

Thermodynamic Interactions of Solvents with Styrene–Butadiene–Styrene Triblock Copolymers

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SYNOPSIS

Fundamental thermodynamic interaction data for various solvents with two styrene–butadiene–styrene triblock copolymers (Kraton D-1101 and Kraton D-1300X) have been collected by the use of inverse gas chromatography at infinite dilution. Experimental results are presented for nine D-1101/solvent systems and nine D-1300X/solvent systems at 308, 328, and 348 K. Weight-fraction activity coefficients and Flory–Huggins χ interaction parameters have been calculated from the retention volumes. The χ parameter is used as a measure of the strength of interaction and therefore as a guide in the prediction of polymer–solvent compatibility. In addition, partial molar heats of mixing, ΔH_m^α , and heats of solution, ΔH_s , were determined. The Hildebrand–Scatchard solubility theory was combined with the Flory theory in order to estimate the solubility parameter of the thermoplastic rubbers at the three different temperatures.

INTRODUCTION

Initially, interest in the thermodynamics of polymer solutions stemmed from the observation that polymer–solvent systems were highly nonideal as opposed to solutions of lower molecular weight substances. As synthetic polymers, in the form of plastics, rubbers, and their composites, became of increasing commercial importance, research on the thermodynamic properties of concentrated polymer solutions took on added significance. In the paint and coating industries, for example, it is often necessary to know the vapor pressure of the solvent over the highly concentrated polymer film during drying. To improve the devolatilization process and to reduce exposure to residual volatile matter, accurate thermodynamic properties such as polymer–solvent interactions and solvent retention by polymer films are valuable to the process designer. Inverse gas–liquid chromatography (IGC) has proven to be very useful for obtaining this information. In this study, the IGC technique is used to gather ex-

perimental data on the behavior of two triblock copolymers with several organic solvents in order to eventually develop methods to correlate and predict this behavior.

EXPERIMENTAL

Apparatus and Procedure

Measurements were carried out on a Varian 3400 gas chromatograph, equipped with an autosampler and a thermal conductivity detector. Helium was used as the carrier gas in all experiments. The temperature of the injection block and the detector assembly were set about 50°C above the column temperature to avoid condensation in the detector assembly. Small amounts of the solvents ($< 0.1 \mu\text{L}$) were injected through the rubber septum of the injection port into the carrier gas using a Hamilton 1 μL syringe. Usually, about 0.8 μL of air was injected along with the liquid sample as the inert component in order to obtain the adjusted retention time. Retention time data were found to be independent of solute sample size below 0.01 μL . The output from the thermal conductivity detector was fed to the printer/plotter built into the gas chromatograph.

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The carrier gas flow rate was measured by means of a soap bubble flowmeter. To eliminate any uncertainty caused by partial saturation from the soap solution in the bubble flowmeter, the carrier gas was saturated with water immediately after passing through the detector. In this work, the retention volumes were independent of carrier gas flow rate for all solutes. After all the solvents were studied at one temperature, the pressure drop across the column was measured by a pressure transducer and the oven set to the next temperature.

Materials

All solutes were of reagent-grade materials supplied by Thomas Scientific Co. and Fisher Scientific Co. All solvents were used without any further purification. Two linear styrene-butadiene-styrene block copolymers were used in this study: Kraton D-1101 and D-1300X. Kraton D-1101 has a styrene content of 31% by weight and a number-average molecular weight of 110,800 ($M_w/M_n = 1.26$) as indicated by gel permeation chromatography analysis. Kraton D-1300X has a lower styrene content (17% by weight) and a number-average molecular weight of 114,800 ($M_w/M_n = 1.64$). The solid support was a diatomaceous earth material (Chromosorb W-HP 80/100 mesh) from Supelco, Inc.

Column Preparation

The chromatographic columns used throughout this study were prepared by first dissolving a weighed sample of D-1101 or D-1300X in toluene and then depositing the solution on a weighed amount of solid support in a Pyrex pan. The mixture was allowed to dry under an infrared heat lamp, being stirred gently and continuously to ensure a uniform mixture. Once all the solvent was evaporated, the coated support was packed into a $\frac{1}{4}$ in.-od, 6.5 ft-long stainless-steel tubing, using a water aspirator at the detector end of the column and a vibrator to gently tap it. Silane-treated glass wool was used to loosely plug both ends of the column. The tubing was then coiled to fit the oven chamber. The percent loading of the coated material packed in column A (D-1101) and column B (D-1300X) was determined by Soxhlet extraction to be 14.0 and 14.1%, respectively. As shown in a previous paper,¹ high percent loadings (i.e., 10–14%) should be used to eliminate surface adsorption on the support.

THEORY

Weight-Fraction Activity Coefficient

At infinite dilution of the solvent, the relation between chromatographic data and the solute activity coefficient is (1 = solvent, 2 = polymer)

$$\Omega_1^\infty = \frac{RT}{V_g P_1^s M_1} \exp \left\{ - \frac{P_1^s (B_{11} - V_1)}{RT} \right\} \quad (1)$$

The standard state in eq. (1) is pure liquid solvent at the system temperature and zero pressure. The exponential term in this equation corrects for the gas-phase nonideality of the solvent. The specific retention volume is given by

$$V_g = Q(t_g - t_r) \frac{f_p}{W_2} \quad (2)$$

where ($t_g - t_r$) is the difference between the air-peak maximum and the solvent-peak maximum as measured directly from the printer/plotter. In eq. (2), Q is the flow rate corrected to the column temperature and the outlet pressure, f_p is a correction term for the pressure gradient across the column and is given by²

$$f_p = \frac{3}{2} \frac{[(P_i/P_o)^2 - 1]}{[(P_i/P_o)^3 - 1]} \quad (3)$$

and W_2 is the mass of the polymer in the column. In the present study, the physical properties of the solvent: P_1^s , M_1 , B_{11} , and V_1 were obtained from Daubert and Danner.³

Flory-Huggins χ Parameters

When eq. (1) is combined with the Flory-Huggins equation,⁴ the χ parameter is obtained:

$$\chi = \ln \Omega_1^\infty - \left(1 - \frac{1}{r} \right) + \ln \frac{\rho_1}{\rho_2} \quad (4)$$

Here r is the ratio of the molar volumes:

$$r = \frac{(\bar{M}_2)_n \nu_2}{V_1} \quad (5)$$

The specific volumes of D-1101 and D-1300X, ν_2 , were determined by using

$$\nu_2 = w_{PS}\nu_{PS} + w_{BR}\nu_{BR} \quad (6)$$

where w_{PS} and w_{BR} are the weight-fractions of polystyrene and polybutadiene, respectively, in the block copolymer. The specific volume of polystyrene, ν_{PS} , was obtained from Höcker et al.⁵ and the specific volume of polybutadiene, ν_{BR} , from Barlow.⁶ The densities of D-1101 and D-1300X determined from eq. (6) are in good agreement with the experimental values reported by Ferdinand and Springer.⁷

Heat of Solution and Partial Molar Heat of Mixing

The heat of solution is determined by using the approximate relation:

$$\Delta H_s = -R \left[\frac{\partial (\ln V_g^0)}{\partial (1/T)} \right] \quad (7)$$

where

$$V_g^0 = V_g \left(\frac{273.2}{T} \right) \quad (8)$$

The partial molar enthalpy of mixing is by definition

$$\Delta \bar{H}_m^\infty = R \left[\frac{\partial (\ln \Omega_1^\infty)}{\partial (1/T)} \right] \quad (9)$$

The heat of vaporization is related to these two quantities by

$$\Delta H_v = \Delta \bar{H}_m^\infty - \Delta H_s \quad (10)$$

Hence, if retention data are available at different temperatures, one can predict the molar enthalpy of vaporization of the solute through eqs. (7), (9), and (10). The assumption made in eq. (10) is that the gas-phase nonideality correction term in eq. (1) is negligible.

Estimation of the Polymer Solubility Parameter

The combination of the Hildebrand–Scatchard regular solution theory⁸ with the Flory theory⁴ yields

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} \right) = \frac{2\delta_2^\infty}{RT} \delta_1 - \left(\frac{\delta_2^{\infty 2}}{RT} + \frac{\chi_S}{V_1} \right) \quad (11)$$

where δ_2^∞ is the polymer solubility parameter at infinite dilution of the solvent and δ_1 is the solubility parameter of the solute given by

$$\delta_1 = \left[\frac{\Delta H_v - RT}{V_1} \right]^{1/2} \quad (12)$$

Since χ , V_1 , and δ_1 are known, the solubility parameter of the polymer, δ_2^∞ , can be determined from the slope of $(\delta_1^2/(RT) - \chi/V_1)$ vs. δ_1 .

RESULTS AND DISCUSSION

Kraton D-1101

Interaction Parameters

Experimental retention volumes on Kraton D-1101 for nine solvents at three different temperatures (308, 328, and 348 K) are shown in Table I. This table also includes the corresponding weight-fraction activity coefficients and the Flory–Huggins χ parameters.

As suggested from stability analysis in terms of the Flory–Huggins theory, the largest permissible value of χ should be 0.5 for complete miscibility of the polymer. Table I shows that for the aromatic hydrocarbons (benzene, toluene, ethyl benzene, *p*-xylene), the χ parameters vary from 0.34 to 0.44, indicating favorable interactions between D-1101 and these solvents. No significant temperature dependence of χ is observed for these D-1101/solvent systems. For cyclohexane, *n*-hexane, and heptane, however, the χ parameters are greater than 0.5, suggesting incompatibility of the polymer with these solvents. A slight dependence of χ on temperature is noticed for the D-1101/cyclohexane system. The relatively higher compatibility of D-1101 with the aromatic hydrocarbons, as opposed to cyclohexane and the alkanes, is probably due to the induction forces with the thermoplastic rubber that are larger for aromatic hydrocarbons by virtue of the mobile π electrons. Also, as the relatively low χ values indicate, chloroform exhibits strong solubility characteristics with D-1101. In fact, chloroform appears to have the lowest value for χ at the three different temperatures; hence, one may predict that chloroform is the most suitable solvent for D-1101. On the other hand, unfavorable interactions are observed between MEK and D-1101 as portrayed through the high values of Ω_1^∞ and χ .

Enthalpy Parameters

Linear regression analysis was used to obtain the heats of solution, ΔH_s , and the partial molar heats of mixing, $\Delta \bar{H}_m^\infty$, over the temperature range 308–348 K, as suggested by eqs. (7) and (9) (Table II). The estimated uncertainty of $\Delta \bar{H}_m^\infty$ and ΔH_s is about ± 0.3 kJ/mol. Values of $\Delta \bar{H}_m^\infty$ ranging from -5 to

Table I Kraton D-1101/Solvent Interaction Data

Solvents	V_g (cm ³ /g)			Ω_1^∞			χ		
	308 K	328 K	348 K	308 K	328 K	348 K	308 K	328 K	348 K
Benzene	376	183	95.7	4.47	4.46	4.63	0.414	0.400	0.423
Toluene	1047	461	228	4.28	4.29	4.31	0.363	0.355	0.348
Ethyl benzene	2513	992	458	4.32	4.39	4.34	0.372	0.379	0.360
<i>p</i> -Xylene	2536	1006	466	4.63	4.65	4.60	0.433	0.429	0.409
Chloroform	279	125	67.4	1.98	2.27	2.41	0.126	0.252	0.297
Cyclohexane	250	128	72.3	6.06	5.88	5.77	0.597	0.555	0.522
Hexane	115	57.9	33.1	8.54	8.79	8.83	0.773	0.785	0.711
Heptane	308	144	74.1	8.53	8.35	8.36	0.812	0.777	0.762
MEK	181	83.9	44.1	10.3	10.6	10.8	1.16	1.17	1.17

+1 kJ/mol were calculated. The experimental heats of vaporization were obtained as suggested by eq. (10) over the temperature range 308–348 K. These values were compared with those obtained from Daubert and Danner³ evaluated at the mid-temperature 328 K, as shown in Table II. Excellent agreement was found between experimental and literature values. These results are a good indicator that the data are internally consistent.

Cyclohexane yielded the lowest value of $-\Delta H_s$, and ethyl benzene, the highest. The heat of solution data exhibit many characteristics of the free energy. For example, the addition of the similar structural unit to an aromatic solute molecule produces a constant increment of about 4 kJ/mol in $-\Delta H_s$. This characteristic could also be seen through the linear molecular weight dependence of $\ln(V_g^0)$ as illustrated for several aromatic hydrocarbons in Figure 1. Accordingly, prediction of interaction data is possible for solutes belonging to a family that has been studied. Figure 2 shows the linear temperature de-

pendence exhibited by several solutes when $\ln(V_g^0)$ is plotted against the reciprocal absolute temperature to determine the corresponding heats of solution.

Estimation of the Solubility Parameter of D-1101

Solute solubility parameters were computed through eq. (12). The latent heat of vaporization, ΔH_v , and the molar volume, V_1 , were both obtained from Daubert and Danner³ for each solvent at the appropriate temperature. The calculated values of δ_1 are compiled in Table III. Using eq. (11) and a least-square analysis, δ_2^∞ values were determined. Figure 3 is a plot of $(\delta_1^2/(RT) - \chi/V_1)$ vs. δ_1 for various solvents in D-1101 at 328 K. The linear correlation coefficient was greater than .997 for all temperatures. The value of δ_2^∞ for D-1101 is estimated to be 17.6 ± 0.4 , 16.9 ± 0.2 , and 16.2 ± 0.2 (J/cm³)^{1/2} at 308, 328, and 348 K, respectively. A range of 16.5–17.8 (J/cm³)^{1/2} has been reported by Brandrup and

Table II Enthalpy Parameters for the D-1101/Solvent Systems between 308 and 348 K (kJ/g mol)

Solutes	$-\Delta H_s$	ΔH_m^∞	ΔH_v	ΔH_v^a	% Deviation in ΔH_v
Benzene	33.2	-0.745	32.4	32.2	0.77
Toluene	36.7	-0.134	36.6	36.7	0.30
Ethyl benzene	40.7	-0.130	40.5	40.5	0.02
<i>p</i> -Xylene	40.5	0.158	40.6	40.7	0.07
Chloroform	34.4	-4.49	29.9	29.8	0.40
Cyclohexane	30.4	1.09	31.5	31.4	0.23
Hexane	30.6	-0.765	29.8	29.7	0.51
Heptane	34.4	0.459	34.9	34.8	0.36
MEK	34.2	-1.11	33.1	32.9	0.45

^a From Daubert and Danner³ at 328 K.

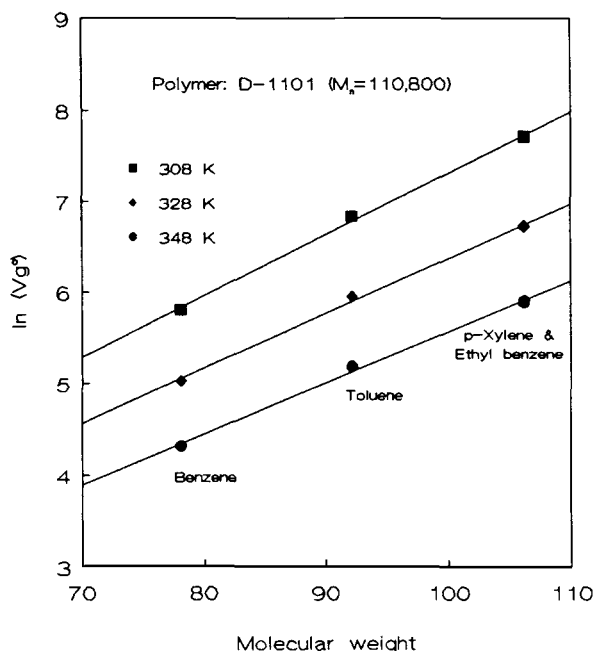


Figure 1 Dependence of $\ln(V_g^0)$ on solute molecular weight for the aromatic hydrocarbons with Kraton D-1101.

Immergut⁹ for several styrene-butadiene copolymers rich in butadiene content (> 60% wt) at 298 K. Our data show that a constant increment of about $0.7 \text{ (J/cm}^3)^{1/2}$ in δ_2^z results for an increase of 20 K in temperature. Assuming a linear relationship, the

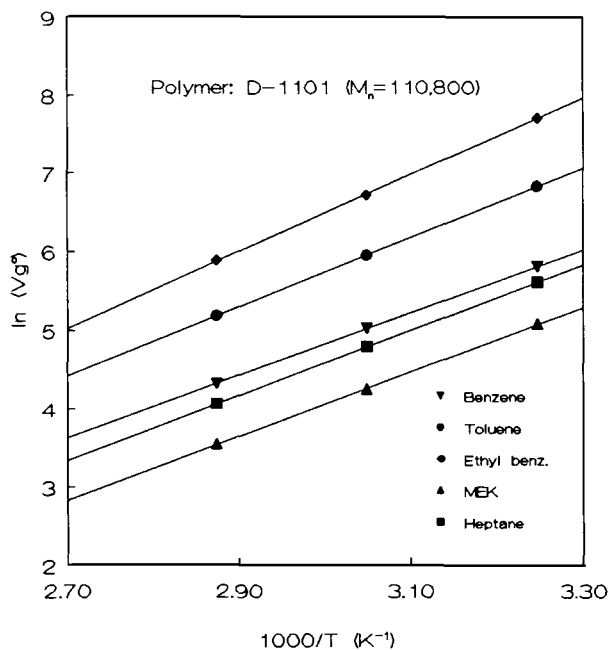


Figure 2 Retention diagram for several D-1101/solvent systems (308–348 K).

Table III Solute Solubility Parameter Data at 308, 328, and 348 K

	$\delta_1 \text{ (J/cm}^3)^{1/2}$		
	308 K	328 K	348 K
Hexane	14.6	14.0	13.4
Heptane	14.9	14.5	13.9
Cyclohexane	16.5	15.9	15.4
<i>p</i> -Xylene	17.7	17.2	16.8
Ethyl benzene	17.8	17.3	16.8
Toluene	18.1	17.6	17.0
Benzene	18.4	17.8	17.2
MEK	18.6	17.9	17.3
Chloroform	18.6	18.0	17.3

value of δ_2^z for D-1101 at 298 K would be $17.9 \text{ (J/cm}^3)^{1/2}$, which falls very close to the value reported by Brandrup and Immergut.⁹

Kraton D-1300X

Interaction Parameters

Values of V_g , Ω_1^z , and χ were determined for nine solvents with Kraton D-1300X at 308, 328, and 348 K. These results are presented in Table IV. Following the same solvency power analysis used for the D-1101/solvent systems, several solubility charac-

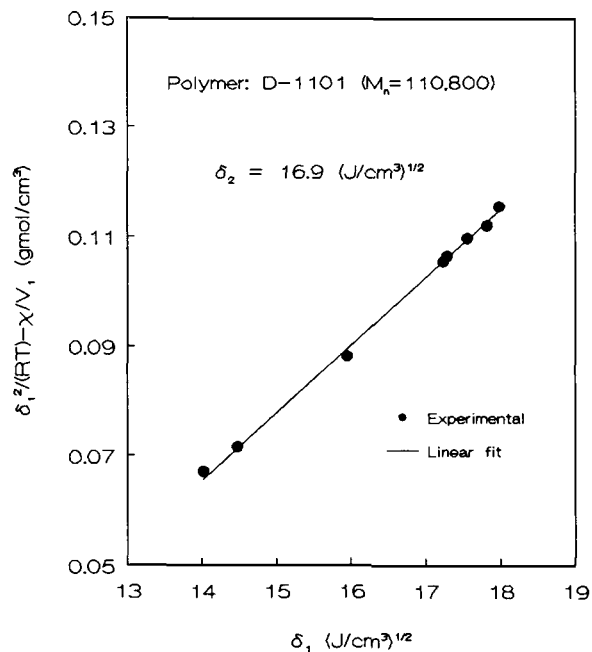


Figure 3 Estimation of the solubility parameter of Kraton D-1101 at 328 K.

Table IV Kraton D-1300X/Solvent Interaction Data

Solvents	V_g (cm ³ /g)			Ω_1^∞			χ		
	308 K	328 K	348 K	308 K	328 K	348 K	308 K	328 K	348 K
Benzene	395	194	103	4.25	4.20	4.30	0.388	0.365	0.375
Toluene	1117	494	243	4.01	4.00	4.03	0.322	0.310	0.306
Ethyl benzene	2687	1090	501	4.04	3.99	3.97	0.329	0.309	0.294
<i>p</i> -Xylene	2727	1103	504	4.31	4.24	4.26	0.385	0.361	0.356
Chloroform	267	131	70.6	2.06	2.18	2.30	0.192	0.234	0.274
Cyclohexane	292	150	82.9	5.19	5.05	5.03	0.467	0.425	0.410
Hexane	131	67.9	38.5	7.51	7.50	7.59	0.669	0.650	0.643
Heptane	363	168	87.4	7.24	7.13	7.09	0.671	0.643	0.621
MEK	182	87.7	47.2	10.2	10.2	10.1	1.17	1.15	1.13

teristics of the D-1300X/solvent systems could be deduced. The Flory–Huggins interaction data compiled in Tables I and IV reveal that D-1300X is slightly more soluble than D-1101 in most of the organic solvents investigated. In fact, all solvents, except chloroform and MEK, show a slightly higher degree of compatibility with D-1300X than with D-1101, in particular, cyclohexane, which exhibits favorable interactions with D-1300X, as opposed to poor affinity to D-1101. *N*-Hexane, heptane, and the aromatic solvents (benzene, toluene, ethyl benzene, *p*-xylene) also exhibit lower χ values with D-1300X than with D-1101. The higher affinity of these solvents to D-1300X, as opposed to D-1101, can be attributed to the higher butadiene content in D-1300X. Previous infinite dilution studies on the homopolymers, polystyrene and polybutadiene,^{1,10} showed that solvents, especially aliphatic hydrocarbons, exhibit stronger solubility characteristics with polybutadiene than with polystyrene. On the other hand, no significant changes are noticed in the interaction behavior of chloroform and MEK with the copoly-

mers. As the relatively low χ values indicate, chloroform is again the most suitable solvent, whereas MEK is the least suitable solvent by virtue of its high Ω_1^∞ and χ values.

Enthalpy Parameters

Values of ΔH_s , ΔH_m^∞ , and experimental ΔH_v were obtained over the temperature range 308–348 K (Table V). The estimated uncertainty on ΔH_m^∞ and ΔH_s is about ± 0.3 kJ/mol. Values of ΔH_m^∞ ranging from -3 to 0.5 kJ/mol were obtained. The highly exothermic value of ΔH_m^∞ for the D-1300X/chloroform system supports the view that chloroform has strong interactions with D-1300X. The experimental heats of vaporization of the various solutes were again compared with those reported by Daubert and Danner.³ The agreement between these two sets of values is excellent for all solvents.

N-Hexane yielded the lowest value of $-\Delta H_s$, and *p*-xylene, the highest. Figure 4 highlights the linear molecular weight dependence of $\ln(V_g^0)$ for several

Table V Enthalpy Parameters for the D-1300X/Solvent Systems between 308 and 348 K (kJ/g mol)

Solutes	$-\Delta H_s$	ΔH_m^∞	ΔH_v	ΔH_v^a	% Deviation in ΔH_v
Benzene	32.7	-0.252	32.4	32.2	0.77
Toluene	36.7	-0.106	36.6	36.6	0.30
Ethyl benzene	40.2	0.397	40.5	40.5	0.01
<i>p</i> -Xylene	40.4	0.270	40.6	40.7	0.07
Chloroform	32.4	-2.467	29.9	29.8	0.39
Cyclohexane	30.8	0.727	31.5	31.4	0.23
Hexane	30.0	-0.228	29.8	29.7	0.52
Heptane	34.4	0.464	34.9	34.8	0.37
MEK	32.8	0.302	33.1	32.9	0.44

^a From Daubert and Danner³ at 328 K.

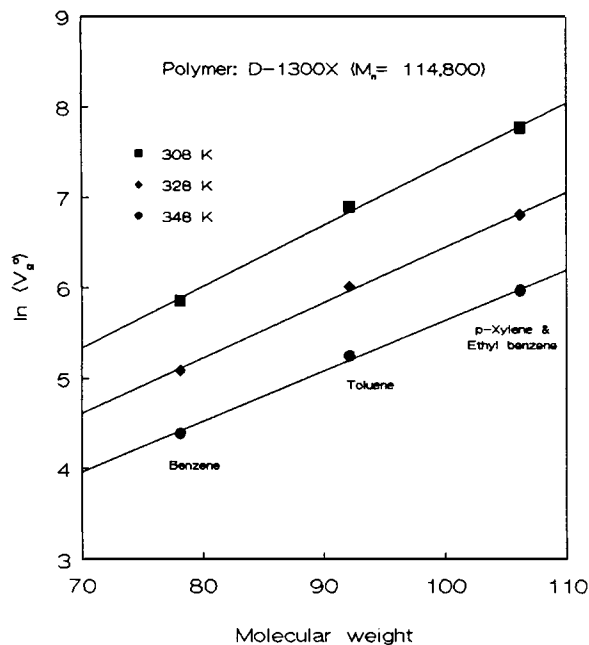


Figure 4 Dependence of $\ln(V_g^0)$ on solute molecular weight for the aromatic hydrocarbons with Kraton D-1300X.

aromatic hydrocarbons at three different temperatures. The heat of solution data for the D-1300X/solvent systems shows that the addition of the similar structural units to an aromatic solute molecule

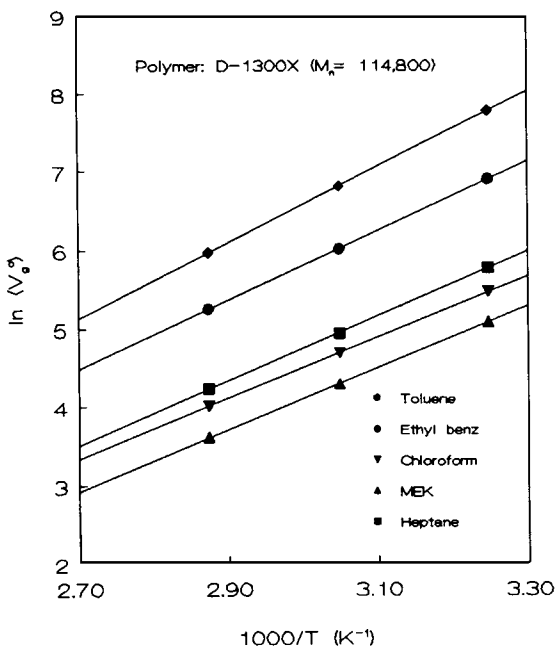


Figure 5 Retention diagram for several D-1300X/solvent systems (308–348 K).

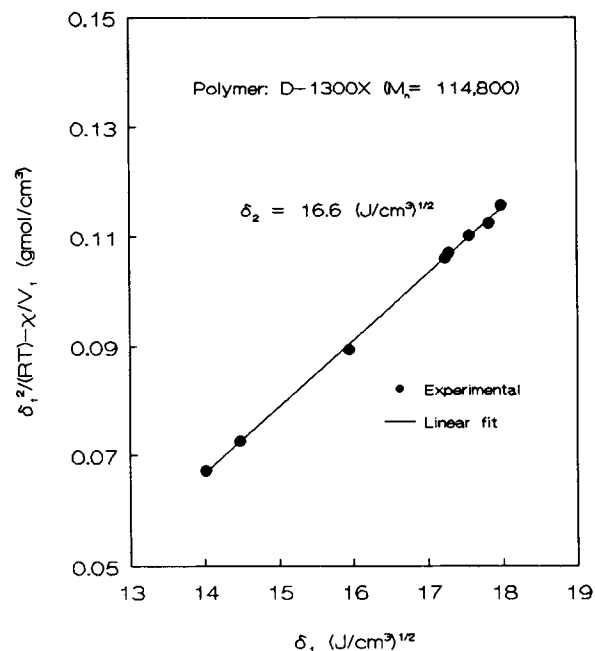


Figure 6 Estimation of the solubility parameter of Kraton D-1300X at 328 K.

produces a constant increment of about 4 kJ/mol in $-\Delta H_s$ just as with D-1101. Figure 5 is a retention diagram representing the linear temperature dependence of $\ln(V_g^0)$ for some solvents with D-1300X.

Estimation of the Solubility Parameter of D-1300X

Carrying out the same analysis done with D-1101, the D-1300X solubility parameters were obtained. The least-square analysis yielded δ_2^∞ values of 17.2 ± 0.3 , 16.6 ± 0.2 , and 15.9 ± 0.2 $(\text{J}/\text{cm}^3)^{1/2}$ at 308, 328, and 348 K, respectively. Figure 6 shows the linear behavior of $(\delta_1^2/(RT) - \chi/V_1)$ with respect to δ_1 at 328 K. The linear correlation coefficient was greater than .999 for all temperatures. As indicated by the error estimates, the difference in the δ_2^∞ values obtained for D-1300X and D-1101 at the different temperatures is not significant.

CONCLUSIONS

Infinite dilution inverse gas chromatography is a convenient and rapid method to obtain thermodynamic interaction data of organic solvents at infinite dilution. When the experimental results are expressed in the form of Flory-Huggins interaction

parameters, their magnitude allow a reasonable ranking of the solvents according to their power of solvency. The results of this study indicate that chloroform and aromatic hydrocarbons are potential solvents for both triblock copolymers. These thermoplastic rubbers show, however, very poor solubility characteristics with *n*-hexane, heptane, and methyl ethyl ketone. Cyclohexane, on the other hand, shows good compatibility with D-1300X and poor affinity to D-1101. The predicted solute heats of vaporization from the experimental interaction data were in excellent agreement with the literature values. Finally, the solubility parameter of Kraton D-1101 and Kraton D-1300X were successfully estimated at various temperatures in this study.

NOMENCLATURE

B_{11}	second virial coefficient of pure solvent, $\text{cm}^3/\text{g mol}$
f_p	pressure correction term
ΔH_s	heat of solution, kJ/g mol
ΔH_m^∞	partial molar heat of mixing at infinite dilution, kJ/g mol
ΔH_v	latent heat of vaporization, kJ/g mol
M_i	molecular weight (MW) of component <i>i</i>
M_n	number-average molecular weight
M_w	weight-average molecular weight
P_1^s	saturation vapor pressure of the solvent, atm
P_i	column inlet pressure, kPa
P_o	column outlet pressure, kPa
Q	flow rate at column outlet pressure and temperature, cm^3/min
R	universal gas constant
r	ratio of molecular volumes of polymer to solvent
T	system temperature, K
t_g	residence time of the solvent, min
t_r	residence time of air, min
V_1	molar volume of liquid solvent at saturation, $\text{cm}^3/\text{g mol}$
V_g	specific retention volume, cm^3/g

V_g^0	specific retention volume corrected to 0°C , cm^3/g
W_2	weight of polymer in column, g

Greek Symbols

δ_1	solvent solubility parameter, $(\text{J}/\text{cm}^3)^{1/2}$
δ_2^∞	polymer solubility parameter at infinite dilution, $(\text{J}/\text{cm}^3)^{1/2}$
ν_2	specific volume of polymer, cm^3/g
ρ_i	mass density of component <i>i</i> , g/cm^3
χ	Flory–Huggins parameter
χ_s	entropic contribution to the Flory–Huggins parameter
Ω_1^∞	weight-fraction activity coefficient of solvent at infinite dilution (WFAC)

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