the blend, whereas this interval is ca. 0.373−0.381 in the present case. The following facts can explain the discrepancy between the two sources of information: (i) our measurements refer to dilute solutions of the blend, whereas the working point of IGC is the nearly solvent-free polymer mixture, (ii) for our evaluation the required information concerning $g_{\mathrm{CHO,PBMA}}$ stems from experiments with lower molar mass PBMA, and (iii) one of many possible mathematical expressions was chosen for the concentration dependence of g (eq 4) and its application to the ternary system. So our fitted $g_{\mathrm{PS,PBMA}}$ values contain all effects of the ternary system, since the two solvent/polymer interaction parameters are not varied in the fitting procedure. Finally, (iv) although this is rather unlikely, influences of polymolecularity (not taken into account in both cases) could also contribute to the discrepancy. The uncommon behavior of PS/poly(*n*-butyl methacrylate), i.e. the maximum of the composition dependence of g, as compared with PS/poly(isobutyl methacrylate) manifests itself in the nonadditivity of the retention volumes in the IGC.[16]

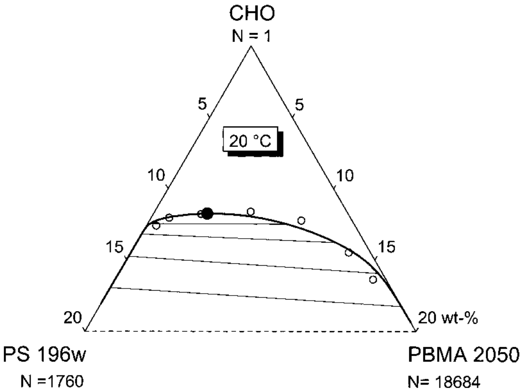

Figure 7. Phase diagram of the system CHO/PS 196w/PBMA 2050 (the numbers of segments are indicated at the edges of the triangle) calculated for 20 °C on the basis of eq 1 and the concentration dependent binary interaction parameters formulated in eqs 2−4. Open symbols represent measured cloud points and the full symbol stands for the measured critical composition.

Table 2. Parameters Describing the Concentration Dependence of $g_{\mathrm{PS,PBMA}}$ (Eq 4)

a	$b \times 10^3$	$c \times 10^3$	T/°C
0.373 28	5.300	8	20
0.373 78	5.330	8	30
0.374 28	5.240	8	40
0.375 39	5.200	8	60
0.376 50	5.110	8	80
0.377 55	5.333	8	100

Irrespective of the above considerations, the experimental results concerning the phase separation behavior of the ternary system can be very well reproduced by the measured $g_{\mathrm{CHO/PS}}$ and $g_{\mathrm{CHO/PBMA}}$ plus the adjusted $g_{\mathrm{PS/PBMA}}$. An example demonstrating the agreement between theory and experiment is shown in Figure 7 for 20 °C.

Rheological Properties. As pointed out in the introduction, rheological information is required for theoretical treatment of the influences of shear on the

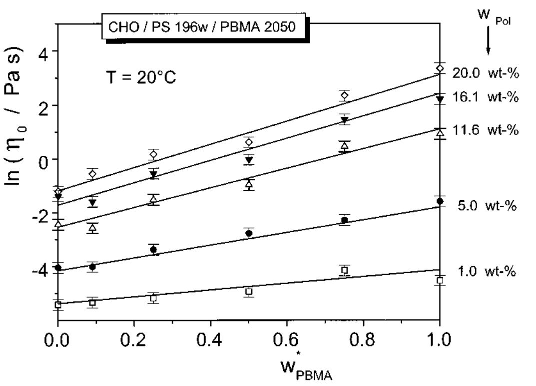

Figure 8. Zero shear viscosities (η_0) of the system CHO/PS 196w/PBMA 2050 as a function of w^*_{PBMA} for 20 °C and for different contents of polymer (w_{pol}). The symbols represent experimental data and the full lines are calculated according to eq 5.

phase diagram of polymer-containing systems. For that reason zero shear viscosities η_0 were measured as a function of blend composition for different overall polymer concentrations of the ternary system at 20 and at 60 °C, respectively.

The straight lines drawn in the above graph correspond to the following mathematical expressions (η_0 in Pa s, T in K):

$$\ln \eta_0 = A + Bw^*_{\mathrm{PBMA}} \tag{5}$$

$$A = \left(-10.8 + \frac{1481}{T}\right) + 33.8w_{\mathrm{pol}} - 56.1w_{\mathrm{pol}}^{\ 2}$$

$$B = 0.93 + \left(95.0 - \frac{1.83 \times 10^4}{T}\right)w_{\mathrm{pol}} - \left(636 - \frac{1.636 \times 10^5}{T}\right)w_{\mathrm{pol}}^{\ 2}$$

This relation was determined the following way: η_0 was measured for several blend compositions, w^*_{PBMA}, in the course of which different overall polymer contents, w_{pol}, were investigated by dilution with CHO. These measurements were carried out at 20 and 60 °C. As can be seen in Figure 8 for the lower temperature, the isothermal semilogarithmic plot $\eta_0(w^*_{\mathrm{PBMA}})$ at constant w_{pol} yields straight lines, i.e. η_0 of a ternary system is related to the η_0 values of the corresponding subsystems by[17]

$$\ln \eta_0 = w^*_{\mathrm{PS}} \ln \eta_{0,\mathrm{CHO/PS}} + w^*_{\mathrm{PBMA}} \ln \eta_{0,\mathrm{CHO/PBMA}} \qquad w_{\mathrm{pol}} = \mathrm{const}, \quad T = \mathrm{const} \tag{6}$$

In the present evaluation A and B are, however, not calculated from the data of the binary subsystems, but all experimental data are fitted by linear regression to guarantee equal treatment of each measurement.

In order to obtain a general and analytical expression for the concentration and temperature dependencies of the zero shear viscosities, A, the intercepts with the ordinate, and B, the slopes of the different lines, were plotted as a function of the overall polymer concentrations, w_{pol}. These experimental results can be described by polynomials of the second order. It was then assumed that these coefficients depend linearly on T^{-1}. This evaluation results in the analytical expression for $\eta_0(w^*_{\mathrm{PBMA}}, w_{\mathrm{pol}}, T)$ given in eq 5.

Conclusions

The thermodynamic results presented in this part demonstrate that the equilibrium phase behavior of the ternary system CHO/PS/PBMA can be modeled quite accurately by means of composition and temperature dependent binary interaction parameters. The corresponding viscometric data supply the basis for the calculation of the stored energy. The input for the theoretical section of part two of this paper dealing with shear influences on the phase diagram is now available.

Acknowledgment. We are very grateful to the DFG (Deutsche Forschungsgemeinschaft) for financial support.

References and Notes

(1) Beyens, D.; Gbadamassi, M.; Moncef-Bouanz, B. *Physical Review A* **1983**, *28*, 2491.
(2) Krause, C.; Horst, R.; Wolf, B. A. *Macromolecules* **1997**, *30*, xx (following paper in this issue).
(3) Meiβner, K.; Ph.D. *thesis*, Johannes Gutenberg-Universität, Mainz, Germany 1994.
(4) Shirataki, H.; Kamide, K. *Polym. Int.* **1993**, *32*, 265−273.
(5) Wagner, M.; Wolf, B. A. *Macromolecules* **1993**, *26*, 6498.
(6) Koningsveld, R. *Macromol. Symp.* **1994**, *78*, 1.
(7) Wolf, B. A. *Makromol. Chem.* **1969**, *128*, 284.
(8) Koningsveld, R.; Staverman, A. J. *J. Polym. Sci.* **1968**, *A-2*, 325.
(9) Boom, R. M.; van den Boomgard, Th.; Smolders, C. A. *Macromolecules* **1994**, *27*, 2034.
(10) Petri, H.-M.; Horst, R.; Wolf, B. A. *Polymer* **1996,** *37*, 2709.
(11) Koningsveld, R.; Kleintjens, L. A. *Macromolecules* **1971**, *4*, 637.
(12) Petri, H.-M.; Wolf, B. A. *Macromol. Chem. Phys.* **1995**, *196*, 2321.
(13) Petri, H.-M. Ph.D. *thesis*, Johannes Gutenberg-Universität, Mainz, Germany, 1994.
(14) Horst, R. *Macromol. Theory Simul.* **1995**, *4*, 449.
(15) Horst, R.; Wolf, B. A. *Macromol. Theory Simul.* **1996**, *5*, 81.
(16) DiPaola-Baranyi, G.; Degré, P. *Macromolecules* **1981**, *14*, 1456.
(17) Sander, U., Ph.D. *thesis*, Johannes Gutenberg-Universität, Mainz, Germany, 1989.

MA9609745