(16) Strauss, U. P.; Ander, P. J. Phys. Chem. 1962, 66, 2235.
(17) Strauss, U. P.; Wineman, P. L. J. Am. Chem. Soc. 1958, 80, 2366.
(18) Brandrup, J.; Immergut, E. H., Eds.; "Polymer Handbook"; Interscience: New York, 1966.
(19) Kowblansky, M.; Zema, P. Macromolecules 1981, 14, 1448.
(20) Stockmayer, W. H.; Fixman, M. J. Polym. Sci., Part C 1963, 1, 137.

Thermodynamic Characterization of Polystyrene–Poly(*n*-butyl methacrylate) Blends

G. DiPaola-Baranyi* and P. Degré[1]

Xerox Research Centre of Canada, 2480 Dunwin Drive, Mississauga, Ontario L5L 1J9, Canada. *Received April 28, 1981*

ABSTRACT: Inverse gas chromatography has been used to investigate the thermodynamic miscibility behavior of molten polystyrene–poly(*n*-butyl methacrylate) blends as a function of blend composition, temperature, and polystyrene molecular weight. A generally consistent and realistic measure of the polymer–polymer interaction has been obtained with this technique. The results suggest that there are no strong attractive forces between these two polymers. The combination of chromatographic and calorimetric data indicates that whereas blends of poly(*n*-butyl methacrylate) with high molecular weight polystyrene are immiscible, the corresponding blends with low molecular weight polystyrene are miscible over the whole range of composition. The resultant miscibility arises from more favorable entropic effects on lowering the molecular weight.

Introduction

Inverse gas chromatography (IGC) is generally recognized as a fast and reliable method for quantitative evaluation of polymer–solute interactions.[2,3] However, the technique can also be used to measure the interaction between two polymers in a mixed stationary phase. This is accomplished by analyzing the interaction between the volatile probe (1) and each of the two nonvolatile components (2 and 3), and then with a mixture of components 2 and 3.

In general, classical Flory–Huggins theory[4] can be used to interpret the results and to determine the χ_{23}' interaction parameter, which is a measure of the thermodynamic miscibility of the two polymers. Some mixtures that have been studied by IGC include poly(vinyl chloride) with di-*n*-octyl phthalate (DOP)[5] and poly(ε-caprolactone),[6] polystyrene with poly(vinyl methyl ether),[7] poly(dimethylsiloxane) with tetracosane and DOP,[8] and styrene–dimethylsiloxane block copolymers and blends.[9]

This report presents self-consistent polymer–solute and polymer–polymer interaction parameters for several polystyrene–poly(*n*-butyl methacrylate) blends.[10] These systems were investigated in the molten state by IGC as a function of temperature, blend composition, and polystyrene molecular weight. In addition, thin films of these blends were prepared and investigated by differential scanning calorimetry (DSC) in order to confirm the results. A previous publication describes the thermodynamic miscibility of the parent homopolymers as well as the behavior of some styrene–butyl methacrylate copolymers.[11]

Experimental Section

Materials. All solutes were chromatoquality or reagent grade and were used without further purification. The polystyrene samples (PS_H: $\bar{M}_w = 110\,000$, $\bar{M}_w/\bar{M}_n < 1.06$; PS_L: $\bar{M}_n = 1709$, $\bar{M}_w/\bar{M}_n < 1.06$) were obtained from Polysciences and Pressure Chemical Co., respectively. Poly(*n*-butyl methacrylate) (PnBMA: $\bar{M}_w = 320\,000$, $\bar{M}_n = 73\,500$) was obtained from Aldrich.

Columns. The columns were prepared in the usual manner. The polymers were coated from a benzene solution onto Chromosorb G (AW-DMCS treated, 70/80 mesh). After drying in a vacuum oven for ca. 48 h at 60 °C, the coated support was resieved and then packed into 48-mm-i.d. copper columns. The total percent loading of polymer on the support was determined by calcination using a suitable blank correction. The relative concentration of polymers in the blends is assumed to be identical with that in the original solution prior to deposition on the inert support. Columns were conditioned under nitrogen for 3 h at 100 °C above their glass transition. A description of the columns is given in Table I.

Table I
Stationary Phase and Column Parameters

polymer	loading, % w/w	wt of polymer, g	column length, cm
PS_H	7.45	1.1778	152
PS_L	10.72	1.3120	116
PnBMA	8.19	1.2656	152
PS_H–PnBMA blends			
30 wt % PS_H	9.47	1.1399	114
58 wt % PS_H	9.80	1.1658	117
PS_L–PnBMA blends			
15 wt % PS_L	10.51	0.9908	91
27 wt % PS_L	9.42	0.8090	91
30 wt % PS_L	10.20	1.0404	91
35 wt % PS_L	10.36	0.9813	91
40 wt % PS_L	10.34	0.9985	91
58 wt % PS_L	10.60	1.1893	107
80 wt % PS_L	10.36	1.2432	107

Instrumentation. The gas chromatographic (IGC) measurements were carried out with a Hewlett-Packard 5830A gas chromatograph, which was equipped with a dual flame ionization detector. The experimental setup and procedure have been described in a previous publication.[11]

The calorimetric measurements (DSC) were carried out with a Du Pont 990 thermal analyzer (approximately 10 mg of sample) at a scan rate of 5 °C/min (second run). The glass transition temperature was taken as the onset of the transition.

Data Reduction. Specific retention volumes, $V_g°$ (cm^3/g), were computed in the usual manner[11,12]

$$V_g° = t_N F J / w_L \quad (1)$$

where t_N is the net retention time for the probe, F is the carrier gas flow rate at 0 °C and 1 atm (STP), J is a correction factor for gas compressibility, and w_L is the weight of polymer in the column.

0024-9297/81/2214-1456$01.25/0 © 1981 American Chemical Society

Table II
Flory-Huggins χ Parameter for the Interaction between Vapor Phase Probes with PS_H, PnBMA, and Their Blends at 140 °C

solute	wt % PS_H			
	0	30	58	100[a]
n-octane	0.796	0.825	0.906	1.077
n-decane	0.833	0.871	0.935	1.115
2,2,4-trimethylpentane	0.732	0.813	0.962	1.162
3,4,5-trimethylheptane	0.687	0.755	0.838	0.992
cyclohexane	0.564	0.558	0.592	0.581
benzene	0.259	0.246	0.246	0.282
toluene	0.207	0.228	0.226	0.320
n-butylbenzene	0.280	0.296	0.323	0.370
tert-butylbenzene	0.215	0.260	0.312	0.398
carbon tetrachloride	0.313	0.343	0.338	0.427
chloroform	−0.047	0.021	0.106	0.311
methylene chloride	0.187	0.257	0.258	0.407
2-pentanone	0.481	0.520	0.567	0.687
1-butanol	0.662	0.836	0.968	1.194

[a] Obtained by extrapolation of data between 170 and 190 °C.

From the Flory–Huggins treatment of solution thermodynamics,[14,15] one can obtain the χ parameter, which is a measure of the residual free energy of interaction between solute and polymer. χ is determined from the following relationship:[13]

$$\chi_{12} = \ln (273.16Rv_2/V_g^\circ p_1^\circ V_1) - (1 - V_1/V_2)\Phi_2 - p_1^\circ(B_{11} - V_1)/RT \quad (2)$$

where v_2, V_2, and Φ_2 refer to the specific volume, molar volume, and volume fraction of the polymer. The molar volume of the polymer was taken as the product of its specific volume and number-average molecular weight. All other symbols have their usual meanings.[11]

It has been shown,[8] using Scott's ternary solution treatment[16] of the Flory–Huggins theory, that the overall interaction parameter between the volatile probe (1) and the binary stationary phase (2-3) is given by

$$\chi_{1(23)} = \ln [273.16R(w_2v_2 + w_3v_3)/V_g^\circ p_1^\circ V_1] - (1 - V_1/V_2)\Phi_2 - (1 - V_1/V_3)\Phi_3 - p_1^\circ(B_{11} - V_1)/RT \quad (3)$$

where w_2 and w_3 refer to the weight fractions of PS and PnBMA in the blend. The sources of the required physical data for the probes and polymers were described previously.[11]

Results and Discussion

Specific retention volumes, V_g° (cm^3/g), have been measured for a variety of polar and nonpolar probes in several pure and mixed stationary phases containing PS and PnBMA. The vapor phase probes include several aliphatic and aromatic hydrocarbons, as well as chlorinated and oxygenated solutes. The stationary phases studied by IGC include two PS_H–PnBMA blends containing 30 and 58 wt % PS_H (130–180 °C) and seven PS_L–PnBMA blends containing 15, 27, 30, 35, 40, 58, and 80 wt % PS_L (100–140 °C). Except for PS_L, results for the other pure stationary phases (PS_H, PnBMA) were reported in a previous publication.[11] The precision of the experimental V_g° values is better than 3%.

Flory–Huggins χ parameters have been determined from the measured retention data in order to examine the extent of polymer–probe and polymer–polymer interaction in various PS–PnBMA mixtures. These values are summarized in Tables II and III for 140 °C.

Polymer–Probe Interaction. The behavior of the thermodynamic polymer–probe interaction parameters illustrates the influence of molecular weight on polymer solubility. Although similar trends in polymer–probe interactions are observed for both PS_H and PS_L blends (see Tables II and III), a distinct increase in polymer–probe solubility is observed for the low molecular weight PS_L blends. This reflects the observed increase in solubility of both solvent and nonsolvent probes in pure PS_L (see Tables II and III). There is a significant decrease in χ (10–30%) on going from PS_H to PS_L for any given vapor phase component. This behavior is probably due to a decrease in the free-volume difference between the probes and PS_L as compared to the higher molecular weight PS_H.[17] Covitz and King[18] have also reported a definite variation of activity coefficients with polystyrene molecular weight.

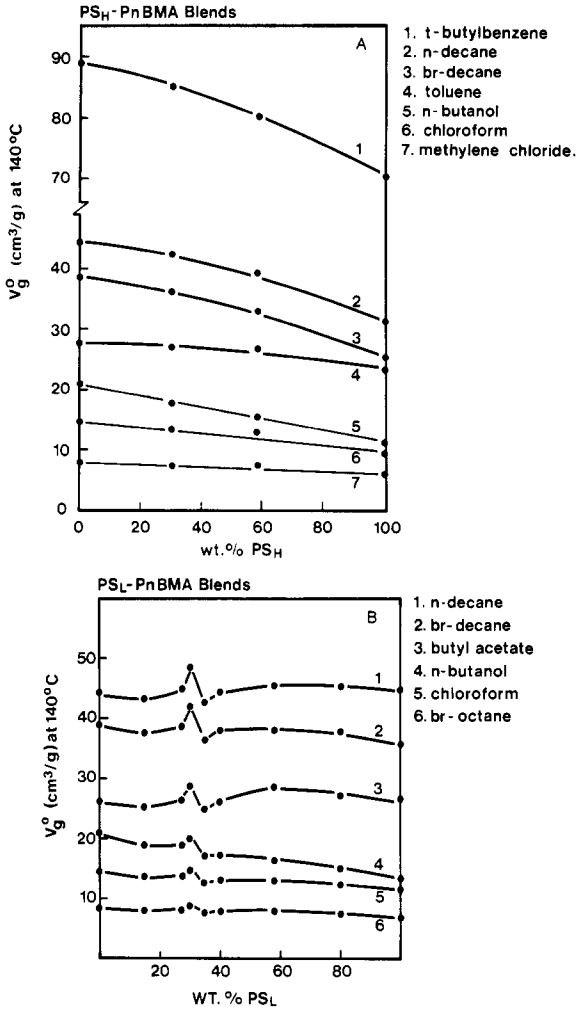

Figure 1. Composition dependence of the specific retention volume for various probes in (A) PS_H–PnBMA blends (the uncertainty on V_g° is 2–3%) and (B) PS_L–PnBMA blends (the uncertainty on V_g° is 1–2%).

The thermodynamic properties of the PS_H–PnBMA blends can generally be approximated from the properties of the parent homopolymers. Experimental V_g° values for all the probes are within 5% of the value predicted by the following relationship between V_g° and blend composition:

$$V_g^\circ{}_{23} = w_2V_g^\circ{}_2 + w_3V_g^\circ{}_3 \quad (4)$$

where w refers to the weight fraction of each polymer in the blend. This is illustrated for several probes at 140 °C (Figure 1A). This additivity, however, is not generally observed for the corresponding lower molecular weight PS_L blends. The composition dependence of V_g°, as illustrated in Figure 1B, is a more complex function of the homopolymer properties which could not have been predicted a priori. Measured retention volumes for several of the blends are consistently larger than expected (>5%).

Polymer–Polymer Miscibility. In order to qualitatively demonstrate the effects of molecular weight on

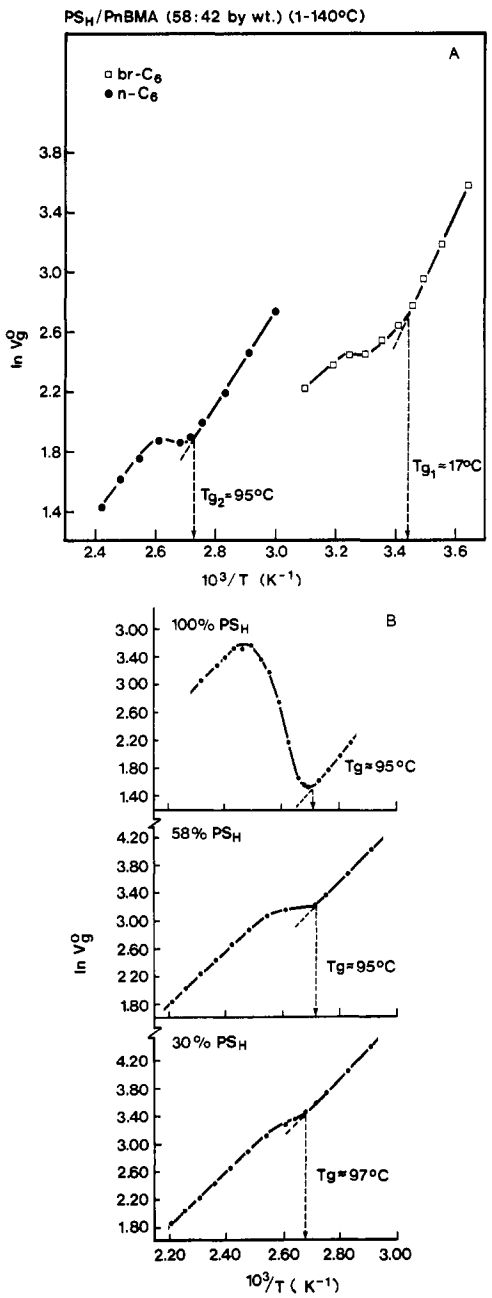

Figure 2. (A) Retention diagram illustrating the two glass transitions of a PS_H–PnBMA blend. T_g was taken as the first deviation from linearity. Branched hexane and *n*-hexane were used as probes in the low- and high-temperature range, respectively. (B) IGC determination of T_g for PS_H in several PS_H–PnBMA blends.

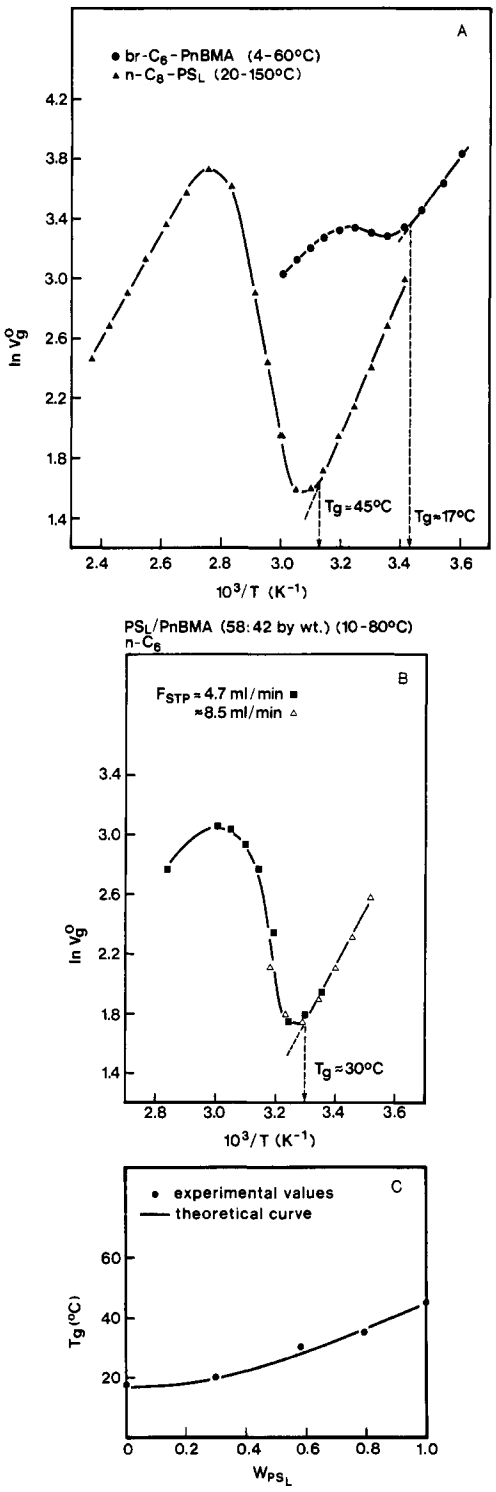

Figure 3. (A) Retention diagrams for the homopolymers PnBMA and PS_L. (B) Retention diagram for a PS_L–PnBMA blend. (C) Composition dependence of T_g for PS_L–PnBMA blends as observed by IGC.

polymer–polymer miscibility for PS–PnBMA blends, optical and T_g criteria of miscibility were employed. Both IGC studies of coatings prepared from benzene solutions and DSC studies of thin films cast from methylene chloride solutions were used to investigate the existence of single or multiple glass transitions in these blends. Both techniques yield similar results. However, only the IGC data are presented here since the calorimetric study was a relative one. Blends of PS_H with PnBMA produce cloudy films exhibiting two T_g's which are characteristic of each homopolymer[21] and are independent of blend composition. This behavior, which is indicative of phase separation,[22] is illustrated in Figure 2. Lowering the molecular weight of PS yields miscible blends over the whole range of composition. PS_L–PnBMA blends produce transparent films which are characterized by a single composition-dependent T_g. This behavior is illustrated in Figure 3. Parts A and B of Figure 3 illustrate the chromatographic determination of T_g for PS_L and PnBMA and the resulting single, intermediate T_g which characterizes a blend of these two polymers (e.g., 58 wt % PS_L). If the T_g of each blend is plotted as a function of composition, as shown in Figure 3C, the resulting curve shows a composition dependence for T_g which is analogous to that observed for copolymers and low molecular weight plasticizers.[22] The experimental data are in good agreement with the predictions of an

Table III
Flory-Huggins χ Parameter for the Interaction between Vapor Phase Probes with PS_L, PnBMA, and Their Blends at 140 °C

solute	wt % PS_L								
	0	15	27	30	35	40	58	80	100
n-octane	0.796	0.824	0.802	0.738	0.877	0.831	0.823	0.863	0.894
2,2,4-trimethylpentane	0.732	0.807	0.794	0.722	0.882	0.844	0.856	0.946	1.030
n-decane	0.833	0.875	0.840	0.780	0.911	0.875	0.877	0.912	0.933
3,4,5-trimethylheptane	0.687	0.741	0.714	0.625	0.794	0.755	0.778	0.800	0.878
cyclohexane	0.564	0.590	0.547	0.460	0.603	0.555	0.523	0.525	0.524
benzene	0.259	0.273	0.224	0.145	0.287	0.240	0.218	0.219	0.209
carbon tetrachloride	0.313	0.342	0.306	0.223	0.372	0.322	0.298	0.310	0.325
chloroform	−0.047	0.023	0.006	−0.054	0.090	0.063	0.081	0.161	0.217
2-pentanone	0.481	0.534	0.494	0.429	0.575	0.537	0.535	0.580	0.586
1-butanol	0.662	0.786	0.783	0.737	0.904	0.878	0.948	1.064	1.158
n-butyl acetate	0.445	0.483	0.441	0.369	0.513	0.465	0.462	0.470	0.492

Table IV
Polymer-Polymer Interaction Parameters (χ_{23}') for Various PS_H-PnBMA Blends at 140 °C

solute	wt % PS_H	
	30	58
n-octane	0.25	0.20
n-decane	0.21	0.24
2,2,4-trimethylpentane	0.21	0.06
3,4,5-trimethylheptane	0.10	0.09
cyclohexane	0.05	−0.08
n-butylcyclohexane		0.05
benzene	0.09	0.10
toluene	0.06	0.19
n-butylbenzene	0.05	0.04
tert-butylbenzene	0.04	0.03
carbon tetrachloride	0.01	0.16
chloroform	0.17	0.21
methylene chloride	−0.03	0.23
n-butyl chloride		0.04
chlorobenzene		0.13
1-butanol	−0.09	−0.01
n-butyl acetate		−0.07
2-pentanone	0.10	0.13

empirical relationship deomonstrated by Jenckel and Heursch:[23]

$$T_g = w_1 T_{g1} + w_2 T_{g2} + w_1 w_2 b(T_{g1} - T_{g2}) \quad (5)$$

where w_1 and w_2 refer to the weight fractions of PnBMA and PS_L, respectively, and b is a constant equal to 0.9. Recently, Massa[24] demonstrated that low molecular weight PS ($M \sim 600$) exhibits limited miscibility with another methacrylate, poly(methyl methacrylate).

Thermodynamic parameters characterizing the interaction between the components of a blend (χ_{23}') have been calculated from the measured polymer–probe interactions in the corresponding pure and mixed stationary phases[8]

$$\chi_{1(23)} = \chi_{12}\Phi_2 + \chi_{13}\Phi_3 - \chi_{23}'\Phi_2\Phi_3 \quad (6)$$

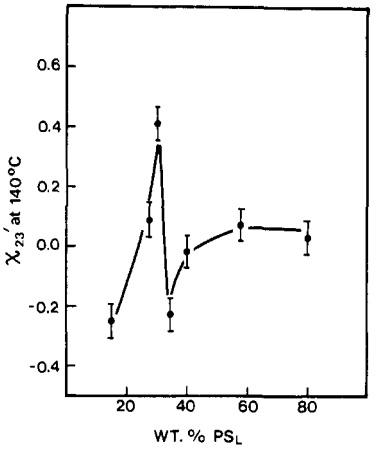

Figure 4. Composition dependence of the polymer–polymer interaction parameter for PS_L-PnBMA blends.

where $\chi_{23}' = \chi_{23} V_1 / V_2$.

The interaction parameter χ_{23}' is thus normalized to the size of the probe molecule. A negative interaction parameter is required in order to ensure miscibility of two high molecular weight polymers.[19] Since eq 6 assumes random mixing of the polymers in the stationary phase, as well as random sensing of the interactions in the mixture by the probe, it should be strictly valid for compatible systems only.[5,7] Galin and Rupprecht have recently indicated that this approach might also be used as a rough approximation for determining χ_{23}' for biphasic mixtures with small domain sizes.[9]

Table IV summarizes the apparent polymer–polymer interaction parameters for the PS_H-PnBMA blends at 140 °C. Although the values vary with the particular probe, the average value of χ_{23}' is small and positive (ca. 0.1). No significant temperature (140–160 °C) or blend composition dependence is observed. These results are consistent with

Table V
Polymer-Polymer Interaction Parameters (χ_{23}') for Various PS_L-PnBMA Blends at 140 °C

solute	wt % PS_L						
	15	27	30	35	40	58	80
n-octane	−0.11	0.10	0.42	−0.21	0.01	0.11	0.07
2,2,4-trimethylpentane	−0.25	0.09	0.47	−0.21	0.02	0.19	0.14
n-decane	−0.22	0.10	0.40	−0.20	−0.01	0.06	0.00
3,4,5-trimethylheptane	−0.21	0.12	0.43	−0.18	0.03	0.07	0.06
cyclohexane	−0.25	0.04	0.44	−0.24	−0.03	0.07	0.04
benzene	−0.17	0.11	0.47	−0.20	0.00	0.05	0.00
carbon tetrachloride	−0.22	0.05	0.45	−0.24	−0.02	0.09	0.08
chloroform	−0.25	0.09	0.41	−0.21	−0.03	0.09	0.01
2-pentanone	−0.30	0.08	0.40	−0.25	−0.06	0.02	−0.09
1-butanol	−0.41	0.06	0.35	−0.32	−0.08	−0.01	−0.03
n-butyl acetate	−0.25	0.08	0.43	−0.23	−0.08	0.04	0.08

the observed immiscibility of these two polymers.

Table V summarizes χ_{23}' for PS_L–PnBMA blends at 140 °C. It is apparent that the probe-to-probe variations are considerably smaller than before and that the interaction parameter is now a complex function of composition. In order to represent this concisely, χ_{23}' values for each of the seven blend compositions at 140 °C were averaged for the 11 probes and the resulting values plotted as a function of PS_L content (Figure 4). These interaction parameters are slightly more positive at 120 °C, but a similar composition dependence is observed. In view of the generally positive χ_{23}' values measured (at high PS_L content), there are no strong attractive forces between these two polymers. The miscibility observed with optical and T_g criteria must therefore be due to more favorable combinatorial entropy effects on lowering the molecular weight of the PS. Further work is required in order to determine the generality and the implications of the composition dependence of χ_{23}' in such polymer blends.

Acknowledgment. We wish to acknowledge helpful discussions with Dr. M. Croucher and to thank Dr. M. Breton for helpful comments.

References and Notes

(1) Co-op student from the Université de Sherbrooke, Sherbrooke, Quebec.
(2) Braun, J. M.; Guillet, J. E. *Adv. Polym. Sci.* **1976**, *21*, 108.
(3) Gray, D. G. *Prog. Polym. Sci.* **1977**, *5*, 1.
(4) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.
(5) Su, C. S.; Patterson, D.; Schreiber, H. P. *J. Appl. Polym. Sci.* **1976**, *20*, 1025.
(6) Olabisi, O. *Macromolecules* **1975**, *8*, 316.
(7) Su, C. S.; Patterson, D. *Macromolecules* **1977**, *10*, 708.
(8) Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. *Macromolecules* **1974**, *7*, 530.
(9) Galin, M.; Rupprecht, M. S. *Macromolecules* **1979**, *12*, 506.
(10) Preliminary results for this system were presented at the Second Chemical Congress of the North American Continent which was held in Las Vegas, Nev. (Aug 24–29, 1980) and are summarized in: DiPaola-Baranyi, G. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1980**, *21*, 214.
(11) DiPaola-Baranyi, G. *Macromolecules* **1981**, *14*, 683.
(12) Littlewood, A. B.; Phillips, C. S. G.; Price, D. T. *J. Chem. Soc.* **1955**, 1480.
(13) Patterson, D.; Tewari, Y. B.; Schreiber, H. P.; Guillet, J. E. *Macromolecules* **1971**, *4*, 356.
(14) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660.
(15) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440.
(16) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 279.
(17) χ represents a residual free energy of interaction term which is composed of an enthalpic or contact energy contribution as well as an entropic contribution arising from the difference in free volume or degree of thermal expansion between the two components.[19] Since the enthalpic contribution is expected to be similar for both low and high molecular weight polystyrene and the thermal expansion coefficient of the former exceeds that of the latter,[20] the observed differences in χ therefore probably arise from the decrease in free volume dissimilarity between a probe and PS_L as compared to the corresponding PS_H system.
(18) Covitz, F. H.; King, J. W. *J. Polym. Sci.* **1972**, *10*, 689.
(19) Patterson, D.; Robard, A. *Macromolecules* **1978**, *11*, 690.
(20) Fox, T. G., Jr.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
(21) Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook", 2nd ed.; Wiley: New York, 1975; pp 111, 147, 154.
(22) Olabisi, O.; Robeson, L. M.; Shaw, M. T. "Polymer–Polymer Miscibility"; Academic Press: New York, 1979.
(23) Meares, P. "Polymers. Structure and Bulk Properties"; Van Nostrand: Princeton, N.J., 1965; Chapter 10.
(24) Massa, D. J. In *Adv. Chem. Ser.* **1979**, *No. 176*.

Main-Chain Rotational Contributions in the Glass–Liquid Transition[1]

A. A. Miller

Department of Chemistry, State University of New York, Albany, New York 12222.
Received January 21, 1981

ABSTRACT: Main-chain rotational contributions to the increments in thermal expansivity and heat capacity in the glass-to-liquid transition, derived via a three-state rotational model, are compared for five vinyl-type polymers. For linear polyethylene and polyisobutylene these contributions are about 40% while for polystyrene and poly(vinyl acetate), both with "articulate" substituents, these contributions are only about 20%. Poly(dimethylsiloxane) gives anomalous results with this rotational model. Considering the glass transition as an isomobility state, it is shown that the second Ehrenfest relation need not apply, but may appear to do so in the limited cases where the pressure coefficients of the Vogel T_0 and B are equal.

In a series of recent papers we have been developing a kinetic model for mobility and the glass transition of polymer[2–4] and copolymer[5] liquids. In this model the important molecular motion is the cooperative rotational isomerization about main-chain bonds. This motion becomes virtually "frozen" when the temperature is lowered to T_g, which we consider to be an isomobility state.[6]

On the other hand, despite the recognized time dependence of this transition there has been much effort on strictly thermodynamic approaches. Intensive discussions of these have recently been reported for polystyrene (PS)[7] and for poly(vinyl acetate) (PVAc).[8–10]

Following the earlier Gibbs and DiMarzio concepts,[11] Adam and Gibbs[12] in 1965 combined the thermodynamic and kinetic aspects of the glass transition in their theory for cooperative relaxation. We have modified[2] (or perhaps clarified) this theory to make it conform to the Vogel or Tammann–Hesse equation[13]

$$-\ln(\mu/\mu_0) = B/(T - T_0) \quad (1)$$

which still appears to be the best empirical relationship describing the temperature dependence of mobility for polymers.[14]

For a three-state rotational model it was shown[2,3] that $U = mRT_0$ and $E_0 = RB$, where U is the energy difference between the trans (t) state and two equivalent higher gauche (g^+, g^-) states and E_0 is related to the energy barriers against rotation between these states in the for-

0024-9297/81/2214-1460$01.25/0 © 1981 American Chemical Society