(21) Friday, A.; Booth, C. *Polymer* **1978**, *19*, 1035.
(22) Ashman, P. C.; Booth, C.; Cooper, D. R.; Price, C. *Polymer* **1975**, *16*, 897.
(23) Hirata, E.; Ijitsu, T.; Soen, T.; Hashimoto, T.; Kawai, H. *Polymer* **1975**, *16*, 249.
(24) Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. *Macromolecules* **1974**, *7*, 530.
(25) Galin, M. *Macromolecules* **1977**, *10*, 1239.
(26) Galin, M., to be submitted for publication.
(27) Su, C. S.; Patterson, D.; Schreiber, H. P. *J. Appl. Polym. Sci.* **1976**, *20*, 1025.
(28) Su, C. S.; Patterson, P. *Macromolecules* **1977**, *10*, 708.
(29) Booth, C.; Devoy, C. J. *Polymer* **1971**, *12*, 309.
(30) Galin, M.; Rupprecht, M. C. *Macromolecules* **1979**, *12*, 506.

Thermodynamic Miscibility of Various Solutes with Styrene–Butyl Methacrylate Polymers and Copolymers

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ABSTRACT: Inverse gas chromatography has been used to determine the thermodynamic miscibility of molten poly(styrene–*n*-butyl methacrylate) (58 wt % styrene), poly(styrene–isobutyl methacrylate) (80 wt % styrene), and the corresponding homopolymers with various polar and apolar solutes. Infinite-dilution weight fraction activity coefficients, Flory–Huggins χ parameters, and excess partial molar heats of mixing are used as measures of the polymer–probe interaction. The thermodynamic interaction parameters obtained for these systems are self-consistent; i.e., the miscibility of the copolymer is in qualitative agreement with the interpolated behavior of the parent homopolymers. However, this agreement is generally not quantitative. This probably reflects the effects of nearest-neighbor segment interactions on the solution thermodynamics of the copolymer. In addition, a comparison of homopolymer properties reveals only minor differences between molten poly(*n*-, iso-, and *sec*-butyl methacrylates).

Introduction

Since the pioneering work of Smidsrod and Guillet,[1] numerous investigators have used inverse gas chromatography (IGC) to determine physicochemical parameters characterizing the interaction of small amounts of volatile solutes with polymers.[2-4] It has been established that reliable infinite-dilution weight fraction activity coefficients, Flory–Huggins χ parameters, and excess partial molar heats of mixing can be readily determined with this technique. In the present work, the sensitivity of these thermodynamic interaction parameters to structural modifications of several poly(butyl methacrylates) is investigated. In addition, the melt behavior of two styrene–butyl methacrylate copolymers has been investigated, and the results have been compared with those for the corresponding homopolymers. This investigation is part of a continuing study of the thermodynamic properties of styrene–methacrylate homopolymers, copolymers, and blends.

Experimental Section

Materials. All solutes were chromatoquality or reagent grade and were obtained from standard laboratory supply sources. Polystyrene (PS: $\bar{M}_w$ = 110000, $\bar{M}_w/\bar{M}_n$ < 1.06) was obtained from Polysciences. Poly(*n*-butyl methacrylate) (PnBMA: $\bar{M}_w$ = 320000, $\bar{M}_n$ = 73500), poly(isobutyl methacrylate) (PiBMA: $\bar{M}_w$ = 300000, $\bar{M}_n$ = 140000), and poly(*sec*-butyl methacrylate) (PsBMA: density = 1.052 g cm^{-3}) were obtained from Aldrich. Poly(styrene–*n*-butyl methacrylate) ($\bar{M}_w$ = 70000–75000, $\bar{M}_w/\bar{M}_n \simeq$ 2.0–2.3, MI = 15.5) containing 58 wt % styrene and poly(styrene–isobutyl methacrylate) ($\bar{M}_w \simeq$ 70000) containing 80 wt % styrene are random copolymers which were obtained from internal sources (Xerox Corp.). Chromosorb G (AW-DMCS treated, 70/80 mesh) was obtained from Johns-Manville.

Columns. The polymers were coated from a benzene solution onto Chromosorb G. After drying in a vacuum oven for ca. 72 h at 60 °C, the coated support was resieved and the packed into 0.25-in o.d. copper columns. Silanized glass wool was used to block the ends of the column. The exact percent loading of polymer on the support (weight of polymer/weight of polymer plus support) was determined by calcination, using a suitable blank correction. A complete description of the columns is given in Table I.

Table I
Stationary Phase and Column Parameters

polymer	loading, % (w/w)	wt of polymer, g	length of column, cm
PS	7.45	1.1778	152.4
PnBMA	8.19	1.2656	152.4
PiBMA	8.20	0.9860	121.9
		0.3463	50.8
PsBMA	8.00	1.0194	121.9
P(S-nBMA)	8.03	1.2763	152.4
P(S-iBMA)	10.62	1.2987	119.4

Instrumentation. IGC measurements were carried out on a Hewlett-Packard 5830A gas chromatograph equipped with a dual flame ionization detector. The oven temperature was measured with a precision of ±0.01 °C with a Hewlett-Packard platinum resistance thermometer. Carrier gas (prepurified nitrogen) flow rates were measured from the end of the column with a water-jacketted soap bubble flowmeter. The net retention time of the probe (±0.01 min) was determined from the peak maxima retention times for the probe and methane (a marker to correct for dead volume in the column). Column inlet and outlet pressures were read from a mercury manometer (±0.05 mmHg).

The solutes and marker were injected manually with a 10-μL Hamilton syringe (<0.01 μL). The solutes were characterized by symmetrical elution peaks and generally exhibit little sample size dependence at low injection volumes, low carrier gas flow rates (5–20 cm^3/min), and moderate column loadings ($\simeq$8%). Galin and Rupprecht[5] have shown that under these conditions the opposite influences of surface adsorption and gas flow rate are nearly equivalent, so that the experimental $V_g°$ value is quite close to the bulk $V_g°$ value. Columns were conditioned at temperatures ca. 100 °C above T_g for 2–3 h prior to use.

Data Reduction. Specific retention volumes, $V_g°$ (cm^3/g), were computed from the relation[6]

$$V_g° = t_N F J / w_L \quad (1)$$

where t_N is the net retention time for the probe, w_L is the weight of polymer in the column, J is the James–Martin correction factor

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Table III
Thermodynamic Interaction Parameters for PnBMA and Several Solutes at Infinite Dilution

solute[a]	120 °C		130 °C		140 °C	
	$(a_1/w_1)^\infty$	χ	$(a_1/w_1)^\infty$	χ	$(a_1/w_1)^\infty$	χ
n-octane			9.92	0.814	9.81	0.793
2,2,4-trimethylpentane			9.39	0.747	9.29	0.729
cyclohexane			7.13	0.579	7.08	0.563
n-butylcyclohexane	7.60	0.718	7.43	0.693	7.27	0.667
benzene	4.56	0.265	4.58	0.261	4.61	0.257
n-butylbenzene	4.64	0.294	4.60	0.284	4.60	0.280
tert-butylbenzene	4.28	0.221	4.26	0.213	4.28	0.215
carbon tetrachloride	2.73	0.346	2.70	0.326	2.68	0.312
chloroform	1.93	−0.087	1.99	−0.067	2.05	−0.048
methylene chloride	2.80	0.169	2.84	0.175	2.90	0.187
n-butyl chloride	5.07	0.325	5.10	0.315	5.13	0.305
chlorobenzene	3.18	0.161	3.19	0.160	3.23	0.168
1-butanol	7.96	0.752	7.56	0.693	7.37	0.661
cyclohexanol	5.53	0.582	5.31	0.540	5.10	0.500
2-pentanone	6.29	0.499	6.28	0.488	6.28	0.479
n-butyl acetate	5.49	0.466	5.46	0.453	5.43	0.443

[a] *n*-Decane and 3,4,5-trimethylheptane were investigated between 150 and 180 °C.

for gas compressibility,[7] and F is the carrier gas flow rate at 0 °C and 1 atm, which is obtained as follows:

$$F = 273.16f(P_A - P_w)/760(273.16 + \theta_A) \quad (2)$$

where P_A is the atmospheric pressure (mmHg), f is the flow rate measured from the end of the column (cm³/min), and P_w is the water pressure (mmHg) at temperature θ_A (°C) of the flowmeter.

At temperatures above T_g, the magnitude of $V_g°$ is a measure of the solubility of the probe in the stationary phase. By applying thermodynamic theory to gas chromatography, one can relate the measured $V_g°$ to the weight fraction activity coefficient at infinite dilution of the probe, $(a_1/w_1)^\infty$, a fundamental parameter of solution thermodynamics which indicates deviation from ideal-solution behavior

$$\ln (a_1/w_1)^\infty = \ln (273.16R/V_g°p_1°M_1) - p_1°(B_{11} - V_1)/RT \quad (3)$$

where V_1, M_1, and $p_1°$ refer to the solute molar volume, molecular weight, and saturated vapor pressure, respectively, R is the gas constant, T is the column temperature (K), and B_{11} is the second virial coefficient which is used to correct for vapor phase nonideality of the probe.[8] Values of B_{11} were estimated from corresponding equations of state.[9,10] Solute vapor pressures were obtained from Dreisbach's compilation.[11] Solute densities were obtained from various sources, including the compilations by Orwoll and Flory[12] and Timmermans,[13] as well as ref 14.

From the Flory–Huggins treatment of solution thermodynamics[15,16] 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 relationship

$$\chi = \ln (273.16Rv_2/V_g°p_1°V_1) - (1 - V_1/M_2v_2)\Phi_2 - p_1°(B_{11} - V_1)/RT \quad (4)$$

where v_2, M_2, and Φ_2 are the specific volume, molecular weight, and volume fraction of the polymer. At infinite dilution of probe and for high molecular weight polymer, the second term of eq 4 approaches 1. Volumetric data for PS and PnBMA were obtained from the work of Hocker et al.[17] and Olabisi et al.,[18] respectively. Specific volumes of PiBMA and PsBMA were estimated from the Simha–Boyer relation.[19]

The volumetric data for the copolymers were determined by assuming that the specific volume of the copolymer is the weight average of the specific volumes of the parent homopolymers.

Results and Discussion

Specific retention volumes were measured at 5–10 °C intervals for various solutes of differing molecular structures and polarities in PS (170–190 °C) and the BMA homopolymers (120–150 °C). The copolymers P(S–nBMA) and P(S–iBMA) were investigated between 120 and 150 °C and between 140 and 180 °C, respectively. These temperature ranges were chosen in order to ensure the attainment of thermodynamic equilibrium for each polymer melt.

In all cases investigated, $V_g°$ decreases with increasing temperature. The linear correlation observed for the temperature dependence of ln $V_g°$ is illustrated for several probes in P(S–nBMA) (Figure 1; supplementary material).

The measured retention data for various PS–solute systems are in excellent agreement (better than 3% agreement for $V_g°$) with the results of DiPaola-Baranyi and Guillet[20] and in good agreement (within 3–10%) with the results of Galin and Rupprecht[5] (Table II; supplementary material). It is difficult to compare the present data for PnBMA[21] with the data reported by Newman and Prausnitz, since their $V_g°$ values are not corrected to 0 °C. However, derived activity coefficients for several of the common probes agree to within 5%. The other polymers have not been investigated by IGC in these temperature ranges.

In order to assess the extent of molecular interactions between probe and polymer, weight fraction activity coefficients and Flory–Huggins χ parameters at infinite dilution of probe have been evaluated. Tables II–V summarize these parameters for PS, PnBMA, and the two copolymers. Values of $(a_1/w_1)^\infty$ range from 2 to 13. Generally speaking, low values indicate polymer–solute miscibility, whereas values greater than 5 usually characterize poor solvent systems in these temperature ranges. Values of χ range from −0.1 to +1.0. In order to ensure polymer–solute miscibility, χ should be less than the critical value, 0.5.[15,16]

In addition to these thermodynamic interaction parameters, excess partial molar heats of mixing have been evaluated from a linear least-squares analysis of the temperature dependence of the activity coefficient

$$\Delta\bar{H}_1^\infty = R\,\partial \ln (a_1/w_1)^\infty/\partial(1/T) \quad (5)$$

Figure 2 illustrates these trends for various probes in P(S–nBMA). A linear temperature dependence is also observed for χ (Figure 3). The temperature coefficients are summarized for PS, PnBMA and P(S-nBMA) in Tables VI–VIII (Tables VI and VII are available as supplementary material). The estimated uncertainty of these values is ±0.1 kcal/mol.

Because of the small combinatorial entropy of mixing associated with the formation of polymer solutions, $\Delta\bar{H}_1^\infty$ plays an important role in determining polymer miscibility. Exothermic or nearly athermal partial molar heats of

Table IV
Thermodynamic Interaction Parameters for P(S-iBMA) and Several Solutes at Infinite Dilution

solute	150 °C		160 °C		170 °C		180 °C	
	$(a_1/w_1)^\infty$	χ	$(a_1/w_1)^\infty$	χ	$(a_1/w_1)^\infty$	χ	$(a_1/w_1)^\infty$	χ
n-octane	11.83	0.943	11.59	0.910	11.33	0.873	11.29	0.855
n-decane	11.66	0.991	11.39	0.958	11.06	0.919	10.85	0.889
2,2,4-trimethylpentane	13.29	1.053	12.51	0.983	12.25	0.952	11.78	0.904
3,4,5-trimethylheptane	10.43	0.925	10.02	0.878	9.79	0.847	9.57	0.817
cyclohexane	7.56	0.592	7.46	0.567	7.49	0.558	7.31	0.521
benzene	4.89	0.279	4.91	0.270	4.94	0.265	4.96	0.256
tert-butylbenzene	4.97	0.333	4.95	0.322	4.94	0.314	4.92	0.304
carbon tetrachloride	2.93	0.364	2.93	0.351	2.92	0.336	2.92	0.324
chloroform	2.71	0.187	2.73	0.177	2.79	0.182	2.81	0.170
methylene chloride	3.44	0.321	3.50	0.324	3.54	0.325	3.64	0.339
n-butyl chloride	6.01	0.418	6.07	0.408	6.06	0.384	6.18	0.380

Table V
Thermodynamic Interaction Parameters for P(S-nBMA) and Several Solutes at Infinite Dilution

solute	120 °C		130 °C		140 °C		150 °C	
	$(a_1/w_1)^\infty$	χ	$(a_1/w_1)^\infty$	χ	$(a_1/w_1)^\infty$	χ	$(a_1/w_1)^\infty$	χ
n-octane	11.16	0.925	10.84	0.886	10.53	0.848	10.29	0.816
n-decane	11.10	0.975	10.67	0.928	10.31	0.888	10.02	0.852
n-dodecane	11.25	1.022	10.80	0.975	10.42	0.935	10.06	0.895
2,2,4-trimethylpentane	11.99	0.983	11.42	0.927	10.93	0.878	10.61	0.839
3,4,5-trimethylheptane	9.80	0.891	9.29	0.830	8.98	0.793	8.73	0.759
cyclohexane	7.29	0.600	7.13	0.563	7.02	0.539	6.93	0.516
methylcyclohexane	7.47	0.619	7.24	0.580	7.12	0.556	6.95	0.524
n-butylcyclohexane	7.67	0.713	7.44	0.677	7.23	0.646	7.07	0.619
benzene	4.50	0.237	4.46	0.217	4.49	0.215	4.52	0.212
ethylbenzene	4.46	0.238	4.45	0.228	4.46	0.225	4.45	0.217
n-butylbenzene	4.64	0.280	4.62	0.271	4.62	0.268	4.61	0.262
tert-butylbenzene	4.53	0.263	4.49	0.250	4.47	0.243	4.44	0.232
carbon tetrachloride	2.70	0.319	2.68	0.302	2.70	0.302	2.68	0.288
chloroform	2.12	−0.007	2.17	0.004	2.22	0.017	2.31	0.039
methylene chloride	2.95	0.209	3.02	0.221	3.05	0.223	3.10	0.224
n-butyl chloride	5.26	0.347	5.30	0.338	5.35	0.331	5.42	0.328
chlorobenzene	3.13	0.133	3.13	0.127	3.17	0.134	3.18	0.132
1-butanol	9.64	0.929	9.32	0.886	8.85	0.828	8.68	0.801
cyclohexanol	6.12	0.670	5.95	0.638	5.69	0.593	5.41	0.540
2-pentanone	6.35	0.495	6.42	0.494	6.50	0.498	6.50	0.488
n-butyl acetate	5.49	0.450	5.33	0.412	5.46	0.432	5.51	0.434

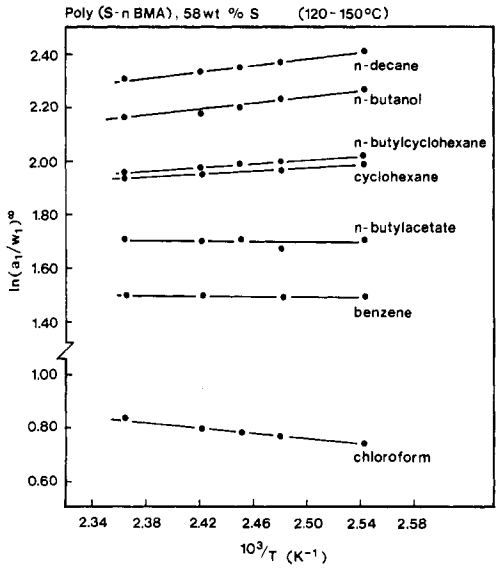

Figure 2. Temperature dependence of the weight fraction activity coefficient for several solutes in P(S-nBMA).

Table VIII
Excess Partial Molar Heats of Mixing ($\Delta\bar{H}_1^\infty$) and Temperature Dependence of the χ Parameter for Various P(S-nBMA)–Solute Systems between 120 and 150 °C

solute	ΔH_1^∞, kcal/mol	$R\,\partial\chi/\partial(1/T)$, kcal/mol
n-octane	0.91	1.22
n-decane	1.13	1.36
n-dodecane	1.23	1.41
2,2,4-trimethylpentane	1.37	1.61
3,4,5-trimethylheptane	1.27	1.45
cyclohexane	0.57	0.88
methylcyclohexane	0.77	1.04
n-butylcyclohexane	0.92	1.04
benzene	−0.06	0.25
ethylbenzene	0.03	0.22
n-butylbenzene	0.06	0.20
tert-butylbenzene	0.20	0.33
carbon tetrachloride	0.02	0.31
chloroform	−0.94	−0.50
methylene chloride	−0.53	0.20
n-butyl chloride	−0.33	0.21
chlorobenzene	−0.18	−0.01
1-butanol	1.22	1.47
cyclohexanol	1.37	1.44
2-pentanone	−0.28	0.05
n-butyl acetate	−0.11	0.11

mixing are usually required in order to ensure solubilization of a polymer. In this work, $\Delta\bar{H}_1^\infty$ values ranging from −1 to +3 kcal/mol have been measured.

It is evident from Tables VI–VIII that the magnitude of $R\,\partial\chi/\partial(1/T)$ is always larger than $\Delta\bar{H}_1^\infty$ by 0.3–0.5 kcal/mol. This is due to the free energy characteristics of χ; i.e., its temperature dependence reflects the excess heat of mixing as well as entropic contribution due to the

Table IX
Specific Retention Volumes of Selected Solutes in Poly(butyl methacrylates) at 140 °C

solute	V_g°, cm³/g		
	PnBMA	PiBMA	PsBMA
n-octane	14.77	14.85	15.45
n-decane	44.39	46.88	44.94
2,2,4-trimethylpentane	8.59	8.14	7.98
3,4,5-trimethylheptane	38.84	38.38	34.40
cyclohexane	9.53	9.62	9.81
n-butylcyclohexane	69.20	68.49	69.35
benzene	14.95	14.03	15.84
n-butylbenzene	123.88	118.03	
tert-butylbenzene	89.08	82.43	
carbon tetrachloride	12.40	12.00	13.63
chloroform	14.64	13.79	15.80
methylene chloride	8.10	7.50	8.73
1-chlorobutane	11.21	10.96	
chlorobenzene	51.96	46.99	
1-butanol	20.91	19.19	

free volume dissimilarity between solute and polymer.

Homopolymers. In order to compare the PS and PnBMA data, the PS results have been extrapolated to 140 °C. In general, most probes display a higher miscibility with PnBMA than PS. Although the alkanes (linear and branched) display nonsolvent characteristics for both polymers, there is a marked decrease in $(a_1/w_1)^\infty$ and χ, as well as in the endothermicity of these probes with the polymethacrylate. This trend is in agreement with expectations of solubility parameter theory.

Both the aromatic and chlorinated probes are good solvents for PS and PnBMA. These probes also exhibit increased miscibility with PnBMA (i.e., lower values of $(a_1/w_1)^\infty$ and χ and more exothermic $\Delta\bar{H}_1^\infty$ values). This is most clearly seen in the case of $CHCl_3$, where χ values decrease from 0.31 in PS to −0.05 in PnBMA at 140 °C. This increased specificity is probably due to hydrogen bond formation between $CHCl_3$ and PnBMA.

Excess partial molar heats of mixing for butanol and cyclohexanol are approximately 1 and 2 kcal/mol lower (respectively) in PnBMA than in PS. This again reflects hydrogen bond formation between the alcohols and PnBMA. However, since these alcohols self-associate, they mix endothermically with both polymers and are thus poor solvents.

Several probes of varying molecular structure and polarity were employed in order to determine whether the structural differences among PnBMA, PiBMA, and PsBMA would be reflected in their melt solubilities. Table IX summarizes the measured specific retention volumes for these systems at 140 °C. Most of the probes in PiBMA and PsBMA were characterized by values of V_g° which agree to within 2 and 7% of those observed in PnBMA. In view of the reliability of the V_g° values (2–3%), the observed differences lie on the border of the experimental uncertainty. In addition, no significant or systematic trends emerge in either V_g° or the derived thermodynamic interaction parameters.

Copolymers. The thermodynamic interaction parameters for the various classes of probes in the S–BMA copolymers are self-consistent. The observed trends in miscibility for these probes are in qualitative agreement with their behavior in the corresponding homopolymers. Both solvent and nonsolvent probes exhibit interaction parameters which are sensitive to the styrene content of the copolymer. Activity coefficients and χ parameters generally decrease as the styrene content decreases (Table X (supplementary material) summarizes the χ values) and approach the value measured in the BMA polymer. This reflects the increased miscibility of these probes with the methacrylate units of the copolymer.

Table XI
Comparison of Specific Retention Volumes of Selected Solutes in Styrene-Butyl Methacrylate Polymers and Copolymers at 140 °C

solute	V_g°, cm³/g			
	P(S-iBMA)		P(S-nBMA)	
	measd	pred[a]	measd	pred[a]
n-octane	11.91	11.71	13.79	12.54
n-decane	35.52	34.76	41.21	37.05
2,2,4-trimethylpentane	5.75	5.89	7.29	6.70
3,4,5-trimethylheptane	28.62	28.20	34.41	31.19
cyclohexane	8.66	9.12	9.63	9.22
benzene	14.32	14.06	15.30	14.44
tert-butylbenzene	74.98	72.65	85.15	78.13
carbon tetrachloride	11.20	10.99	12.28	11.44
chloroform	11.34	10.65	13.48	11.87
methylene chloride	6.91	6.52	7.68	7.04
1-chlorobutane	9.61	9.40	10.75	9.93

[a] $V_{g(23)}^\circ = w_2 V_{g2}^\circ + w_3 V_{g3}^\circ$.

Comparison of Copolymer and Homopolymer Properties. A comparison of V_g° values for various probes in the styrene–isobutyl methacrylate copolymer (80 wt % styrene) and in the parent homopolymers indicates that the specific retention volumes can be predicted to within 2–5% by simple interpolation of homopolymer properties (Table XI).

However, this additivity is not observed in the case of the styrene–*n*-butyl methacrylate copolymer (58 wt % styrene). The measured retention volumes of both solvent and nonsolvent probes in this copolymer melt are consistently and significantly higher (6–20% at 140 °C) than predicted by a linear relationship between V_g° and copolymer composition (Table XI). These differences are only slightly lower at 180 °C.

Although the reason for this behavior is not clear, it is nevertheless interesting to speculate on the nature of the observed nonadditive effects of the S–BMA system. Significant deviations are observed for the copolymer containing a higher proportion of sequential S–BMA segments.[22] This suggests that nonadditive effects may arise from nearest-neighbor segment interactions in the copolymer melt. Further work is in process to determine the generality of these trends in other S–BMA copolymers and blends.

It is clear from the present discussion, however, that copolymer properties are not generally a simple function of homopolymer properties and that care should be exercised in "tailor-making" copolymers with specific miscibility characteristics based on a knowledge of homopolymer properties.

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Supplementary Material Available: ln V_g° (Figure 1) and χ (Figure 3) as functions of $1/T$ for several solutes in P(S–nBMA), thermodynamic interaction parameters for PS and several solutes at infinite dilution (Table II), $\Delta\bar{H}_1^\infty$ and $R\,\partial\chi/\partial(1/T)$ for various PS–solute systems between 170 and 190 °C (Table VI) and various PnBMA–solute systems between 120 and 150 °C (Table VII), and comparison of the Flory–Huggins χ parameter of selected solutes in PS and P(S–nBMA) at 140 °C (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Smidsrod, O.; Guillet, J. E. *Macromolecules* **1969**, *2*, 272.
(2) Guillet, J. E. In "New Developments in Gas Chromatography"; Purnell, H., Ed.; Wiley: New York, 1973.

(3) Braun, J. M.; Guillet, J. E. *Adv. Polym. Sci.* **1976**, *21*, 108.
(4) Gray, D. G. *Prog. Polym. Sci.* **1977**, *5*, 1.
(5) Galin, M.; Rupprecht, M. C. *Polymer* **1978**, *19*, 506.
(6) Littlewood, A. B.; Phillips, C. S. G.; Price, D. T. *J. Chem. Soc.* **1955**, 1480.
(7) Cruikshank, A. J. B.; Windsor, M. L.; Young, C. L. *Proc. R. Soc. London, Ser. A* **1966**, *295*, 259, 271.
(8) Patterson, D.; Tewari, Y. B.; Schreiber, H. P.; Guillet, J. E. *Macromolecules* **1971**, *4*, 356.
(9) McGlashan, M. L.; Potter, D. J. B. *Proc. R. Soc. London, Ser. A* **1962**, *267*, 478.
(10) Guggenheim, E. A.; Wormald, C. J. *J. Chem. Phys.* **1965**, *42*, 3775.
(11) Dreisbach, D. R. *Adv. Chem. Ser.* **1955**, *No. 15*. *Ibid.* **1959**, *No. 22*. *Ibid.* **1961**, *No. 29*.
(12) Orwoll, R. A.; Flory, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 6814.
(13) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950; Vol. 1. *Ibid.*, 1965, Vol. 2.
(14) "International Critical Tables"; McGraw-Hill: New York, 1928; Vol. 3.
(15) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660.
(16) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440.
(17) Hocker, H.; Blake, G. J.; Flory, P. J. *Trans. Faraday Soc.* **1971**, *67*, 2251.
(18) Olabisi, O.; Simha, R. *Macromolecules* **1975**, *8*, 206.
(19) Simha, R.; Boyer, R. F. *J. Chem. Phys.* **1962**, *37*, 1003.
(20) DiPaola-Baranyi, G.; Guillet, J. E. *Macromolecules* **1978**, *11*, 228.
(21) Newman, R. D.; Prausnitz, J. M. *J. Paint Technol.* **1973**, *45*, 33.
(22) Private communication with Dr. L. Alexandru.

Photochemical Behavior of Poly(organophosphazenes). 3. Role of the Charge-Transfer Process in the Photolysis of Poly[bis(*p*-tolylamino)phosphazene] in Halogenated Solvents

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ABSTRACT: The photochemical behavior of poly[bis(*p*-tolylamino)phosphazene] in halogenated solvents is the result of two concurrent processes: the homolytic scission of side-chain *p*-tolylamino moieties and the charge-transfer reaction from these groups to the solvent in which the polymer is dissolved. Moreover, three parameters determine the reaction path of the excited polymer in solution: the concentration of molecular oxygen, the presence of species which may supply hydrogen atoms, and the electron affinity of the solvent in which the photolysis is carried out. The relative importance of these parameters to the overall photochemical behavior of poly[bis(*p*-tolylamino)phosphazene] in solution has been evaluated.

Introduction

Since the pioneering work of Allcock on the preparation of poly(organophosphazenes),[1] interest in these polymers with a phosphorus–nitrogen backbone has markedly grown. Due to the fact that poly(organophosphazenes) are prepared by nucleophilic substitution of the chlorines of poly(dichlorophosphazene), a wide variety of substituents can be inserted in the inorganic backbone, and polymers with variable chemical and physical properties are obtainable. Since some of these polymers have high resistance to flammability,[2] commercial application of these materials as fire-resistant coatings and flame-retardant additives is currently being considered.[3] Recently, other research areas, such as biomedical applications,[4] have begun to be explored, so increasing scientific interest in these polymers.

To date, most of the experimental work in the field of poly(organophosphazenes) has been done on the synthesis, characterization, and thermal properties of these polymers. Moreover, several studies on the thermal degradation of poly[(aryloxy)phosphazenes] have been reported[5–8] and their photochemical stability has begun to be explored.[9]

In our laboratory, the activity on poly(organophosphazenes) is mainly focused on the behavior of these polymers in solution under γ and UV irradiation. Irradiation with γ rays of air-saturated solutions of poly[bis(arylamino)phosphazenes] in various solvents leads to degradation of the polymers, induced mainly by the free radicals formed by the action of the γ rays on the solvent.[10] The photochemical behavior of poly[bis(*p*-tolylamino)phosphazene] and poly[bis(β-naphthoxy)phosphazene], as examples of arylamino- and aryloxy-substituted poly(organophosphazenes), has been investigated in previous papers of this series.[11,12] It could be demonstrated that, for both polymers, the primary photochemical act is the homolytic cleavage of the bond between the phosphorus atom of the inorganic backbone and the arylamino or aryloxy substituent. In the absence of oxygen, interchain linkage of the macroradicals formed is the dominant process: this leads to an increase of molecular weight and to gel formation. In air-saturated solutions, a peroxidic intermediate on the phosphorus atom can be formed and the breaking of the O–OH bond induces chain scission of the polymer and a decrease in molecular weight.

In a recent communication,[13] we presented some preliminary results concerning the influence of the solvent on the photochemistry of arylamino-substituted polyphosphazenes. The results were that the electron affinity of the solvent plays an important role in the photoreactivity of poly[bis(arylamino)phosphazenes] and, in this paper, we give a more detailed account of our investigation.

Experimental Section

Poly[bis(*p*-tolylamino)phosphazene] (PTAP) was prepared according to a known procedure[14] and was purified by repeated dissolution in THF and precipitation with CH_3OH. The elemental analysis data of the polymer are as follows (calculated values in

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