Solvent-Polymer Interactions in Polybutadienes

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ABSTRACT: Infinite-dilution activity coefficients of 26 solvents in three polybutadienes were determined by inverse gas chromatography in the temperature range 40-100 °C. The polybutadienes have well-characterized structures and different molecular weights. The data are useful for the development of thermodynamic models for polymer-solvent interaction and for characterization. The results were fitted to the PHCT equation of state. The data indicate that activity coefficients depend on polymer molecular weight and structure.

Introduction

In polymer processing there is a growing need for knowledge of the phase behavior of polymer solutions.

The literature provides correlative and predictive methods for the activity of solvents in polymer solutions. Correlative models, like the well-known Flory-Huggins, need specific experimental data for the estimation of the parameters.

Predictive methods,[1] on the other hand, are based on a group-contribution hypothesis and need no specific information about the particular system. Despite the generality of these methods, they are not able to distinguish among polymer isomers.

In this work, three samples of well-characterized polybutadiene polymers were studied by inverse gas chromatgraphy[2-4] to determine the effect of structure and molecular weight on the activity coefficient at infinite dilution for 26 volatile organic liquids with different polarities.

Experimental Section

1. **Apparatus.** A thermal-conductivity chromatograph (Fractovap Model B, Carlo Erba, Italy) was employed. The thermostat stability of the oven was better than 0.05 deg, measured by an electronic thermometer Systemteknik AB, Sweden, Series S1220. The flow of the carrier gas (helium) was measured with a soap-film meter. The pressure drop in the column was read in a U mercury manometer.

The measured experimental conditions were retention time of solvent, dead time (retention time of air), carrier flow, column temperature, flow meter temperature, ambient pressure, and pressure drop in the column. The carrier flow was set ranging from 20 to 40 mL/min, and the pressure drop was about 40-150 mbar.

For all three polymers the influence of carrier gas flow rate was evaluated by extrapolating to zero flow rate the retention volumes: no influence of the flow rate was observed for all the stationary phases.

Because the peaks did not show notable asymmetry, retention times were read using peak maxima.

The uncertainties are estimated to be as follows: carrier flow, ±0.005 mL/s; column temperature, ±0.05 deg; soap-film meter temperature, ±0.1 deg; inlet and outlet pressures, ±2 mbar; solvent mass, ±0.001 g. The effect of these variables in the activity coefficients is estimated to be about 2%. The linearity in the plots of the logarithm of V_g^0 vs $1/T$ was always satisfactory to better than ±0.024 in the natural logarithm of V_g^0, which gives an uncertainty of about 3% in activity coefficients.

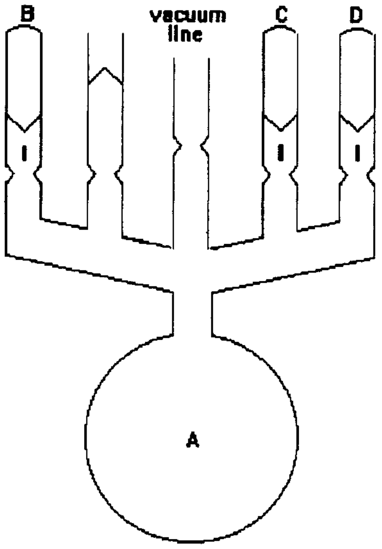

Figure 1.

Table I. Molecular Weights of Polybutadienes Determined by Low-Angle Laser Scattering (LALLS), Gel Permeation (GPC), Vapor Pressure Osmometry (VPO), and Membrane Osmometry (MO)

	LALLS	GPC			VPO	MO
no.	M_w	M_n	M_w	M_w/M_n	M_n	M_n
1		11 900	12 200	1.02	12 200	
2	13 100	11 800	12 300	1.04		
3	108 000	88 000	96 000	1.09		98 000

Table II. Molecular Weights and Vinyl Contents of Polybutadienes

		% of isomer		
no.	M_w used	trans	cis	vinyl
1	12 200	45.5	46.5	8.0
2	13 100	10.2	20.8	69.0
3	108 000	46.5	40.6	12.9

2. **Polymer Synthesis and Characterization.** Three narrow molecular weight distribution polybutadienes differing in molecular weight and vinyl content were anionically polymerized in a vacuum system at room temperature under high purity conditions.[5] The reaction was initiated by *tert*-butyllithium and terminated with dry 2-propanol. The polymerization reactor (A) is shown in Figure 1 with the vials containing the initiator (C), termination agent (D), and purge (B). The reactor was joined

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Table III. Activity Coefficients at Infinite Dilution (Ω_1^∞), Specific Retention Volume (V_g^0), and Flory–Huggins Parameters (χ) for Different Organic Solvents in the Polybutadienes at Different Temperatures

		polymer 1			polymer 2			polymer 3		
component	T (°C)	V_g^0 [mL/(g·K)]	Ω_1^∞	χ	V_g^0 [mL/(g·K)]	Ω_1^∞	χ	V_g^0 [mL/(g·K)]	Ω_1^∞	χ
n-pentane	40.0				46.3	6.2	0.442			
	60.0	21.2	7.5	0.611	26.2	6.0	0.399			
	80.0	12.9	7.4	0.582	15.8	6.0	0.374			
	100.0	8.2	7.5	0.565	10.1	6.1	0.361			
n-hexane	40.0				132.6	5.5	0.385			
	60.0	52.8	6.8	0.590	66.0	5.4	0.366			
	80.0	29.7	6.6	0.547	35.6	5.5	0.365			
	100.0	17.8	6.6	0.522	20.5	5.7	0.379			
n-heptane	40.0				365.2	5.1	0.357			
	60.0	131.3	6.3	0.560	166.9	4.9	0.319	107.3	7.7	0.751
	80.0	66.5	6.2	0.532	83.4	4.9	0.305	56.0	7.4	0.694
	100.0	36.3	6.2	0.523	44.9	5.0	0.310	31.3	7.2	0.660
n-octane	40.0				988.6	4.9	0.342			
	60.0	321.8	6.0	0.535	408.8	4.7	0.294	268.0	7.1	0.707
	80.0	147.1	5.9	0.517	186.8	4.6	0.277	125.1	6.9	0.668
	100.0	73.1	6.0	0.521	92.9	4.7	0.281	63.4	6.9	0.653
1-hexene	40.0				125.1	4.9	0.319			
	60.0	53.5	5.8	0.473	64.3	4.8	0.289			
	80.0	29.1	6.0	0.480	35.7	4.9	0.277			
	100.0	16.9	6.2	0.498	21.1	5.00	0.280			
1-heptene	40.0				345.4	4.5	0.253			
	60.0	129.7	5.5	0.433	159.7	4.5	0.224	111.9	6.4	0.571
	80.0	65.3	5.5	0.429	80.6	4.5	0.218	57.8	6.3	0.542
	100.0	35.4	5.7	0.442	43.8	4.6	0.229	32.0	6.3	0.532
1-octene	40.0				938.7	4.3	0.226			
	60.0	315.1	5.2	0.412	390.7	4.2	0.196	263.6	6.2	0.580
	80.0	146.7	5.2	0.396	179.6	4.2	0.193	125.9	6.0	0.538
	100.0	74.2	5.3	0.400	89.7	4.4	0.208	65.1	6.0	0.519
cyclohexane	40.0				285.8	3.9	0.218			
	60.0	118.4	4.5	0.357	141.6	3.8	0.177	104.4	5.1	0.475
	80.0	63.1	4.5	0.344	76.0	3.7	0.157	56.2	5.1	0.452
	100.0	36.0	4.6	0.346	43.6	3.8	0.154	32.4	5.1	0.445
methylcyclohexane	40.0				511.4	4.2	0.168			
	60.0	199.0	4.9	0.317	238.4	4.1	0.136			
	80.0	100.6	4.9	0.312	121.2	4.1	0.126			
	100.0	54.7	5.0	0.322	66.2	4.1	0.131			
ethylcyclohexane	40.0				1507.0	3.6	0.085			
	60.0	528.0	4.2	0.226	632.9	3.5	0.044			
	80.0	242.3	4.2	0.222	293.3	3.5	0.030			
	100.0	120.8	4.3	0.236	147.6	3.5	0.035			
benzene	40.0				325.4	3.7	0.255			
	60.0	146.8	3.9	0.291	158.9	3.6	0.212	144.3	3.9	0.302
	80.0	76.2	3.9	0.291	84.1	3.5	0.191	76.9	3.9	0.275
	100.0	42.4	4.0	0.304	47.7	3.6	0.186	43.8	3.9	0.265
toluene	40.0				946.9	3.3	0.140			
	60.0	370.1	3.6	0.225	414.0	3.2	0.112	357.4	3.8	0.253
	80.0	178.8	3.6	0.214	198.8	3.3	0.107	176.1	3.7	0.221
	100.0	93.3	3.7	0.219	103.2	3.3	0.117	93.6	3.7	0.208
acetone	40.0				45.9	15.6	1.640			
	60.0	22.2	16.1	1.660	25.9	13.8	1.506			
	80.0	13.2	15.0	1.567	15.6	12.7	1.402			
	100.0	8.3	14.2	1.496	9.9	12.0	1.321			
2-propanol	40.0				47.0	58	2.943			
	80.0	14.0	30.2	2.247	15.6	27.2	2.145			
	80.0	14.0	30.2	2.247	15.6	27.2	2.145			
	100.0	9.3	22.0	1.909	9.8	20.8	1.855			
1-butanol	40.0				263.4	48	2.756			
	60.0	120.2	32.4	2.348	126.8	30.7	2.294	242.5	16.0	1.640
	80.0	59.7	23.9	2.035	66.4	21.5	1.929	105.0	13.6	1.464
	100.0	31.9	19.0	1.791	37.2	16.3	1.637	49.7	12.2	1.341
acetonitrile	40.0				42.0	61	2.862			
	60.0	21.9	55	2.749	24.0	50	2.660			
	80.0	13.4	47	2.578	14.6	43	2.493			
	100.0	8.6	41	2.435	9.4	38	2.355			
propionitrile	40.0				103.6	31.8	2.246			
	60.0	47.4	30.9	2.209	54.6	26.9	2.069	76.7	19.1	1.724
	80.0	27.0	27.1	2.067	30.9	23.7	1.930	42.2	17.3	1.613
	100.0	16.3	24.6	1.955	18.6	21.5	1.821	24.8	16.1	1.529
butyronitrile	40.0				268.4	21.8	1.901			
	60.0	109.4	21.9	1.899	126.2	19.0	1.756			
	80.0	57.2	19.4	1.769	64.6	17.2	1.647			
	100.0	32.0	17.7	1.670	35.5	16.0	1.566			
methyl acetate	40.0				71.2	11.2	1.138			
	60.0	36.5	10.7	1.080	38.1	10.3	1.036			
	80.0	15.3	14.0	1.324	21.9	9.7	0.965			
	100.0	7.1	18.0	1.559	13.4	9.5	0.917			
ethyl acetate	40.0				161.0	6.5	0.861			
	60.0	67.3	7.1	0.935	79.0	6.0	0.775	76.4	6.2	0.802
	80.0	34.6	7.0	0.916	42.0	5.8	0.721	40.0	6.1	0.764
	100.0	19.1	7.2	0.918	23.9	5.7	0.691	22.4	6.1	0.748
propyl acetate	40.0				433.5	5.4	0.669			
	60.0	156.0	6.3	0.808	191.8	5.1	0.601	176.5	5.6	0.677
	80.0	75.9	6.1	0.768	93.1	5.0	0.563	86.0	5.4	0.635
	100.0	39.9	6.1	0.750	48.8	5.0	0.548	45.2	5.4	0.617
butyl acetate	40.0				1179.3	4.7	0.520			
	60.0	379.4	5.6	0.682	469.9	4.5	0.468			
	80.0	170.1	5.5	0.646	207.8	4.5	0.445			
	100.0	83.1	5.4	0.634	100.3	4.5	0.445			
chloroform	40.0				208.0	1.95	0.051			
	60.0	100.0	2.02	0.081	105.0	1.93	0.032	119.8	1.69	0.105
	80.0	53.2	2.11	0.115	57.2	1.96	0.042	61.0	1.84	0.028
	100.0	30.3	2.25	0.164	33.3	2.05	0.070	33.4	2.04	0.060
carbon tetrachloride	40.0				309.6	1.71	0.097			
	60.0	136.6	1.88	0.184	148.5	1.73	0.100	127.6	2.01	0.246
	80.0	72.7	1.89	0.183	77.4	1.78	0.120	68.7	2.00	0.233
	100.0	41.4	1.94	0.196	43.3	1.86	0.152	39.6	2.03	0.235
1-chloropropane	40.0				88.0	4.2	0.359			
	60.0	40.6	4.8	0.480	47.5	4.1	0.323	41.1	4.8	0.462
	80.0	23.4	4.8	0.465	27.5	4.1	0.305	23.8	4.7	0.441
	100.0	14.4	4.9	0.462	16.9	4.2	0.301	14.7	4.8	0.434
1-chlorobutane	40.0				246.6	3.9	0.331			
	60.0	102.2	4.5	0.461	122.0	3.7	0.282	102.7	4.5	0.449
	80.0	54.1	4.5	0.446	65.4	3.7	0.257	53.9	4.5	0.444
	100.0	30.7	4.5	0.448	37.5	3.7	0.248	30.3	4.6	0.454

ME ketone	40.0				134.6	10.1	1.194			
	60.0	57.1	11.0	1.267	68.1	9.3	1.091	69.1	9.1	1.071
	80.0	31.7	10.2	1.179	37.2	8.7	1.018	39.9	8.1	0.941
	100.0	18.7	9.7	1.115	21.7	8.4	0.967	24.5	7.4	0.841
MIB ketone	40.0				522.9	7.6	0.953			
	60.0	199.8	7.9	0.995	235.0	6.7	0.832	207.6	7.6	0.948
	80.0	95.7	7.6	0.946	115.6	6.3	0.756	110.3	6.6	0.796
	100.0	49.6	7.6	0.929	61.4	6.1	0.715	62.7	6.0	0.686
DE ketone	40.0				374.7	7.1	0.820			
	60.0	141.1	8.1	0.944	171.5	6.7	0.749	169.2	6.8	0.755
	80.0	70.2	7.8	0.900	85.7	6.4	0.700	85.4	6.4	0.697
	100.0	37.6	7.7	0.873	46.2	6.3	0.667	46.4	6.3	0.656
methanol	40.0				14.1	145	3.850			
	60.0	9.2	95	3.409	9.2	95	3.409			
	80.0	6.3	66	3.026	6.3	66	3.030			
	100.0	4.5	48	2.695	4.5	49	2.702			
ethanol	40.0				30.3	92	3.411			
	60.0	17.1	63	3.019	17.8	60	2.978			
	80.0	10.6	45	2.660	11.1	43	2.611			
	100.0	6.9	33.6	2.355	7.3	31.8	2.298			
1-propanol	40.0				92.9	59	2.973			
	60.0	45.5	41	2.608	47.7	39	2.561	95.3	19.7	1.864
	80.0	25.1	30.3	2.284	26.4	28.8	2.233	45.4	16.7	1.684
	100.0	14.7	23.7	2.025	15.5	22.4	1.970	23.5	14.9	1.553
1-chloropentane	40.0				655.9	3.8	0.373			
	60.0	252.9	4.2	0.477	291.7	3.7	0.334			
	80.0	122.7	4.2	0.467	142.2	3.7	0.319			
	100.0	64.3	4.3	0.476	74.9	3.7	0.324			
tetrahydrofuran	40.0				214.0	3.7	0.352			
	60.0	93.3	4.2	0.457	107.8	3.6	0.313			
	80.0	49.9	4.2	0.456	58.7	3.6	0.293			
	100.0	28.5	4.3	0.469	34.1	3.6	0.289			
diethyl ether	40.0				52.9	5.2	0.425			
	60.0	24.0	6.3	0.598	29.0	5.3	0.411			
	80.0	14.0	6.5	0.597	17.0	5.4	0.404			
	100.0	8.7	6.7	0.599	10.6	5.5	0.402			
dipropyl ether	40.0				246.4	5.5	0.510			
	60.0	117.7	5.2	0.446	58.7	10.5	1.142			
	80.0	59.6	5.2	0.435	16.5	19.0	1.722			
	100.0	32.5	5.4	0.442	5.3	33.0	2.257			
dibutyl ether	60.0	672.4	4.6	0.368						
	80.0	287.8	4.5	0.337						
	100.0	134.9	4.5	0.336						

to the vacuum line to obtain a high vacuum. Then it was separated from the line to be washed with the purge containing a dilute solution of *n*-butyllithium in cyclohexane. The washing solution was then returned to vial B, frozen, and separated from the reactor that was joined again to the line. The previously dried solvent and the monomer were subsequently distilled into the reactor. The whole system was then separated from the vacuum line, and the initiator was added to A by breaking the seal between C and A with a magnetic hammer. The reaction was allowed to proceed for about 120 h and was finalized by the addition of the 2-propanol contained in vial D. The polymer was precipitated from the cyclohexane solution with methanol. A 20 ppm quantity of antioxidant (Santonox) was added to the polymer at this stage. The polymer was finally dried under vacuum for several hours until no traces of methanol were detected.

Two initiator concentrations were used to obtain the low (10^4) and high (10^5) molecular weight polymers. Changing the polarity of the reaction medium provides a method to increase the vinyl content of the polymer. For this reason, tetrahydrofuran (THF) was added to the cyclohexane solution of the monomer in one of the low molecular weight polymerizations to obtain two polymers with similar molecular weights differing in content of the 1,2 vinyl isomer.

The double-bond microstructure of the polybutadienes was determined by infrared spectroscopy. The absorption bands used to resolve the content of the different double bonds in the polymer chains were 966 cm^{-1} for 1,4 trans, 910 cm^{-1} for 1,2 vinyl, and 735 cm^{-1} for the 1,4 cis.[6,7] The infrared measurements were made using 2% (weight) solutions in carbon disulfide.

Several techniques were used to determine the molecular weights and molecular weight distribution (M_w/M_n) of the polymers. Gel permeation chromatography (GPC) was performed using a Waters 150-C ALC-GPC instrument. A set of five μ-Styragel columns was used with nominal pore sizes 10^6, 10^5, 10^4, 10^3, and 500 Å. Toluene was the carrier solvent, and the flow rate was 1.0 mL/min. The universal calibration curve was used with linear polystyrene standards (Pressure Chemicals). A Chromatrix KMX-6 low-angle laser light scattering instrument was used to determine the weight-average molecular weights (M_w) of the samples. Number-average molecular weights were measured by membrane (Knauer) and vapor pressure osmometry (Wescan 233).

The results of these characterizations are summarized in Tables I and II.

3. Columns. The polymer samples were solubilized in toluene or in chloroform and mixed with a known quantity of silanized Chromosorb (WDMCS 100/120 mesh) which allows no adsorption on the support. The solvent was then removed by vacuum and nitrogen stripping, and the coated support was fed into 60-cm-long, $^1/_4$-in.-O.D. copper tubes. The solvent was further removed once the column was installed, by flowing helium at 80 °C for about 30 h. The weight percent of polymer in the impregnated support was over 15% for all columns: in these conditions the effect of adsorption is negligible.[3] The mass of polymer in the columns was calculated by emptying them and calcining the stationary phases in an oven at 800 °C for more than 8 h.

Solute (0.1 μL) was injected with a Hamilton syringe. All the solvents were reagent grade from C. Erba, Fluka, and Merck.

Results and Discussion

In polymer solutions, activity coefficients are more conveniently based in mass rather than in molar fraction.[8] As discussed in numerous references (e.g. ref 9), the activity coefficient at infinite dilution of a solvent in a polymer at temperature T and zero pressure, Ω_1^∞, is related to the specific retention volume corrected to 273.15 K, V_g^0, by

$$\ln(\Omega_1^\infty) = \ln\left(\frac{R273.15}{M_1 V_g^0 P_1^s}\right) - \frac{(B_{11} - \upsilon_1^0)P_1^s}{RT} \qquad (1)$$

where B_{11}, P_1^s, and υ_1^0 are, respectively, the second virial coefficient, the vapor pressure, and the molar volume of the solvent at the column absolute temperature T; R is the universal gas constant. The specific retention volume is given by

$$V_g^0 = (t_r - t_a)\frac{F}{W}\left(\frac{273.15}{T_f}\right)j_3^2\left(\frac{P_f - P_w^s}{P_o}\right) \tag{2}$$

In eq 2, W is the mass of polymer in the column, F is the carrier gas flow, T_f and P_f are the absolute temperature and pressure at the flow meter, P_w^s is the vapor pressure of water at T_f, t_r and t_a are the retention time of the solvent and the dead time, respectively. j_3^2 represents the correction factor for gas compressibility inside the column; it is given by

$$j_3^2 = \frac{3}{2}\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \tag{3}$$

where P_i and P_o are the pressure at the input and at the output of the column.

For all the volatile liquids, saturation pressures were calculated with the Antoine equation,[10] second virial coefficients with the correlation of Hayden–O'Connell,[11] and liquid molar volumes with the correlation of Yen–Woods.[12]

The dead time t_a is repeatedly measured by air injections during the isothermal runs to avoid errors due to possible variations in carrier flow. The flow rate is also measured several times, because its variation produces an important source of error.

As the Flory χ parameter is extensively used in polymer solutions, it is useful to report also the χ values calculated from the experimental V_g^0 data. The Flory parameter χ can be calculated directly from Ω_1^∞:[13]

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

with

$$r = \frac{(M_2)_n^\infty \rho_1}{M_1 \rho_2} \tag{5}$$

Where ρ and M are the mass density and molecular weight, respectively, subscript 2 refers to polymer, and subscript n indicates number average. The following expression was used to calculate the densities of the polymers:[7]

$$\rho_2\ (\mathrm{g/mL}) = 0.895 \exp(-0.00075(t\ (^\circ\mathrm{C}) - 25)) \tag{6}$$

In Table III, experimental results for V_g^0, Ω_1^∞, and χ are listed at different temperatures for several volatile liquids in the different polymer samples. The activity coefficients and specific retention volumes are different for the three polymers; the differences are in general much wider than the experimental uncertainties.

To compare our experimental data with those in the literature, we calculated V_g^{100} ($V_g^{100} = V_g^0 \times 373.15/273.15$) at 100 °C for solvents in polymers 1 and 3 of this work and in a polybutadiene reported by Romdhane et al.[14]

The characteristics of this polybutadiene (PBD[14]) are M_n = 22 600, M_w/M_n = 1.06, with the following composition: trans(1,4) 52%, cis(1,4) 40%, vinyl(1,2) 8%. We also compared the retention values in polymer 2 (which has the higher content of vinylic isomer) with the ones in the wholly vinylic polybutadiene, PVE (molecular weight not reported), reported by Du et al.[13]

Agreement is good according to both structures and molecular weight. Values for polymer 1 are closer to those for PBD, in agreement with their similar structure. For methanol and acetonitrile, there is a disagreement; the values in ref 14 are much higher. Values for polymer 2 agree well also with those for PVE.

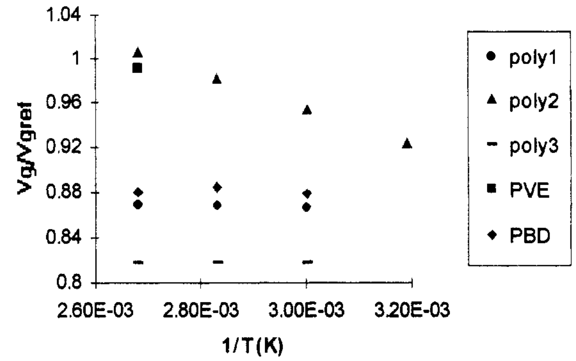

Figure 2.

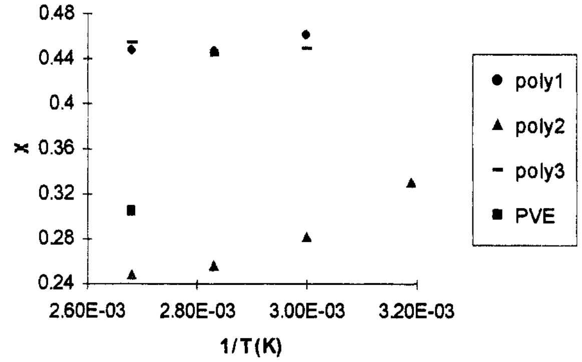

Figure 3.

Differences in solvent–polymer interactions are evident from one polymer to another.

To indicate differences in polymer interactions, Figure 2 shows the ratio between the V_g for cyclohexane and that for carbon tetrachloride at different temperatures, for the polymers in this work and for PBD.[14] In this figure, the effect of different structures is shown more strongly than the effect of different molecular weights. Moreover the good agreement between polymer 1 and PBD is also evident.

In Table III, the observed variation of the χ Flory parameter with temperature is low for the three polymers, for almost every solvent, and it is generally higher for polymer 3.

For systems with χ less than 0.4, χ increases with decreasing temperature.

In Figure 3, the χ parameter is plotted as a function of temperature for 1-chlorobutane and the polymers investigated in this work. The value at 373.15 K from ref 13 for PVE is also reported. For a relatively good solvent, the effect of the different structures between polymers 1 and 2 is more important than that of different molecular weights between 1 and 3.

With the V_g^0 data, partial molar enthalpies of solution of the solutes at infinite dilution in the polymers, namely $\overline{H}_1^{s,\infty}$, can be calculated from the slope of $\ln(V_g^0)$ versus $1/T$ lines, as follows:[2]

$$\overline{H}_1^{s,\infty} = -R\frac{\partial(\ln(V_g^0))}{\partial(1/T)} \tag{7}$$

In eq 7 it is assumed that the correction for nonideality of the solvent (in eq 1, second term in the right hand side), does not vary appreciably with temperature. The $\overline{H}_1^{s,\infty}$ values in the temperature range investigated (see Table III) are reported in Table IV, together with values obtained in ref 14 for PBD. The data for polymer 1 and PBD are similar except for methanol and acetonitrile.

Table IV. Partial Molar Enthalpies at Infinite Dilution of the Solutes in the Polymers, $(\overline{H}_1^{S\infty})$, kJ/(g mol)

component	POLY1	POLY2	POLY3	PBD[14]
n-pentane	24	25		
n-hexane	28	30		29
n-heptane	33	34	32	
n-octane	38	38	37	
1-hexene	30	29		
1-heptene	34	33	32	
1-octene	37	38	36	
cyclohexane	31	30	30	30
methylcyclohexane	33	33		
ethylcyclohexane	38	38		
benzene	32	31	31	31
toluene	36	36	35	36
acetone	25	25		28
methyl ethyl ketone	29	30	27	29
methyl isobutyl ketone	36	35	31	35
diethyl ketone	34	34	33	
methanol	18	18		43
ethanol	23	23		
1-propanol	29	29	36	
2-propanol	23	25		27
1-butanol	34	32	41	34
acetonitrile	24	24		32
propionitrile	28	28	29	
butyronitrile	32	33		
methyl acetate	42	27		
ethyl acetate	33	31	32	32
propyl acetate	35	35	35	
butyl acetate	39	40		
chloroform	31	30	33	30
carbon tetrachloride	31	32	30	31
1-chloropropane	27	27	27	
1-chlorobutane	31	30	31	
1-chloropentane	35	35		
tetrahydrofuran	31	30		31
diethyl ether	26	26		
dipropyl ether	33	62		
dibutyl ether	41			

Table V. PHCT Parameters for Some Polybutadiene Polymers and Organic Compounds

	T^* (K)	V^* (cm^3/mol)	C
Poly1 (12 200)	451.41	8471.7	257.5
Poly2 (13 100)	451.41	9096.6	276.5
PBD (23 956)	451.41	16635.0	505.7
Poly3 (108 000)	451.41	74995.2	2279.8
cyclohexane	321.84	83.28	2.01
benzene	368.10	51.61	1.68
1-butanol	360.74	20.67	2.43
toluene	376.25	67.56	1.80
ethyl acetate	304.27	66.99	2.31
ME ketone	247.0	168.6	3.17

The effect of different polymer structures on their interactions with infinitely dilute solutes was investigated also using the PHCT equation of state.[15,16]

In this equation the parameters of the polymer, T^*, v^*, and c, are related to the molecular weight; they are connected with the temperature, the molar volume, and the form and flexibility of the compound, respectively, and obtained from *PVT* data.

Due to the very few *PVT* data available in literature, the PHCT parameters for polybutadiene polymers were calculated using the density correlation reported in eq 6. For pure solutes the parameters were directly calculated from vapor pressure data. All parameters are reported in Table V.

The extention to a mixture of the equation of state requires the definition of combining and mixing rules.[16] A binary interaction parameter K_{ij} (function of the temperature) is included in the geometric combining rule of the pure component ϵ (potential energy per unit area).

Table VI. Binary Interaction Coefficients K_{ij} at 90 °C of Organic Compounds (i) in Polybutadiene Polymers (j) for the PHCT Equation

	Poly1 (12 200)	Poly2 (13 100)	PBD (23 956)	Poly3 (108 000)
cyclohexane	0.162	0.157	0.182	0.229
1-butanol	0.408	0.405	0.437	0.498
ME ketone	0.084	0.082	0.094	0.121
benzene	0.517	0.499	0.534	0.580
toluene	0.186	0.185	0.209	0.267
ethyl acetate	0.197	0.192	0.217	0.274

By fitting the weight fraction infinite-dilution activity coefficient data (Table III), it was possible to calculate the interaction coefficients for binary mixtures of polybutadiene polymers and volatile liquids. The binary coefficients (at 90 °C), for polymers of similar structure (Poly 1, Poly 3, PDB), grow with increasing polymer molecular weight. For Poly 2, of different structure, the values obtained do not follow the same trend (see Table VI).

Conclusions

Retention volumes were measured at several temperatures for 26 volatile liquids in different polybutadienes of different structure and molecular weight. Mass-fraction activity coefficients, Flory χ parameters, and infinite-dilution partial molar enthalpies were calculated. The data show the effect of polymer molecular weight and structure. Binary interaction parameters of the PHCT equation of state were obtained for several volatile liquids with the polymers.

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