Macromolecules 1984, *17*, 619–625

Thermodynamic Studies on Polystyrene–Solvent Systems by Gas Chromatography†

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ABSTRACT: Partial molar sorption as well as mixing functions were derived from gas chromatography for linear and branched alkanes, cyclohexane, isomeric octenes, and alkylbenzenes up to hexylbenzene in molten atactic polystyrene within the temperature range 403–463 K. Both types of functions are discussed with respect to (i) the chain length, (ii) the group contributions of methyl, methylene, and phenyl to the solute–PS sites of interaction, and (iii) the influence of branching in the solute molecules. The pronounced nonsolvent character of linear and branched alkanes is governed by large negative entropies of mixing in parallel to small endothermic enthalpies. The good solvents in the alkylbenzene series—benzene, toluene, and ethylbenzene—exhibit negative heats of mixing, which turn into positive heats of mixing with increasing length of alkyl chain. Flory's equation of state theory enables a consistent interpretation of the data: The segment interaction parameter, χ^*, and the corresponding enthalpy term, χ_H^*, are consistent with the related mixing functions, while χ and χ_H are not. The contact interaction parameters, X_{12}, are discussed for the n-alkanes as well as for the exothermically interacting alkylbenzenes.

Introduction

Gas chromatography (GC) is an effective alternative to static methods for studies of solute–solvent interactions.[1] Soon after its first application to polymer research,[2] the method was used extensively for thermodynamic studies above the glass transition temperature, T_g, of polymers.[3,4]

It is now well established that weight fraction activity coefficients[5] and heats of dilution may be derived accurately for polymer–solute systems above T_g.[6–8] These thermodynamic functions are determined by interactions between the solvent molecule and short sequences within the polymeric chain.[9] Consequently, the structure of both solvent and solute influence the thermodynamic sorption and mixing functions.

Over the past decade, gas chromatography has expanded the range of thermodynamic studies on polystyrene (PS) solutions to maximum polymer concentrations and high temperatures. In a series of notable papers[10–14] activity coefficients, heats of solution and χ and χ_H values have been reported for molten PS–solute systems. Randomly selected solutes, however, have been used in many of these studies, for example, nonpolar hydrocarbons, ketones, alcohols, esters, and alkyl halides.

In the present work the results of GC investigations of PS–solute interactions are given for a number of systematically selected solutes without polar groups: linear and branched alkanes, alkenes, cyclohexane, and linear alkylbenzenes. The aim of these investigations is to demonstrate the enthalpic and entropic consequences of changes in the nature and structure of the solute molecule. This work represents an extension of light scattering and swelling investigations of related systems.[15–17]

Experimental Part

Materials. Low-polydispersity atactic polystyrene (PS, M_w = 53 700, M_w/M_n = 1.06) was a Pressure Chemical Co. product. Reagent grade solutes, linear and branched alkanes (C_6–C_9), alkenes (C_8), and alkylbenzenes (Ph-H to Ph-C_6H_{13}), were used without further purification (Fluka and Roth).

Column Preparations. The polymer was deposited onto Chromosorb A (Supelco, mesh size 45/60, specific surface 2.7 m^2 g^{-1}) from toluene solution by continuous stirring over 48 h and then slow evaporation of the solvent at 65 °C under dry nitrogen. The coated support was dried in a vaccuum oven at 130 °C for 72 h and then resieved, packed in a stainless steel column (i.d. 2 mm, length 1.2 m), and conditioned (at least 48 h at 160 °C). During the measurements the column weight remained constant within the limits ±0.3 mg. The column loading was determined by calcination, using the required blank correction. The amount of polystyrene was found to be 0.1194 ± 0.0002 g (5.78% by weight).

Instrumentation. Measurements were carried out on a Perkin-Elmer Sigma 3 dual-column gas chromatograph, equipped with a thermal conductivity detector. Column temperature was controlled within 0.1 °C. Solutes were introduced by manual injection or with a heated sampling valve. The pressures at the inlet and outlet of the column were measured by a high-performance piezoelectric pressure gauge (Wika, FRG). Dry, prepurified nitrogen was used as the carrier gas.

A large range of carrier gas flow rates (3–50 mL min^{-1}) was measured within an error limit of ±0.1% using three calibrated soap film flowmeters. The chart speed of the recorder was calibrated.

Measurement Procedure. GC measurements were started after thermal and flow equilibrium in the column were stabilized (2–3 h). To facilitate rapid vaporization of the liquid solute sample (0.01 μL) the injector temperature was kept 30 °C above the boiling point of the solute. The carrier gas flow rate was controlled before and after sample injection. Measurements were made at five different carrier gas flow rates and inlet pressures for each solute. Retention volumes for six runs for each solute and twenty runs for the marker (H_2) at a given flow rate were averaged. The values obtained were extrapolated to zero flow rate in order to eliminate the pressure (or flow rate) dependence of the retention data.[1,13]

The net retention time (t_R) is defined as the time difference between the first statistical moment of the solute peak and that of the marker gas.[18] Thus t_R was calculated by statistical peak analysis rather than from the retention time at the peak maximum ($t_{R,max}$). This eliminates inaccuracies arising from slight peak asymmetry, which occurs even for inert and well-coated supports.[19,20] The specific retention volumes ($V_g°$) derived from t_R and $t_{R,max}$ can differ up to 2–5% for small retention times and slightly skewed peaks.

Data Treatment. Specific retention volumes ($V_g°$) were calculated from the expression[21]

$$V_g° = t_R(F/w_2)(3/2)[(p_i/p_o)^2 - 1][(p_i/p_o)^3 - 1]^{-1}(1 - p_{H_2O}/p_a) \quad (1)$$

where t_R is the net retention time, w_2 is the mass of the polymer in the column, F is the carrier gas flow rate at 273 K and atmospheric pressure (p_a), p_i and p_o are the inlet and outlet pressures, and p_{H_2O} is the water vapor pressure at room temperature.

The partial molar free energy of sorption ($\Delta\bar{G}_1^s$) was derived from the relation[22,23]

$$\Delta\bar{G}_1^s = -RT \ln (M_1 V_g°/273R) \quad (2)$$

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† Dedicated to Professor W. H. Stockmayer with the best regards and wishes on his 70th birthday.

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where M_1 is the molar mass of the solute and R is the universal gas constant (1 atm K^{-1} mol^{-1}). Consequently, the partial molar heat of solution ($\Delta\bar{H}_1{}^s$) is given by

$$\Delta\bar{H}_1{}^s = -R\ \partial \ln V_g{}^\circ / \partial(1/T) \tag{3}$$

The weight fraction activity coefficient of the solute probe at "infinite dilution", $\Omega_1{}^\infty$, was calculated from the expression[5]

$$\Omega_1{}^\infty = (273R/V_g{}^\circ p_1{}^\circ M_1) \exp[-p_1{}^\circ(B_{11} - v_1)/RT] \tag{4}$$

where v_1 represents the solute molar volume,[6] $p_1{}^\circ$ is the saturated vapor pressure, and B_{11} is the second virial coefficient of the solute probe. The partial molar heat of mixing at "infinite dilution" of the solute follows from

$$\Delta\bar{H}_1{}^\infty = R\ \partial \ln \Omega_1{}^\infty / \partial(1/T) \tag{5}$$

For high molecular weight the link between $\Omega_1{}^\infty$ and the reduced free energy parameter χ is given for unit volume fraction of the polymer by

$$\chi = \ln \Omega_1{}^\infty - 1 + \ln (v_2{}^{sp}/v_1{}^{sp}) \tag{6}$$

v^{sp} is the specific volume of the solute (1) and the polymer (2), respectively. Separation of χ into an enthalpy (χ_H) and an entropy (χ_S) term leads from

$$\chi_H = -T(\partial\chi/\partial T) \tag{7}$$

to the relations

$$\Delta\bar{H}_1{}^\infty = -RT^2[(\partial\chi/\partial T) + T(\alpha_1 - \alpha_2)] \tag{8}$$

and

$$\chi_H = \frac{\Delta\bar{H}_1{}^\infty}{RT} + T^2(\alpha_1 - \alpha_2) = T^2(\alpha_1 - \alpha_2) - \frac{\partial \ln \Omega_1{}^\infty}{\partial \ln T} \tag{9}$$

where α is the thermal expansion coefficient of the component indicated by the subscript. This is usually defined by

$$\alpha = (v^{sp})^{-1}(\partial v^{sp}/\partial T)_p \tag{10}$$

Replacing volume fractions by segment fractions and the specific volumes (v^{sp}) by the characteristic specific volumes (v^*), the interaction parameter based on segment fractions, χ^*, according to Flory's equation of state theory[24,25] is related to $\Omega_1{}^\infty$ through an equation similar to eq 6:

$$\chi^* = \ln \Omega_1{}^\infty - 1 + \ln (v_2{}^*/v_1{}^*) \tag{11}$$

The interaction parameter, χ^*, is connected to that denoting the energy change for the formation of contacts between unlike species, X_{12}.[24] In the GC region the corresponding equation becomes

$$X_{12} = RT(\tilde{v}_2/v_1{}^*)\chi^* - P_1{}^*\tilde{v}_2\{3\tilde{T}_1 \ln [(\tilde{v}_1{}^{1/3} - 1)/(\tilde{v}_2{}^{1/3} - 1)] + \tilde{v}_1{}^{-1} - \tilde{v}_2{}^{-1}\} \tag{12}$$

where $\tilde{v}$ and $\tilde{T}$ are reduced equation of state parameters and $P_1{}^*$ is the characteristic pressure of the solute.

The equation of state parameters are defined by[24]

$$\tilde{v} = v/v^* = \{(4\alpha T + 3)/(3\alpha T + 3)\}^3 \tag{13}$$

$$\tilde{T} = T/T^* = v^{-4/3}(v^{1/3} - 1) \tag{14}$$

$$P^* = (\alpha/\beta)T\tilde{v}^2 \tag{15}$$

where α is the thermal expansion coefficient and β the isothermal compressibility.

Solute densities were taken from various sources.[26-28] The density of polystyrene at elevated temperatures was obtained from the work of Höcker.[29] The thermal expansion coefficient and v and T were calculated from the density data. Compressibility data were taken from the literature.[26,30,31]

Solute vapor pressures were computed from standard sources.[26,27] Values of B_{11} were estimated from the corresponding equation of state.[32] It was found that the critical parameters T_c and V_c of the alkylbenzenes vary with the carbon number of the alkyl chain.

$$V_c\ (\text{cm}^3) = 252.35 + 68.89n - 2.113n^2 \tag{16}$$

$$T_c\ (\text{K}) = 562.59 + 29.79n - 1.366n^2 \tag{17}$$

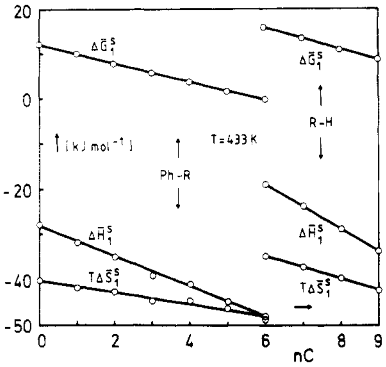

Figure 1. $\Delta\bar{G}_1{}^s$, $\Delta\bar{H}_1{}^s$, and $T\Delta\bar{S}_1{}^s$ vs. carbon number of *n*-alkanes and alkylbenzenes at 433 K.

The B_{11} values of alkylbenzenes are functions of the carbon number and the temperature.

$$\ln (-B_{11}) = a + bn + cn^2 \tag{18}$$

Within the temperature range 373–473 K the coefficients of eq 18 are functions of the absolute temperature:

$$a = 10.2625 - 1.2544 \times 10^{-2}T + 8.28 \times 10^{-6}T^2 \tag{19}$$

$$b = 9.9993 - 2.1271 \times 10^{-3}T + 1.842 \times 10^{-6}T^2 \tag{20}$$

$$c = -5.262 \times 10^{-2} + 1.567 \times 10^{-4}T - 1.656 \times 10^{-7}T^2 \tag{21}$$

Results and Discussion

A. Specific Retention Volumes. Specific retention volumes of selected hydrocarbons in atactic polystyrene (PS) from 403 to 463 K were measured at 10 °C intervals. To ensure thermodynamic equilibrium for the polymer melt, measurements were carried out 40–50 °C above the T_g of polystyrene. The $V_g{}^\circ$ obtained (extrapolated to zero flow rate) are summarized for alkanes and alkylbenzenes (Tables I and II; Supplementary Material).

In all investigated systems, $V_g{}^\circ$ decreases with increasing temperature as expected for an exothermic sorption process. The $V_g{}^\circ$ derived for PS–benzene, –toluene, –ethylbenzene, and –cyclohexane are slightly higher than those reported by Galin and Rupprecht,[13] Newman and Prausnitz,[10] and Lipatov and Nesterov[12] but considerably lower than those published by Covitz and King.[11] The data obtained are in good agreement with those derived by DiPaola-Baranyi and Guillet.[14] The published values for $V_g{}^\circ$ scatter probably because of nonstandardized determinations.

B. Thermodynamic Sorption Functions. The sorption process involves the transfer of a solute molecule from the vapor phase into a highly diluted solution, with the polymer as the solvent. The enthalpy change of this process is dependent on the solute–polymer interactions and the energy due to the formation of cavities in the polymeric solvent which accommodate the solute molecules. Consequently, the sorption functions $\Delta\bar{G}_1{}^s$, $\Delta\bar{H}_1{}^s$, and $T\Delta\bar{S}_1{}^s$ allow meaningful comparisons of solutes in a given polymeric solvent. A linear relationship between the carbon number of the alkanes and of the alkyl chain of alkylbenzenes and the sorption functions $\Delta\bar{G}_1{}^s$, $\Delta\bar{H}_1{}^s$, and $T\Delta\bar{S}_1{}^s$ has been established (see Figure 1). The slope of these linear functions may be understood as the contribution to $\Delta\bar{G}_1{}^s$, $\Delta\bar{H}_1{}^s$, and $T\Delta\bar{S}_1{}^s$, of the dispersive interactions between CH_2 groups and the PS sites.

Upon closer examination the CH_2 groups contribute comparably to the partial molar heat of sorption $\Delta\bar{H}_1{}^s$ for linear alkanes (4.1 ± 0.5 kJ mol^{-1}) and for the alkylbenzenes (3.4 ± 0.5 kJ mol^{-1}). The minor difference between the CH_2 sorption enthalpies of the two solute groups is compensated for by the corresponding sorption entropies

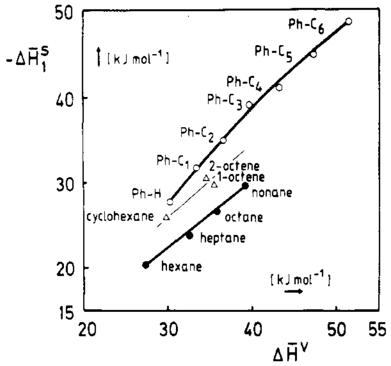

Figure 2. $\Delta\bar{H}_1^{s}$ vs. the heat of vaporization of the solutes.

$T\Delta\bar{S}_1^{s}$ of the CH_2 groups (alkanes, −1.8 kJ mol^{-1}; alkylbenzenes, −0.7 kJ mol^{-1}). Therefore the contribution of the CH_2 groups to the partial molar free enthalpy $\Delta\bar{G}_1^{s}$ is the same for both solute series:

$$\Delta\bar{G}_1^{s}(CH_2) = 2.2 \pm 0.5 \text{ kJ mol}^{-1}$$

The enthalpic contribution of the phenyl groups was evaluated from the intercept differences of the corresponding linear functions of both solute series (−28 kJ mol^{-1}).

The sorption process of alkylbenzenes in molten PS is therefore governed by interactions between the phenyl groups of both components.

From a comparison of the $\Delta\bar{H}_1^{s}$ values of octane and the isomeric octenes, the contribution of the interaction between a double bond and the PS segments to the sorption process may be estimated:

$$\Delta\bar{H}_1^{s}(C{=}C) = \Delta\bar{H}_1^{s}(\text{octene}) - \{\Delta\bar{H}_1^{s}(\text{octane}) - 2\Delta\bar{H}_1^{s}(CH_2)\}$$

The average contribution of the double bond to $\Delta\bar{H}_1^{s}$ is two times greater than of a methylene group. The more exothermic value of 2-octene (*cis*) (−30.4 kJ mol^{-1}) compared with that of 1-octene (−29.6 kJ mol^{-1}) may be caused by the inductive effect +I of the terminal methyl group.

From the values of the thermodynamic sorption functions it is obvious that the pronounced negative entropy values are responsible in all cases for the endothermic $\Delta\bar{G}_1^{s}$ of both solute series. The $\Delta\bar{H}_1^{s}$ values, however, lower the $\Delta\bar{G}_1^{s}$ with the chain length of the solute molecule.

During sorption, the alkane molecules effect favorable but weak dispersive contacts with the PS backbone, whereas the alkylbenzenes can interact also with the saturated backbone and, dominantly, with the phenyl rings. This difference due to the specific interactions of the phenyl group with the PS sites can be derived, for example, from a plot of $\Delta\bar{H}_1^{s}$ vs. the heat of vaporization of the solutes, ΔH_1^{v}.

Comparing the $\Delta\bar{H}_1^{s}$ values for the solutes with the identical heat of vaporization (that is, with similar interaction energies for solute–solute contacts), it becomes evident that the phenyl group of the alkylbenzenes contributes significantly to the interactions with the PS sites. As can be seen from Figure 2 the unlike contacts between solute molecules and PS segments are more exothermic for the alkylbenzenes than for the alkanes at constant ΔH^{v}. For members higher than butylbenzene, however, the relationship of $\Delta\bar{H}_1^{s}$ vs. ΔH^{v} indicates a trend to the alkane-like dispersive-type behavior. The intermediate character of the octenes and cyclohexane is once more evident from this representation.

The electron perturbations of the solute molecule during collisions with the solvent sites, represented by the molar polarization (P), can also be related to $\Delta\bar{H}_1^{s}$.[22] Including dipole moment contributions[26] to P, the plot of $\Delta\bar{H}_1^{s}$ vs. P (see Figure 3) shows a linear dependence for each solute series. The vertical difference of the two graphs illustrates the contribution of dipole and induced-dipole interaction forces to the unlike contact formation between alkylbenzenes and PS sites.

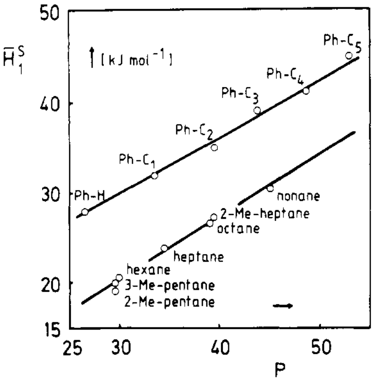

Figure 3. Heats of solution as a function of the molar polarization. Solutes are indicated.

Table III
Partial Molar Heats $\Delta\bar{H}_1^{s}$ (kJ mol^{-1}) and Entropies $T\Delta\bar{S}_1^{s}$ (kJ mol^{-1}) of Sorption at 433 K for Selected Hydrocarbons

solute	$\Delta\bar{H}_1^{s}$	$-T\Delta\bar{S}_1^{s}$
n-hexane	−20.2	36.0
2-methylpentane	−18.5	39.1
3-methylpentane	−19.2	38.9
cyclohexane	−25.6	38.8
n-octane	−28.1	38.9
2-methylheptane	−27.1	38.6
2,2,4-trimethylpentane	−24.3	37.3
1-octene	−29.6	40.5
2-octene (*cis*)	−30.4	40.5

The structure of the dispersive interacting solute molecules undoubtedly has an influence on sorption. Branching the hydrocarbon backbone of alkanes causes more endothermic $\Delta\bar{G}_1^{s}$ and $\Delta\bar{H}_1^{s}$ (see Table III). The effect is more pronounced if (i) a smaller molecule is branched ($C_6 > C_8$), (ii) the branching is near the chain end (2-methylpentane > 3-methylpentane), and (iii) the number of side methyl groups increases (2,2,4-trimethylpentane > 2-methylpentane). This effect may be explained by assuming that a methyl group contribution to the $\Delta\bar{H}_1^{s}$ is less exothermic than that of a methylene group. Sterically unfavorable arrangements for the branched solute–PS site contacts cannot be excluded. Furthermore, the $\Delta\bar{G}_1^{s}$ and $\Delta\bar{H}_1^{s}$ values obtained for cyclohexane are more exothermic than those of *n*-hexane or *n*-heptane (see Figure 2).

C. Weight Fraction Activity Coefficients and Partial Molar Free Energies of Mixing. Quantitative thermodynamic analysis of the polymer–solute miscibility was made and the weight fraction activity coefficients were computed according to eq 4. Calculation of Ω_1^{∞} requires knowledge of neither the molecular weight of the polymer nor its polydispersity. The activity coefficient, however, is not independent of these factors. While keeping the molecular weight of the polymer and the column loading constant, we studied the solute–PS miscibilities. The results are presented in Tables IV and V for both solute series.

Even for carefully obtained retention data the activity coefficients vary at high temperatures as a consequence of (i) the small retention times of low-boiling solutes, (ii)

Table IV
Weight Fraction Activity Coefficients, Ω_1^∞, of Alkanes in Molten Atactic PS at Several Temperatures

	T, K						
solute	403	418	423	433	443	448	463
n-hexane	12.38	11.61	11.36	11.00	10.46	10.33	9.83
n-heptane	11.53	10.91	10.76	10.26	9.84	9.80	9.43
n-octane	10.38	9.80	9.54	9.34	9.04	8.99	8.73
n-nonane	9.94	9.58	9.50	9.32	8.94	8.89	8.61
cyclohexane	7.33	7.03	6.95	6.85	6.95	6.98	6.95
2-methylpentane	15.36	13.03	13.71	12.95	12.96	13.40	12.31
3-methylpentane	13.51	12.98	12.70	12.29	11.91	11.42	11.46
2-methylheptane	10.99	10.09	10.13	9.72	9.54	9.54	9.03
2,2,4-trimethylpentane	11.71	10.92	10.95	10.52	10.41	10.29	9.95
1-octene	9.44	8.81	8.72	8.89	8.45	8.39	8.21
2-octene (*cis*)	8.28	8.03	7.96	7.98	7.69	7.95	7.63

Table V
Weight Fraction Activity Coefficients, Ω_1^∞, of the Alkylbenzenes in Molten Atactic PS at Several Temperatures

	T, K					
solute	413	423	433	443	453	463
benzene	4.82	4.85	4.84	4.86	4.90	4.91
toluene	4.87	4.90	4.93	4.96	4.99	4.98
ethylbenzene	5.01	5.01	5.02	5.04	5.04	5.06
propylbenzene	5.15	5.13	5.13	5.15	5.15	5.15
butylbenzene	5.30	5.28	5.25	5.24	5.23	5.16
pentylbenzene	5.50	5.48	5.41	5.35	5.33	5.30
hexylbenzene	5.83	5.74	5.69	5.67	5.56	5.50

Table VI
Partial Molar Free Energies and Heats and Entropies of Mixing (kJ mol^{-1}) at Infinite Dilution of Alkanes in Molten Atactic PS at 433 K

solute	$\Delta\bar{G}_1^\infty$	$\Delta\bar{H}_1^\infty$	$T\Delta\bar{S}_1^\infty$
n-hexane	8.63	6.01	−2.62
n-heptane	8.38	5.42	−2.96
n-octane	8.04	4.49	−3.55
n-nonane	8.00	3.80	−4.20
cyclohexane	6.92	1.13	−5.79
2-methylpentane	9.22	4.37	−4.85
3-methylpentane	9.03	4.84	−4.19
2-methylheptane	8.22	4.66	−3.56
2,2,4-trimethylpentane	8.51	4.00	−4.51
1-octene	7.78	3.34	−4.44
2-octene (*cis*)	7.45	1.86	−5.58

Table VII
Temperature Dependence of the Weight Fraction Activity Coefficients Reported for Alkylbenzenes

solute	d ln Ω_1^∞/d(1/*T*)	ref
benzene	>0	11, 12, 34
	<0	10, 13, 14, 35
toluene	>0	11, 12, 34
	<0	10, 13, 14
ethylbenzene	>0	11
	<0	10, 13, 35

the relative uncertainity of p_1°, and v^{sp} at elevated temperatures, and (iii) the extremely temperature-sensitive correction term for the nonideal behavior of the solute vapor.

The activity coefficient Ω_1^∞ and the related thermodynamic mixing functions prove to be more sensitive to changes in the structure of the solute molecules than the sorption functions. Large Ω_1^∞ values of the alkanes illustrate typical nonsolvent characteristics (see Table IV). The regularities concerning the influence of chain and branching of the alkanes, as discussed for the sorption process, are once more observed. In addition, information about the more complex solute–polymer mixing can be obtained.

The alkylbenzenes (see Table V) show markedly low activity coefficients, a general indication of solute–polymer miscibility. The slightly increasing Ω_1^∞ values with the alkyl chain length indicate that the dispersive-type interactions of CH_2 groups contribute to a decline of the miscibility with PS. Thus alkylbenzenes offer a possibility for tailoring desired Ω_1^∞ values in the range between those of benzene and a polymethylenic compound. From the definition of the partial molar free energy of mixing

$$\Delta\bar{G}_1^\infty = RT \ln \Omega_1^\infty$$

it becomes evident that the observations mentioned above are also valid for $\Delta\bar{G}_1^\infty$.

D. Partial Molar Heat and Entropy of Mixing. Due to the scattered Ω_1^∞ values (especially for the alkanes) the average partial molar enthalpy of mixing, $\Delta\bar{H}_1^\infty$, was calculated by linear regression over the entire temperature range (see Figures 4–6; Supplementary Material).

The endothermic $\Delta\bar{H}_1^\infty$ for the alkanes decreases with increasing carbon number of the solute (see Table VI). The larger negative $T\Delta\bar{S}_1^\infty$ values of the higher *n*-alkanes, however, counter this effect and accentuate the demixing tendency. Surprisingly, the branched alkanes have smaller endothermic $\Delta\bar{H}_1^\infty$ values than the linear ones. Once again, the differences between the linear and branched alkanes depend on the position and number of methyl side groups as well as on the chain length. From Table VI it becomes obvious that the larger partial molar entropies of mixing of the branched solutes are responsible for the more endothermic ΔG_1^∞, as discussed in the previous section.

Cyclohexane contrasts with the alkanes by having a small endothermic $\Delta\bar{H}_1^\infty$ value (1.1 kJ mol^{-1}) and a large negative entropy term $T\Delta\bar{S}_1^\infty$ (−5.8 kJ mol^{-1}). This indicates that the cyclohexane–PS system tends toward a LCST. Significantly, near the critical temperature, the compressibility of the mixture rises quickly. According to Sanchez[33] this causes an unfavorable contribution to an entropic equation of state term, which finally determines the LCST. Plausibly, the differences between the entropies of mixing of the branched alkanes (lower T_c) and linear ones (higher T_c) are due to corresponding effects. A similar explanation may be advanced for cyclohexane. Its ring conformation may be relevant in this connection. Investigations at higher temperatures may furnish supplementary information.

For alkylbenzene–PS systems, it must be noted that in the past only benzene, toluene, and ethylbenzene have been used in GC investigations using PS as the stationary phase. Consequently, a substantial disagreement concerning the temperature dependence of the Ω_1^∞ values and of $\Delta\bar{H}_1^\infty$ is found in the literature on alkylbenzenes (see

Table VIII
Reduced Free Energy and Enthalpy Parameters for the Solute-PS Systems at 433 K

solute	χ	χ^*	χ_H eq 7	χ_H eq 9	χ_H^*	X_{12}
n-hexane	0.726	1.043	2.69	2.68	1.59	17.9
n-heptane	0.787	1.005	2.04	2.21	1.29	16.7
n-octane	0.693	0.911	1.78	1.79	1.13	14.0
n-nonane	0.740	0.906	1.47	1.42	1.09	13.7
cyclohexane	0.474	0.715	0.93	0.94	0.35	9.8
2-methylpentane	0.875	1.181	2.15	2.24	1.23	
3-methylpentane	0.852	1.145	1.99	2.22	1.36	
2-methylheptane	0.733	0.939	1.79	1.79	1.25	
2,2,4-trimethylpentane	0.794	1.019	1.72	1.68	1.13	
1-octene	0.671	0.871	1.41	1.40	0.92	
2-octene	0.559	0.766	1.00	0.99	0.43	
benzene	0.258	0.468	0.41	0.38	−0.16	4.0
toluene	0.286	0.472	0.10	0.10	−0.30	5.2
ethylbenzene	0.320	0.475	0.21	0.21	−0.12	5.5
propylbenzene	0.345	0.483	0.26	0.28	−0.02	
butylbenzene	0.385	0.496	0.41	0.40	0.25	
pentylbenzene	0.408	0.519	0.57	0.57	0.36	
hexylbenzene	0.462	0.563	0.71	0.69	0.53	

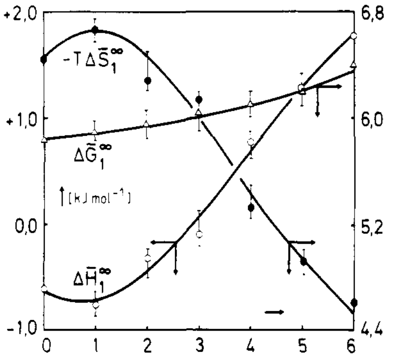

Figure 7. Partial molar free energy and heat and entropy of mixing of alkylbenzenes vs. the carbon number of the alkyl chain.

Table VII). We extended these investigations to hexylbenzene. The activity coefficients (Table V) demonstrate clearly that the interaction of PS with benzene, toluene, and ethylbenzene is characterized by exothermic partial molar heats of mixing (see Figure 7). Propylbenzene behaves nearly athermically in this temperature range and the higher alkylbenzenes steadily approach the partial molar heats of mixing of the alkanes.

Toluene exhibits the most exothermic heat of mixing. This effect might be caused by increased electron density of the aromatic nucleus due to the methyl group of toluene compared with benzene. It is worthwhile to note that the favorable enthalpy situation for toluene does not contribute substantially to an improvement of the mixing process with PS as a consequence of the larger negative $T\Delta\bar{S}_1^\infty$. Finally, benzene has the lowest $\Delta\bar{G}_1^\infty$ of all alkylbenzenes.

The mixing entropy contribution of the higher alkylbenzenes becomes less negative with increasing alkyl chain length. From Figure 7 it is evident that solute as well as polymer structure generates entropy effects which determine the final outcome of the process.

E. Interaction Parameter. In order to discuss the reduced residual free energy of mixing it has to be decided whether the interaction parameter χ or χ^* is consistent with the $\Delta\bar{G}_1^\infty$ values. In this connection we made some observations concerning the common χ and the equation of state interaction parameter χ^* (see Tables IX and X; Supplementary Material).

First, all χ values are substantially smaller than the corresponding χ^* ones. This is due to the fact that the ratio of the specific volumes v_2^{sp}/v_1^{sp} is in all cases smaller than that of the characteristic volumes v_2^*/v_1^*.

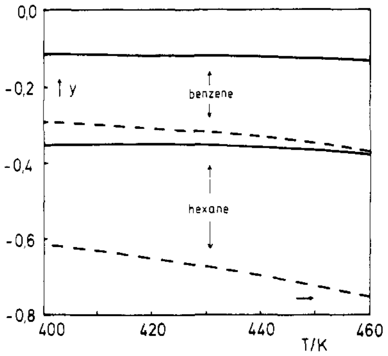

Figure 8. Temperature dependence of the logarithmic term (Y) for *n*-hexane and benzene: dashed line, $Y = \ln (v_2^{sp}/v_1^{sp})$; solid line, $Y = \ln (v_2^*/v_1^*)$.

Second, the order of sucession of the χ's in a homologous series, i.e., the alkanes, can be altered as a consequence of the magnitude of the solute specific volume (v_1^{sp}). Table VIII shows that hexane and octane establish lower χ values than their neighboring heptane and nonane, respectively. Another example of such irregularities is cyclohexane, which exhibits approximately the same χ as hexylbenzene. At elevated temperatures the low-boiling solutes have higher specific volumes. Thus, the observed inversions of the χ values in the alkane series are caused by the value of $\ln (v_2^{sp}/v_1^{sp})$, which contributes to χ following eq 6. They do not reflect any unexpected changes of interactions between solute and polymer sites. In contrast, χ^* shows a similar trend like the weight fraction activity coefficient or the free enthalpy function.

Third, the term $\ln (v_2^{sp}/v_1^{sp})$ in eq 6 alters significantly with temperature, whereas the equation of state term $\ln (v_2^*/v_1^*)$ is temperature insensitive over a wider range (see Figure 8). This has consequences on the temperature dependence of χ and χ^*. In order to derive the enthalpy parameter χ_H the temperature dependence of $\ln (v_2^{sp}/v_1^{sp})$ has to be considered in addition to that of $\ln \Omega_1^\infty$. As expected, the χ_H calculated according to eq 7 and 9 agree well (see Table VIII, columns 4 and 5). The test for the consistency of the derived χ_H is obtained from the alkylbenzenes. The generally positive χ_H values in this series contrast to the partial molar heats of mixing presented in the previous section (Table VI). Our χ_H of ethylbenzene (0.21) agrees with that reported by Höcker and Flory[36] at

25 °C for the same system. χ and χ_H are not able to describe the thermodynamic behavior of the systems in the studied temperature and concentration range. The reduced residual free energy parameter χ^* and the corresponding enthalpy term χ_H^* are more consistent with the observed effects. The $\Delta\bar{H}_1^\infty$, derived from χ_H^* and Ω_1^∞, agree within experimental error. No inconsistencies occur comparing χ^* with $\Delta\bar{G}_1^\infty$. Thus, the argumentation drawn for these thermodynamic functions can be transduced to χ^* and χ_H^*.

The discussion can be extended for some solutes to the contact interaction parameter X_{12} according to Flory's equation of state theory.[24] Unfortunately, the calculations are restricted to few solutes because only poor data are available about the isothermal compressibility or the compressibility coefficients. Risky extrapolations of these values to high temperatures must be accepted in some cases. The equation of state parameters used for our calculations of X_{12}, $\tilde{v}_1$, $\tilde{v}_2$, $\tilde{T}_1$, V_1^*, and P_1^* will be published in the near future.[37]

The last column of Table VIII contains the calculated contact interaction parameters X_{12} at 433 K. The differences between alkanes and cyclohexane on the one hand and cyclohexane and alkylbenzenes on the other are more accentuated than for the χ^* values. The trend toward more favorable exothermic contact energies of the alkylbenzenes becomes evident.

Considering the temperature dependence of X_{12} (see Table X; Supplementary Material) an attempt was made to extrapolate the values toward low temperatures. The data obtained at 298 K for X_{12} (J cm^{-3}) are as follows: hexane, 69; heptane, 53; octane, 38; nonane, 30; cyclohexane, 28; benzene, 5.2; toluene, 7.2; ethylbenzene, 9.3. The value for ethylbenzene is in good agreement with those obtained by Flory and Höcker[36] from volumetric investigations (8.8 J cm^{-3}). In contrast, for the system cyclohexane–PS the extrapolation leads to a value considerable lower than that reported by Höcker, Shih, and Flory[38] (42 J cm^{-3}). On the other hand, Koningsveld et al.[39] derived a much smaller contact interaction parameter (17 J cm^{-3}) from the spinodal and critical point conditions, which explain the upper critical solution temperature of the system. This disagreement may be caused by the uncertainity of P_1^* and T_1^* at high temperatures as well as by limitations of the equation of state theory.

Conclusion

Partial molar sorption and mixing functions for polystyrene and a wide variety of nonpolar solvents via gas chromatographic retention data were derived in the temperature range 403–463 K. The sorption functions ($\Delta\bar{G}_1^s$, $\Delta\bar{H}_1^s$, and $T\Delta\bar{S}_1^s$) vary linearly with the chain length of alkanes and alkylbenzenes. From this was derived the incremental contribution of the CH$_2$ groups and of the phenyl group to the solute sorption in molten atactic polystyrene. The influence of the dipole and induced-dipole interactions of the phenyl group with the PS sites was shown by plots of $\Delta\bar{H}_1^s$ vs. the molar polarization of the solute. It was shown that branching of the hydrocarbon backbone of alkanes causes more endothermic partial molar free energies and heats of sorption. The effect is dependent on the position and the number of branches.

The thermodynamic mixing functions prove to be more sensitive to changes of structure of the solute molecule than are sorption functions. Large values of the weight fraction activity coefficient and of the partial molar free energy of mixing established for the alkanes illustrate their typically nonsolvent characteristics in molten PS. The endothermic $\Delta\bar{H}_1^\infty$ for alkanes become smaller if the carbon number of the solute is higher or if the molecule is branched. In both cases large negative partial molar entropies of mixing contribute a strong demixing tendency. Cyclohexane and the octene isomers occupy an intermediate position between alkanes and alkylbenzenes. The alkylbenzenes have markedly low activity coefficients, a general indication of solute–polymer miscibility.

The slightly increasing values of Ω_1^∞ and $\Delta\bar{G}_1^\infty$ with the dispersive interacting alkyl chain indicate a decrease in miscibility. Benzene, toluene, and ethylbenzene were clearly shown to have negative heats of mixing with the molten PS. The higher members of the series show endothermic $\Delta\bar{H}_1^\infty$. The solute as well as the polymer structure generates entropy effects which determine the overall mixing process. The reduced residual free energy parameter χ^* (segment fraction) and the corresponding enthalpy term χ_H^* are consistent with $\Delta\bar{G}_1^\infty$ and $\Delta\bar{H}_1^\infty$, respectively. The contact interaction parameter X_{12}, derived according to Flory's equation of state theory for the alkanes, cyclohexane, and alkylbenzenes, indicates substantial differences in the energy of solute–PS site contacts.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft within Sonderforschungsbereich 60 is gratefully acknowledged.

Registry No. PS, 9003-53-6; cyclohexane, 110-82-7; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0; 2-methylheptane, 592-27-8; 2,2,4-trimethylpentane, 540-84-1; 1-octene, 111-66-0; 2-octene (*cis*), 7642-04-8; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; propylbenzene, 103-65-1; butylbenzene, 104-51-8; pentylbenzene, 538-68-1; hexylbenzene, 1077-16-3.

Supplementary Material Available: Weight fraction activity coefficients of hexane isomers (Figure 4), octane isomers (Figure 5), and alkylbenzenes (Figure 6) as functions of $1/T$ in PS, specific retention volumes (cm^3 g^{-1}) of alkanes (Table I) and alkylbenzenes (Table II) between 403 and 463 K, segment fraction interaction parameters for solute–PS systems at all temperatures investigated (Table IX), and contact interaction parameters X_{12} for selected solute–PS systems (Table X) (7 pages). Ordering information is given on any current masthead page.

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Mean Square Dipole Moments in Rotational Isomeric State Chains Containing Atoms That Behave as Hard Spheres

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Received June 14, 1983

ABSTRACT: Response of the mean square dipole moment, $\langle\mu^2\rangle$, to excluded volume has been evaluated for several chains via Monte Carlo methods. In the unperturbed state, configurational statistics are those specified by the usual rotational isomeric state model for linear polymethylene chains. Excluded volume is introduced by requiring chain atoms participating in long-range interactions to behave as hard spheres. Dipole moment vectors are affixed to chain bonds in various patterns. Patterns are found for which $\langle\mu^2\rangle$ is unaffected by excluded volume. In these cases the long unperturbed chain has $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$, where $\mathbf{r}$ and μ are the end-to-end vector and dipole moment vector, respectively. However, adherence to the condition $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$ does not guarantee that the mean square dipole moment is independent of chain expansion. Patterns are found for which, even though $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$, the perturbed chain has $1 < \alpha_\mu^2 < \alpha_r^2$ or $\alpha_\mu^2 < 1 < \alpha_r^2$. Properties of these latter chains are not in harmony with previous theoretical work (Nagai, K.; Ishikawa, T. *Polym. J.* **1971**, *2*, 416. Doi, M. *Ibid.* **1972**, *3*, 252), which led to the equation $\alpha_\mu^2 - 1 = \langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2(\langle r^2\rangle_0\langle\mu^2\rangle_0)^{-1}(\alpha_r^2 - 1)$. The combination of $\alpha_\mu^2 \neq 1$ and $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$ can be obtained when the dipole moment vector assigned to bond i has a component perpendicular to the planes of bonds i and $i - 1$. The chain giving $\alpha_\mu^2 < 1 < \alpha_r^2$ contains subchains which have a zero dipole moment when fully extended.

The mean square end-to-end distance, $\langle r^2\rangle$, is well-known to be sensitive to excluded volume. However, the mean square dipole moment, $\langle\mu^2\rangle$, is often found to be independent of chain expansion. An unambiguous test of insensitivity to perturbation is obtained if $\langle\mu^2\rangle/n$ is measured as a function of the number, n, of bonds in the chain. The ratio $\langle\mu^2\rangle/n$ has been shown to attain an asymptotic limit at large n for poly(dimethylsiloxane) in a good solvent.[1] In contrast, $\langle\mu^2\rangle/n$ has been reported to increase with n for poly(vinyl chloride)[2] and poly(vinyl bromide).[3] The reported inconstancy of $\langle\mu^2\rangle/n$ might arise if the fractions studied varied in stereochemical structure as well as degree of polymerization.[1,4] Essentially identical $\langle\mu^2\rangle/n$ were obtained for two samples of poly(vinyl bromide) which differed in molecular weight by nearly a factor of 2, but had the same isotactic content.[5]

Some time ago $\langle\mu^2\rangle$ was proposed to be insensitive to excluded volume if every repeat unit has a resultant dipole moment vector which lies in a plane bisecting the bond angle at a chain atom.[6-8] Nagai and Ishikawa[9] later employed perturbation theory to obtain the interesting relationship

$$\alpha_\mu^2 - 1 = \langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2(\langle r^2\rangle_0\langle\mu^2\rangle_0)^{-1}(\alpha_r^2 - 1) \qquad (1)$$

The term $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2(\langle r^2\rangle_0\langle\mu^2\rangle_0)^{-1}$ is to be evaluated for an infinite chain. Nagai and Ishikawa point out that $\langle\mu^2\rangle$ is unaffected by excluded volume when $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0$ is zero. They further describe symmetry conditions (symmetry planes, twofold symmetry axes, and symmetry points) which, when present in the all-trans configuration, lead to $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$. Additionally, they call attention to the prediction that chains for which $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0$ is nonzero will have $\alpha_\mu^2 > 1$ if $\alpha_r^2 > 1$. The situation $\alpha_\mu^2 < 1 < \alpha_r^2$ is forbidden because $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2(\langle r^2\rangle_0\langle\mu^2\rangle_0)^{-1}$ cannot be negative. Doi[10] argues that, for infinite chains, eq 1 is valid for any order of perturbation and any type of interaction, provided $\langle\mu^2\rangle$ is not independent of n.

The current paper examines adherence to eq 1 for several model chains. While recognizing that the reader may have minimal interest in the dipole moment of polyethylene, we have nevertheless adopted a rotational isomeric state model[11,12] of this polymer for the configurational statistics of the unperturbed chain. By so doing we employ a realistic chain model which has well-known unperturbed properties. Dipole moment vectors are affixed to chain bonds in various patterns. Excluded volume is introduced by requiring chain atoms participating in long-range interactions to behave as hard spheres. As might be expected, circumstances are found where $\alpha_r^2 > 1$, $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$, and $\alpha_\mu^2 = 1$. There are also chains for which $\alpha_\mu^2 = \alpha_r^2$, the factor $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2(\langle r^2\rangle_0\langle\mu^2\rangle_0)^{-1}$ being unity in such cases. However, a pattern for the dipole moment vectors is found for which $1 < \alpha_\mu^2 < \alpha_r^2$, even though $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0$ is zero. Furthermore, another pattern has $\alpha_\mu^2 < 1 < \alpha_r^2$, $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0$ being zero in this case also. While the chains were not designed to model any particular real polymer, they define some circumstances under which $\alpha_\mu^2 < 1 < \alpha_r^2$ can be expected with real chains.

0024-9297/84/2217-0625$01.50/0