J. Chem. Eng. Data **1999,** *44,* 839−845

Infinite-Dilution Activity Coefficients of Polar and Nonpolar Solvents in Solutions of Hyperbranched Polymers

Alessandro Polese, Cristina Mio,* and Alberto Bertucco

Istituto di Impianti Chimici, Università di Padova, Via Marzolo 9, I-35131 Padova, Italy

Infinite-dilution activity coefficients are measured for several polar and nonpolar solvents in hyperbranched polymers using inverse gas chromatography in the temperature range 40−160 °C. Two kinds of polymers are studied: comb polymers and dendritic polymers. The combs are poly(styrene-*co*-maleic anhydride) with alkyl side chains of different lengths (C12, C22). The solvents are: acetone, toluene, tetrahydrofuran (THF), and chloroform. Solvent solubility in the combs depends on the ratio between the polar backbone and the nonpolar side chain of the polymer. The dendrimers are amine-terminated poly(propylenimine) of generation 2 to 5. The solvents are: methanol, ethanol, ethyl acetate, toluene, and THF. Solvent activity coefficients change with respect to the dendrimer generation number, reaching a minimum at generation 4. Because the dendrimers are basic, the solvent quality is higher for slightly acidic solvents, such as methanol and ethanol. Flory's interaction parameters are calculated for the solvent/dendrimer systems.

Introduction

Hyperbranched polymers (such as star, comb, brush, and dendritic polymers) have applications in many fields. For example, they can be used as chemical sensors (Wells and Crooks, 1996), catalysts (Knapen et al., 1994), liquid crystals (Allia et al., 1997), chromatographic materials (Dubin et al., 1992; Castagnola et al., 1995), surfactants (Xu et al., 1992; Li et al., 1992), or in the biomedical field as drug-delivery devices or gene vectors (Merrill, 1993; Jansen et al., 1995; Haensler and Szoka, 1993), or also in blends with linear polymers to improve the performance of plastics, coatings, or lubricants (Gersappe et al., 1994; Israels et al., 1995; Simms, 1993; Carr et al., 1996).

Despite the wealth of potential applications, so far few experimental studies of thermodynamic properties of polymers in solution have focused on polymers with a well-characterized branched structure (Cowie et al., 1979; Faust et al., 1989; Yokoyama et al., 1991; Mio et al., 1997; 1998), probably because of the difficulty in manufacturing these macromolecules. Because of recent advances in polymer synthesis, regularly branched polymers are now more easily available (Frechet and Hawker, 1996; Lutz and Rempp, 1988; Newkome et al., 1996; Tomalia and Durst, 1993).

In industrial polymer production, design and development of processes require thermodynamic data, such as vapor pressure as a function of liquid composition. Comparing the experimental solution behavior of well-defined, monodisperse branched, and linear macromolecules may provide insight as to what extent branching affects polymer-solution properties; in addition, it is useful for testing and developing models for branched polymers toward rational design of products with specific characteristics. In particular, comparison of properties of classical linear polymers and dendrimers is of special interest because the globular shape and the high number of surface groups of dendrimers may soon lead to new applications for this type of polymer.

Our work aims to measure activity coefficients of several solvents infinitely dilute in some hyperbranched polymers, using a standard gas-chromatographic technique. Inverse gas chromatography provides a convenient and fast method to obtain infinite-dilution solvent volatilities from concentrated polymer solutions (see, for example, Smidsrod and Guillet, 1969; Newman and Prausnitz, 1973; Romdhane and Danner, 1991).

We studied the thermodynamic behavior of several common organic solvents in two kinds of hyperbranched polymers: comb and dendritic polymers.

Solvent infinite-dilution activity coefficients are provided at temperatures ranging from 40 to 160 °C and Flory's interaction parameters are given for the solvent/dendrimer systems.

Experimental Section

Apparatus. Inverse gas chromatography (gas−liquid chromatography) was applied to study polymer−solvent interactions. The gas chromatograph (GC) was a Shimadzu Model GC-14A. Solvent samples were injected directly into the chromatographic column with a 1-μL Hamilton Microliter No. 7001 syringe. A thermal-conductivity detector (TCD) and a recorder were used to measure solvent concentration in the carrier gas.

The flow rate of the helium carrier gas was measured within ±0.1 mL/min with a bubble flowmeter at the output of the TCD. The carrier-gas flow was controlled with the same accuracy by the manual pressure regulators of the GC. A membrane manometer with precision of 0.1 bar (FM, Marcon, Italy) was used to measure the column-inlet pressure.

The temperature was kept constant within ±0.1 °C by the air bath of the GC equipped with a temperature controller. The chromatographic column was placed in the middle of the bath, where the temperature gradient along the column was checked to be within ± 0.5 °C.

Materials. The column solid support was 100/120 mesh Chromosorb pink, acid washed, and silanized (Supelco, Bellefonte, PA). Because solvent adsorption on the support is prevented because of the silanizing treatment, this support can be used with both polar and nonpolar solvents.

---

* To whom correspondence should be addressed.

10.1021/je9803025 CCC: $18.00

Table 1. Solvent Characteristics

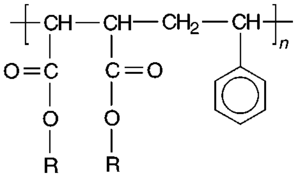
solvent	manufacturer	purity
chloroform	Baker	>99.0%
chloroform	PROLABO	>99.2−99.6%
toluene	PROLABO	>99.7%
methanol	Baker	>99.8%
THF	PROLABO	>99.0%
acetone	PROLABO	>99.8%
ethanol	PROLABO	>99.8%
ethyl acetate	Rudi Pont	>99.5%

In addition, it is characterized by a high surface area, thus allowing higher amounts of stationary phase to be loaded. Solvent characteristics are given in Table 1. All solvents were used without further fractionation.

Two kinds of hyperbranched polymers were studied: comb and dendritic polymers. Comb polymers have a linear backbone and several side chains, also called teeth, attached to it. The degree of branching of comb polymers can be changed by changing either the number of teeth (or their frequency along the backbone) or the tooth length.

The backbone of the combs was the copolymer of polystyrene and poly(maleic anhydride) (PSMA) of 50% molar composition and MW = 116 000 Da. It was obtained through radical polyaddition of styrene and maleic anhydride.

The structure of the comb polymer repeat unit is:



The alkyl side chains were attached by esterification of the anhydride group with alcohols (1-dodecanol and 1-docosanol). The yield of the reaction was approximately 50%; therefore, the molecular weights of the comb, named C12 and C22, were approximately 213 000 and 293 400 Da, respectively. PSMA, C12, and C22 were kindly donated by P. R. Chatterji (Indian Institute of Chemical Technology, Hyderabad, India).

Differential scanning calorimetry (DSC) was performed on the polymers using a Perkin-Elmer calorimeter (model DSC-4). The DSC traces did not show a clear glass transition for the polymers, but the glass-transition temperature T_g was less than 100 °C for PSMA and C12; C22 showed a sharp crystalline peak around 64 °C (the long C22 side chains probably form crystalline structures).

The decomposition temperatures in inert atmosphere were 125, 180, and 150 °C for PSMA, C12, and C22, respectively. The GC experiments were performed below these decomposition temperatures.

Dendrimers are highly branched, tree-like molecules that emanate from a central multifunctional core. They are grown in concentric layers, called generations, through multistep repetitive synthesis (Frechet and Hawker, 1996; Newkome et al., 1996). After several layers, the surface becomes densely packed and the dendrimer assumes a spherical, globular shape. Dendrimers possess three architectural components: a core, an interior, and a surface with numerous end groups that can be functionalized by chemical reaction.

The dendrimers used were poly(propylenimine) with a tetrafunctional diaminebutane core (DSM Fine Chemicals, Geleen, Netherlands). They were synthesized with the divergent method, through successive Michael additions and hydrogenations of the nitrile groups (de Brabander-van den Berg et al., 1994; de Brabander et al., 1996). Their commercial name is Astramol. Four generations were used: Astramol Am 8, MW = 773 Da (generation 2); Astramol Am 16, MW = 1687 Da (generation 3); Astramol Am 32, MW = 3514 Da (generation 4); Astramol Am 64, MW = 7166 Da (generation 5).

Table 2. Mass of Polymer Loaded and GC Column Diameters

polymer	mass of polymer w_2, g	column external diameter, mm
poly(styrene-*co*-maleic anhydride)	0.290	3.17
C12 esterified poly(styrene-*co*-maleic anhydride)	0.683	6.35
C22 esterified poly(styrene-*co*-maleic anhydride)	0.564	6.35
Astramol-Am 8	0.945	6.35
Astramol-Am 16	0.545	6.35
Astramol-Am 32	0.759	6.35
Astramol-Am 64	0.767	6.35

The samples were monodisperse. They were obtained through successive Michael additions of acrylonitrile and subsequent hydrogenation of the surface groups from nitrile to amine. For Am64, 1% of the nitrile surface groups did not react to become amines in the last hydrogenation step. All other samples were highly pure.

All dendrimers were viscous liquid at room temperature; their T_g was approximately −65 °C (de Brabander et al., 1994) and their thermal decomposition temperature was greater than 400 °C.

Column Preparation. The columns were prepared by first dissolving a known mass of polymer in a suitable solvent. PSMA and C12 were dissolved in acetone, C22 in chloroform, and the Astramol dendrimers in methanol.

The solution was stirred with a known mass of solid support to obtain a column packing with about 15% mass polymer. The exact percentage was obtained by calcination of a sample of the coated support at high temperatures (700−800 °C) for 8 h. Because the calcination process removes all polymer coating from the support, the amount of polymer is calculated from the difference in sample weight before and after calcination. The solvent was eliminated using a rotating evaporator (Inlabo, model EVI 90/1), whereas the suspension was stirred continuously for 2−3 h to obtain a perfectly homogeneous coated support. The support was then dried to constant weight in a thermostatic oven for 4−6 days. The oven temperature was kept low enough to prevent polymer melting or flow.

The coated support was packed into 1/4- or 1/8-in. o.d. stainless steel tubings, while vibrating the column to ensure uniform packing. The columns were bent in a U or spiral shape to fit inside the thermostatic bath of the GC. Table 2 gives the diameters of the columns and the amounts of each polymer in them; the loading percentage was always between 14 and 20%, with a precision of ±0.5 mg.

After mounting the columns onto the chromatograph, the connections were checked carefully for leaks. All columns were conditioned overnight to remove any moisture or solvents still present. The process was carried out at 15−20 °C higher than the maximum temperature reached during the GC experiments. The carrier gas flow rate was 60 mL/min and 15 mL/min for 1/4- and 1/8-in. o.d. columns, respectively.

Procedure. A very small amount of the solvent (0.1 μL) was injected into the carrier gas where it was vaporized

Table 3. Experimental Conditions

polymer	temperature *t*,°C	carrier flow rate, mL/min	column pressure drop, bar
poly(styrene-*co*-maleic anhydride)	90−120	1.6−2	0.75
C12 esterified poly(styrene-*co*-maleic anhydride)	90−160	8−12.2	0.15−0.25
C22 esterified poly(styrene-*co*-maleic anhydride)	90−155	7.8−8.6	0.15−0.2
Astramol-Am 8	40−140	9.1−10.1	0.2−0.25
Astramol-Am 16	60−140	10.3−11.1	0.14−0.2
Astramol-Am 32	60−140	9.2−9.9	0.175−0.25
Astramol-Am 64	60−140	10.6−11.3	0.15−0.2

and carried through the chromatographic column, together with air (0.1−0.2 μL), used as reference (air is not absorbed by the polymer).

Table 3 gives the experimental conditions. At the reported (low) values of the carrier flow rate, the solvent injected could distribute between the mobile (helium gas) and fixed (liquid polymer) phase as a series of vapor−liquid equilibrium steps (Heintz et al., 1979).

The detector recorded the air peak, related to the column dead volume, and the solvent peak. For both air and solvent, the maximum of the recorded peak was taken as the retention time. This procedure was correct because of peak symmetry.

For each solvent, 5 to 10 injections were performed to ensure a good reproducibility of the data at any given temperature. This can be checked from the values of σ, the standard deviation reported in the results (Tables 4 to 12).

Reliability of the apparatus was established by reproducing experimental data from the literature for toluene, *n*-heptane, acetone, chloroform, THF, and methanol in poly(styrene) and for methanol, toluene, and THF in poly(methyl methacrylate). The data obtained agreed with those of Alessi et al. (1992) within experimental uncertainty.

Inverse GC can be applied correctly only if the solvent pulse establishes local equilibrium with the polymer throughout the column, and if all the mass of polymer participates in the solvent equilibrium distribution. The first goal was achieved by sufficiently lowering the carrier flow rate. For the second goal, a practical way to check it, according to Smidsrød and Guillet (1969), is to plot the logarithm of the retention volume as a function of the inverse of the absolute temperature: if a straight line is obtained in a large temperature range, the measurement is reliable in that range. This condition was satisfied for all our experiments. Figures 1 and 2 show plots for a comb polymer (C22) and for a dendrimer (Am 32), respectively.

Data Reduction

The mass-based infinite-dilution activity coefficient of the solvent, Ω_1^∞, is obtained from the experimental GC data, i.e., from the retention time, using (Kikic, 1980):

$$\Omega_1^\infty = \frac{W_2RT}{Q(t_{r\infty}-t_m)jMW_1}\,\frac{\hat{\phi}_1^v}{P_1^{sat}\exp\left[\dfrac{P_1^{sat}(B_{11}-v_{1sat}^l)+Pv_{1sat}^l}{RT}\right]} \qquad (1)$$

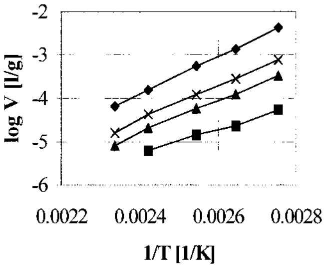


Figure 1. Specific retention volume as a function of temperature for C22 comb polymer: toluene (◆); acetone (■); chloroform (▲); THF (×).

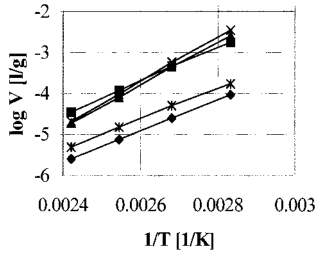


Figure 2. Specific retention volume as a function of temperature for Am 32 dendrimer: ethyl acetate (◆); toluene (■); methanol (▲); ethanol (×); THF (*).

Table 4. Infinite-Dilution Activity Coefficients of Toluene in Comb Polymers

		backbone	C12	C22
$t = 160$ °C	$t_r - t_m$ [min]		0.597	
	$\sigma(t_r - t_m)$		0.0065	
	Ω_1^∞		13.2	
	$\sigma(\Omega_1^\infty)$		0.14	
$t = 155$ °C	$t_r - t_m$ [min]			1.823
	$\sigma(t_r - t_m)$			0.031
	Ω_1^∞			5.44
	$\sigma(\Omega_1^\infty)$			0.091
$t = 140$ °C	$t_r - t_m$ [min]		0.863	2.754
	$\sigma(t_r - t_m)$		0.0073	0.0066
	Ω_1^∞		13.5	5.15
	$\sigma(\Omega_1^\infty)$		0.11	0.012
$t = 120$ °C	$t_r - t_m$[min]	5.801	2.192	4.406
	$\sigma(t_r - t_m)$	0.041	0.046	0.017
	Ω_1^∞	10.5	11.8	4.84
	$\sigma(\Omega_1^\infty)$	0.073	0.24	0.018
$t = 105$ °C	$t_r - t_m$ [min]	7.279	4.187	6.516
	$\sigma(t_r - t_m)$	0.56	0.12	0.035
	Ω_1^∞	10.6	8.97	4.92
	$\sigma(\Omega_1^\infty)$	0.80	0.26	0.026
$t = 90$ °C	$t_r - t_m$ [min]	8.843	7.989	9.959
	$\sigma(t_r - t_m)$	0.62	0.090	0.024
	Ω_1^∞	11.9	7.09	4.70
	$\sigma(\Omega_1^\infty)$	0.86	0.080	0.011

In Eq 1 Ω_1^∞ is the mass fraction solvent activity coefficient at infinite dilution, W_2 is the mass of polymer loaded in the GC column, R is the universal gas constant, T is the absolute temperature, Q is the carrier-gas flow rate, $t_{r\infty}$ is the retention time of solvent at infinite dilution, t_m is the dead time of the column, MW_1 is the solvent molecular weight, j is the James Martin's factor, ϕ_1^v is the vapor-phase solvent fugacity coefficient, P_1^{sat} is the solvent vapor pressure, B_{11} is the solvent second virial coefficient, v_{1sat}^l is the liquid molar volume of solvent at saturation, and P is the total pressure. The gas-phase mixture was considered ideal; therefore: $\phi_1^v = 1$.

Tables 4−12 summarize the experimental solvent infinite-dilution activity-coefficient data.

Table 5. Infinite-Dilution Activity Coefficients of Acetone in Comb Polymers

		backbone	C12	C22
$t = 160$ °C	$t_r - t_m$ [min]		0.265	
	$\sigma(t_r - t_m)$		0.0066	
	Ω_1^∞		13.6	
	$\sigma(\Omega_1^\infty)$		0.34	
$t = 155$ °C	$t_r - t_m$ [min]			
	$\sigma(t_r - t_m)$			
	Ω_1^∞			
	$\sigma(\Omega_1^\infty)$			
$t = 140$ °C	$t_r - t_m$ [min]		0.368	0.685
	$\sigma(t_r - t_m)$		0.014	0.018
	Ω_1^∞		13.3	8.71
	$\sigma(\Omega_1^\infty)$		0.50	0.21
$t = 120$ °C	$t_r - t_m$ [min]	8.036	0.817	0.909
	$\sigma(t_r - t_m)$	0.21	0.069	0.058
	Ω_1^∞	2.79	12.2	9.00
	$\sigma(\Omega_1^\infty)$	0.073	0.99	0.60
$t = 105$ °C	$t_r - t_m$ [min]	11.160	1.350	1.111
	$\sigma(t_r - t_m)$	0.27	0.071	0.081
	Ω_1^∞	2.42	9.86	10.2
	$\sigma(\Omega_1^\infty)$	0.059	0.51	0.70
$t = 90$ °C	$t_r - t_m$ [min]	24.960	2.429	1.496
	$\sigma(t_r - t_m)$	1.45	0.040	0.034
	Ω_1^∞	1.47	7.59	10.2
	$\sigma(\Omega_1^\infty)$	0.089	0.13	0.22

Table 6. Infinite-Dilution Activity Coefficients of Chloroform in Comb Polymers

		backbone	C12	C22
$t = 160$ °C	$t_r - t_m$ [min]		0.285	
	$\sigma(t_r - t_m)$		0.0045	
	Ω_1^∞		7.35	
	$\sigma(\Omega_1^\infty)$		0.11	
$t = 155$ °C	$t_r - t_m$ [min]			0.743
	$\sigma(t_r - t_m)$			0.024
	Ω_1^∞			4.69
	$\sigma(\Omega_1^\infty)$			0.15
$t = 140$ °C	$t_r - t_m$ [min]		0.415	1.156
	$\sigma(t_r - t_m)$		0.0079	0.012
	Ω_1^∞		6.84	3.00
	$\sigma(\Omega_1^\infty)$		0.13	0.030
$t = 120$ °C	$t_r - t_m$ [min]	2.644	0.933	1.657
	$\sigma(t_r - t_m)$	0.099	0.067	0.045
	Ω_1^∞	4.76	6.19	2.85
	$\sigma(\Omega_1^\infty)$	0.18	0.43	0.079
$t = 105$ °C	$t_r - t_m$ [min]	4.676	1.536	2.298
	$\sigma(t_r - t_m)$	0.22	0.072	0.044
	Ω_1^∞	3.72	5.02	2.86
	$\sigma(\Omega_1^\infty)$	0.18	0.23	0.054
$t = 90$ °C	$t_r - t_m$ [min]	8.779	2.737	3.281
	$\sigma(t_r - t_m)$	1.68	0.039	0.033
	Ω_1^∞	2.31	3.89	2.68
	$\sigma(\Omega_1^\infty)$	0.41	0.055	0.027

From Ω_1^∞, the mass-based Henry's constant is calculated using the expression:

$$H_{w1} = \Omega_1^\infty \frac{MW_1}{MW_2} P_1^{\ \mathrm{sat}} \exp\left[\frac{P_1^{\ \mathrm{sat}}(B_{11} - v_{1\mathrm{sat}}^l) + P v_{1\mathrm{sat}}^l}{RT}\right] \quad (2)$$

where MW_2 is the polymer molecular weight. For liquid polymers, Flory's interaction parameter at infinite dilution, χ, can be calculated from the relation:

$$\chi = \ln\Omega_1^\infty - \left(1 - \frac{1}{r}\right) + \ln\frac{\rho_1}{\rho_2} \quad (3)$$

where r, the number of sites occupied by the polymer in Flory's lattice, is given by:

$$r = \frac{MW_2}{MW_1}\frac{\rho_1}{\rho_2} \quad (4)$$

Table 7. Infinite-Dilution Activity Coefficients of THF in Comb Polymers

		backbone	C12	C22
$t = 160$ °C	$t_r - t_m$ [min]		0.377	
	$\sigma(t_r - t_m)$		0.0052	
	Ω_1^∞		9.39	
	$\sigma(\Omega_1^\infty)$		0.13	
$t = 155$ °C	$t_r - t_m$ [min]			0.991
	$\sigma(t_r - t_m)$			0.032
	Ω_1^∞			4.41
	$\sigma(\Omega_1^\infty)$			0.14
$t = 140$ °C	$t_r - t_m$ [min]		0.521	1.577
	$\sigma(t_r - t_m)$		0.015	0.0063
	Ω_1^∞		9.23	3.72
	$\sigma(\Omega_1^\infty)$		0.28	0.015
$t = 120$ °C	$t_r - t_m$ [min]	7.089	1.243	2.320
	$\sigma(t_r - t_m)$	0.22	0.061	0.043
	Ω_1^∞	3.13	7.89	3.53
	$\sigma(\Omega_1^\infty)$	0.097	0.38	0.066
$t = 105$ °C	$t_r - t_m$ [min]		2.203	3.275
	$\sigma(t_r - t_m)$		0.11	0.059
	Ω_1^∞		5.98	3.42
	$\sigma(\Omega_1^\infty)$		0.31	0.062
$t = 90$ °C	$t_r - t_m$ [min]		3.943	4.723
	$\sigma(t_r - t_m)$		0.077	0.068
	Ω_1^∞		4.64	3.20
	$\sigma(\Omega_1^\infty)$		0.090	0.046

Table 8. Infinite-Dilution Activity Coefficients of Toluene in Dendrimers

		Am 8	Am 16	Am 32	Am 64
$t = 140$ °C	$t_r - t_m$ [min]		1.169	2.181	
	$\sigma(t_r - t_m)$		0.0054	0.024	
	Ω_1^∞		8.45	7.24	
	$\sigma(\Omega_1^\infty)$		0.039	0.079	
$t = 120$ °C	$t_r - t_m$ [min]		1.861	3.740	
	$\sigma(t_r - t_m)$		0.021	0.017	
	Ω_1^∞		8.10	6.94	
	$\sigma(\Omega_1^\infty)$		0.091	0.032	
$t = 100$ °C	$t_r - t_m$ [min]		3.287	6.249	
	$\sigma(t_r - t_m)$		0.049	0.017	
	Ω_1^∞		8.11	6.65	
	$\sigma(\Omega_1^\infty)$		0.12	0.018	
$t = 80$ °C	$t_r - t_m$ [min]	0.400	5.774	10.740	0.377
	$\sigma(t_r - t_m)$	0.0035	0.061	0.025	0.015
	Ω_1^∞	224	8.07	7.05	174
	$\sigma(\Omega_1^\infty)$	2.0	0.086	0.017	7.1
$t = 60$ °C	$t_r - t_m$ [min]	0.742	10.070		0.764
	$\sigma(t_r - t_m)$	0.012	0.028		0.0095
	Ω_1^∞	230	8.94		161
	$\sigma(\Omega_1^\infty)$	3.8	0.024		2.0
$t = 40$ °C	$t_r - t_m$ [min]	1.543			
	$\sigma(t_r - t_m)$	0.025			
	Ω_1^∞	247			
	$\sigma(\Omega_1^\infty)$	4.1			

In Eq 4 ρ_1 and ρ_2 are the solvent and polymer density, respectively.

Table 13 gives Flory's interaction parameters for solvent-dendrimer systems.

Results and Discussion

Comb Polymers. The experimental data for the combs show that the solubility of toluene generally increases (i.e., its activity coefficient decreases) from the backbone to C12, to C22 (Figure 3), whereas the solubility of acetone decreases as the polymer side-chain length increases (Figure 4). The solvent activity coefficients have an unusual behavior in C12 at high temperatures (above 105 °C). On the other hand, we did not detect any Z-shape curve when plotting logV_g versus $1/T$ for C12; we cannot explain the rapid rise of the activity coefficients in C12 with temperature.

With respect to one another, the affinity of acetone and toluene changes completely in the backbone and in the two

Table 9. Infinite-Dilution Activity Coefficients of Ethyl Acetate in Dendrimers

		Am 8	Am 16	Am 32	Am 64
$t = 140$ °C	$t_r - t_m$ [min]		0.389	0.698	
	$\sigma(t_r - t_m)$		0.0078	0.031	
	Ω_1^∞		11.5	10.2	
	$\sigma(\Omega_1^\infty)$		0.23	0.47	
$t = 120$ °C	$t_r - t_m$ [min]		0.555	1.130	
	$\sigma(t_r - t_m)$		0.0050	0.010	
	Ω_1^∞		11.6	9.78	
	$\sigma(\Omega_1^\infty)$		0.10	0.089	
$t = 100$ °C	$t_r - t_m$ [min]		0.856	1.770	
	$\sigma(t_r - t_m)$		0.033	0.036	
	Ω_1^∞		12.5	9.52	
	$\sigma(\Omega_1^\infty)$		0.49	0.20	
$t = 80$ °C	$t_r - t_m$ [min]		1.422	2.994	
	$\sigma(t_r - t_m)$		0.040	0.011	
	Ω_1^∞		12.4	9.54	
	$\sigma(\Omega_1^\infty)$		0.35	0.035	
$t = 60$ °C	$t_r - t_m$ [min]	0.349	2.201	5.250	0.386
	$\sigma(t_r - t_m)$	0.0050	0.093	0.016	0.0091
	Ω_1^∞	172	14.4	9.76	112
	$\sigma(\Omega_1^\infty)$	2.4	0.58	0.030	2.7
$t = 40$ °C	$t_r - t_m$ [min]	0.699			
	$\sigma(t_r - t_m)$	0.024			
	Ω_1^∞	179			
	$\sigma(\Omega_1^\infty)$	6.0			

Table 10. Infinite-Dilution Activity Coefficients of THF in Dendrimers

		Am 8	Am 16	Am 32	Am 64
$t = 140$ °C	$t_r - t_m$ [min]		0.527	0.930	
	$\sigma(t_r - t_m)$		0.020	0.029	
	Ω_1^∞		7.76	7.03	
	$\sigma(\Omega_1^\infty)$		0.32	0.22	
$t = 120$ °C	$t_r - t_m$ [min]		0.758	1.533	
	$\sigma(t_r - t_m)$		0.015	0.039	
	Ω_1^∞		7.51	6.39	
	$\sigma(\Omega_1^\infty)$		0.15	0.17	
$t = 100$ °C	$t_r - t_m$ [min]		1.208	2.408	
	$\sigma(t_r - t_m)$		0.021	0.013	
	Ω_1^∞		7.52	5.95	
	$\sigma(\Omega_1^\infty)$		0.13	0.031	
$t = 80$ °C	$t_r - t_m$ [min]		1.888	3.933	
	$\sigma(t_r - t_m)$		0.010	0.048	
	Ω_1^∞		7.50	5.86	
	$\sigma(\Omega_1^\infty)$		0.041	0.070	
$t = 60$ °C	$t_r - t_m$ [min]	0.294	2.830	6.710	0.286
	$\sigma(t_r - t_m)$		0.035	0.041	0.011
	Ω_1^∞	155	8.48	5.77	114
	$\sigma(\Omega_1^\infty)$		0.11	0.036	4.3
$t = 40$ °C	$t_r - t_m$ [min]	0.513			
	$\sigma(t_r - t_m)$	0.031			
	Ω_1^∞	170			
	$\sigma(\Omega_1^\infty)$	11			

combs. In the backbone, the activity coefficients of acetone are lower than those of toluene (Figure 5); in C12 they are similar, whereas in C22 the activity coefficients of acetone are much higher than those of toluene. Because the backbone contains oxygen atoms of the anhydride groups, it is likely that polar solvents, like acetone, are good solvents. However, nonpolar solvents (for example, toluene) are good solvents for the alkyl side chains. Therefore, the polar character of the polymers, i.e., their affinity for acetone, decreases as the comb side-chain length increases, and the opposite happens with toluene. Similar results were obtained in comb-polymer/solvent concentrated solutions (solvent weight fraction from 0.05 to 0.5) by Mio et al. (1997).

The activity coefficients of chloroform and THF do not have a simple, monotonic behavior with side-chain length of the comb polymers. Chloroform is a good solvent in C22, whereas its quality worsens in C12 and in the backbone. The solubility of THF is good in C22 and in the backbone, but it is low in C12. THF and chloroform are better solvents than acetone and toluene in both C12 and C22, whereas in the backbone the solvent quality improves from toluene to chloroform to acetone. THF and chloroform are considered good solvents for both alkyl polymers (such as polyisobutylene and polyethylene) and for polystyrene, and THF (but not chloroform) is a good solvent also for poly(maleic anhydride) (Brandrup and Immergut, 1989). We could not detect any trend in the GC data, probably because there is no specific affinity between these two solvents and a particular portion of the combs.

Table 11. Infinite-Dilution Activity Coefficients of Ethanol in Dendrimers

		Am 8	Am 16	Am 32	Am 64
$t = 140$ °C	$t_r - t_m$ [min]	1.216	0.925	1.745	0.534
	$\sigma(t_r - t_m)$	0.032	0.018	0.016	0.0073
	Ω_1^∞	10.5	6.39	5.41	15.6
	$\sigma(\Omega_1^\infty)$	0.29	0.13	0.048	0.21
$t = 120$ °C	$t_r - t_m$ [min]	1.654	1.753	3.423	0.748
	$\sigma(t_r - t_m)$	0.031	0.028	0.028	0.018
	Ω_1^∞	12.6	5.79	4.78	17.8
	$\sigma(\Omega_1^\infty)$	0.24	0.094	0.040	0.41
$t = 100$ °C	$t_r - t_m$ [min]	2.301	3.515	6.887	1.197
	$\sigma(t_r - t_m)$	0.025	0.021	0.033	0.030
	Ω_1^∞	15.7	5.11	4.06	19.7
	$\sigma(\Omega_1^\infty)$	0.17	0.030	0.020	0.50
$t = 80$ °C	$t_r - t_m$ [min]	3.337	7.650	14.530	2.574
	$\sigma(t_r - t_m)$	0.079	0.040	0.024	0.026
	Ω_1^∞	19.4	4.45	3.80	18.6
	$\sigma(\Omega_1^\infty)$	0.46	0.023	0.0062	0.18
$t = 60$ °C	$t_r - t_m$ [min]		17.080		
	$\sigma(t_r - t_m)$				
	Ω_1^∞		4.21		
	$\sigma(\Omega_1^\infty)$				

Table 12. Infinite-Dilution Activity Coefficients of Methanol in Dendrimers

		Am 8	Am 16	Am 32	Am 64
$t = 140$ °C	$t_r - t_m$ [min]	1.546	0.901	1.674	0.862
	$\sigma(t_r - t_m)$	0.020	0.026	0.018	0.0058
	Ω_1^∞	8.33	6.62	5.70	9.73
	$\sigma(\Omega_1^\infty)$	0.11	0.20	0.062	0.065
$t = 120$ °C	$t_r - t_m$ [min]	2.507	1.659	3.164	1.439
	$\sigma(t_r - t_m)$	0.0043	0.024	0.051	0.018
	Ω_1^∞	8.07	5.93	5.02	8.98
	$\sigma(\Omega_1^\infty)$	0.015	0.089	0.080	0.11
$t = 100$ °C	$t_r - t_m$ [min]	5.142	3.180	6.187	3.330
	$\sigma(t_r - t_m)$	0.013	0.010	0.013	0.060
	Ω_1^∞	6.46	5.21	4.17	6.52
	$\sigma(\Omega_1^\infty)$	0.017	0.017	0.0085	0.12
$t = 80$ °C	$t_r - t_m$ [min]	11.560	6.722	12.630	9.424
	$\sigma(t_r - t_m)$	0.17	0.020	0.013	0.13
	Ω_1^∞	4.80	4.39	3.79	4.40
	$\sigma(\Omega_1^\infty)$	0.075	0.013	0.0040	0.060
$t = 60$ °C	$t_r - t_m$ [min]		14.610		
	$\sigma(t_r - t_m)$				
	Ω_1^∞		4.00		
	$\sigma(\Omega_1^\infty)$				

Dendrimers. The experimental data for the 4 generations of the Astramol dendrimers show that the solubilities of the solvents are higher in Am 16 and Am 32 than in Am 8 and Am 64. It seems that there is a minimum in the infinite-dilution solvent activity coefficients in the fourth dendrimer generation (Am 32) (see Figures 6 and 7). However, Am 64 is not completely hydrogenated and 1% of its terminations are nitrile groups and not primary amines. Therefore, it is possible that the presence of the nitrile groups lowers the affinity of the polymers to the solvents, thus explaining why the activity coefficients are higher in Am 64 than in Am 32.

Table 13. Values of Flory's Parameter for Solvent/Dendrimer Systems

	t [°C]	Am 8	Am 16	Am 32	Am 64
methanol	140	0.767	0.485	0.319	0.848
	120	0.783	0.423	0.240	0.816
	100	0.601	0.335	0.0995	0.539
	80	0.342	0.202	0.0422	0.184
	60		0.133		
ethanol					
	140	1.01	0.441	0.253	1.30
	120	1.23	0.387	0.173	1.48
	100	1.49	0.301	0.0513	1.62
	80	1.73	0.198	0.0214	1.60
	60		0.175		
ethyl acetate					
	140		1.21	1.05	
	120		1.26	1.05	
	100		1.37	1.06	
	80		1.39	1.10	
	60	4.15	1.58	1.15	3.58
	40	4.21			
toluene					
	140		0.908	0.715	
	120		0.893	0.700	
	100		0.919	0.684	
	80	4.36	0.937	0.768	3.96
	60	4.41	1.06		3.90
	40	4.50			
THF					
	140		0.853	0.726	
	120		0.857	0.668	
	100		0.892	0.630	
	80		0.918	0.646	
	60	4.05	1.07	0.660	3.63
	40	4.17			

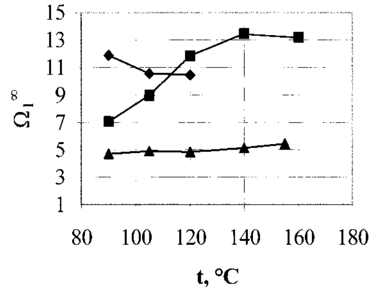


Figure 3. Toluene activity coefficients in comb polymers: backbone (◆); C12 (■); C22 (▲).

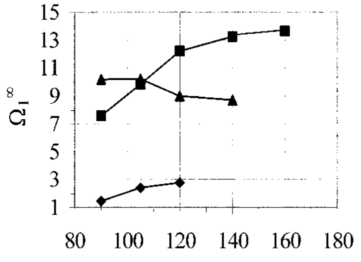


Figure 4. Acetone activity coefficients in comb polymers: backbone (◆); C12 (■); C22 (▲).

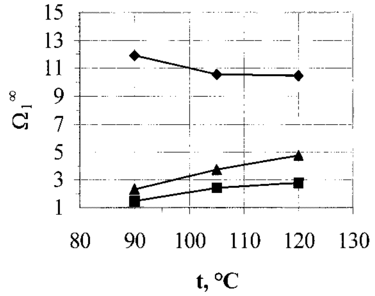


Figure 5. Activity coefficients of toluene (◆), acetone (■), and chloroform (▲) in poly(styrene-*co*-maleic anhydride).

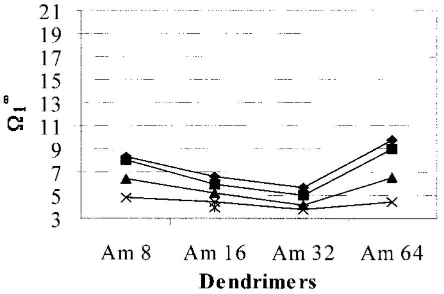


Figure 6. Methanol activity coefficients as a function of dendrimer generation number: *t* = 140 °C (◆); *t* = 120 °C (■); *t* = 100 °C (▲); *t* = 80 °C (×); *t* = 60 °C (*).

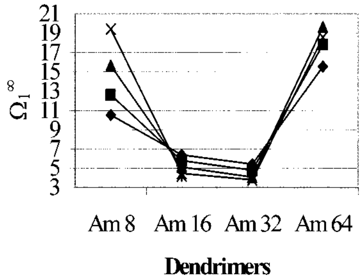


Figure 7. Ethanol activity coefficients as a function of dendrimer generation number: *t* = 140 °C (◆); *t* = 120 °C (■); *t* = 100 °C (▲); *t* = 80 °C (×); *t* = 60 °C (*).

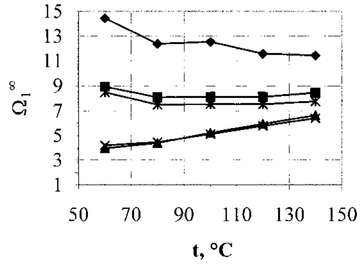


Figure 8. Activity coefficients of ethyl acetate (◆); toluene (■); methanol (▲); ethanol (×); THF (*) in Am 16 Astramol.

In Am16 the solvents studied have solubility behavior similar to that in Am 32. In both Am 16 and Am 32, the solvent solubility decreases in the following order: ethanol, methanol, THF, toluene, and ethyl acetate (Figure 8). The two alcohols have much lower activity coefficients than those of the other solvents.

Methanol and ethanol are the only solvents that are soluble in Am 8 and Am 64, whereas the other solvents had very small retention times and, therefore, very high activity coefficients (above 100).

The high affinity between Astramol and lower alcohols is not surprising. The dendrimers studied have numerous groups with a basic nature (the internal branches are tertiary amines and the surface end groups are primary amines); therefore, they can form strong hydrogen bonds with the OH group of the alcohols. On the contrary, THF and toluene cannot form hydrogen bonds; therefore, their affinity to the polymers is lower. Because ethyl acetate has a slightly basic character (it contains electron-donor oxygen atoms), it is a poor solvent for the dendrimers.

Generally, the activity coefficients of methanol and ethanol increase with temperature (Figure 8). Because hydrogen bonding is exothermic, alcohols can make hydrogen bonds with the dendrimer more easily at low temperatures. Therefore, their solubility decreases when passing from 60 to 140 °C.

Conclusions

The new experimental data show that the chemical composition of the comb polymers (i.e., the ratio of polar backbone/nonpolar side chains) strongly affects solvent solubility.

In the dendrimers, a maximum in solvent solubility was found in the fourth generation in the temperature range 60 to 140 °C. Because the dendrimers are basic, slightly acidic solvents are better solvents than the others studied; in particular, THF, toluene, and ethyl acetate are poor solvents for these polymers.

Our infinite-dilution experimental data are a useful starting point to study and understand the effect of comb-polymer side chains, dendrimer-generation number, and surface-end groups on polymer−solvent interactions.

Literature Cited

Alessi, P.; Hao, W.; Elbro, H. S. *Polymer Solution Data Collection*; DECHEMA: Frankfurt (D), 1992.

Allia, P.; Taverna, P.; Trossi, L.; Gallot, B.; Siyuan, H. Optical noise and dynamical properties of liquid crystal comb polymers with different mesogenic groups. *Liq. Cryst.* **1997**, *22*, 279−286.

de Brabander-van den Berg, E. M. M.; Nijenhuis, A.; Mure, M.; Keulen, J.; Reintjens, R.; Vanderbooren, F.; Bosman, B.; de Raat, R.; Frijns, T.; v.d. Wal, S.; Castelijns, M.; Put, J.; Meijer, E. W. Large scale production of polypropylenimine dendrimers. *Macromol. Symp.* **1994**, *77*, 51−62.

de Brabander, E. M. M.; Brackman, J.; Mure-Mak, M.; de Man, H.; Hogeweg, M.; Keulen, J.; Scherrenberg, R.; Coussens, B.; Mengerink, Y.; van der Wal, Sj. Polypropylenimine dendrimers: improved synthesis and characterization. *Macromol. Symp.* **1996**, *102*, 9−17.

Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.

Carr, P. L.; Davies, G. R.; Feast, W. J.; Stainton, N. M.; Ward, I. M. Dielectric and mechanical characterization of aryl ester dendrimers/PET blends. *Polymer* **1996**, *37*, 2395−2401.

Castagnola, M.; Cassiano, L.; Lupi, A.; Messana, I.; Patamia, M.; Rabino, R.; Rossetti, D. V.; Giardina, B. Ion-exchange electrokinetic capillary chromatography with starburst (PAMAM) dendrimers: a route towards high-performance electrokinetic capillary chromatography. *J. Chromatogr. A* **1995**, *694*, 463−469.

Cowie, L. M. G.; Horta, A.; McEwen, I. J.; Prochazka, K. Upper and lower critical solution temperatures for star branched polystyrene in cyclohexane. *Polym. Bull.* **1979**, *1*, 329−336.

Dubin, P. L.; Edwards, S. L.; Kaplan, J. I.; Mehta, M. S.; Tomalia, D.; Xia, J. Carboxylated starburst dendrimers as calibration standards for aqueous size exclusion chromatography. *Anal. Chem.* **1992**, *64*, 2344−2347.

Faust, A. B.; Sremicich P. S.; Gilmer, J. W.; Mays, J. W. Influence of star-core exclusion on polymer−polymer miscibility. *Macromolecules* **1989**, *22*, 1250−1258.

Frechet, J. M. J.; Hawker, C. J. *Synthesis and Properties of Dendrimers and Hyperbranched Polymers, Comprehensive Polymer Science* (Suppl. 2); Aggarwal, S., Russo, S., Eds.; Pergamon Press: Oxford, 1996.

Gersappe, D.; Irvine, D.; Balazs, A. C.; Liu, Y.; Sokolov, J.; Rafailovih, M.; Schwarz, S.; Peiffer, D. G. The Use of Graft Copolymers to Bind Immiscible Blends. *Science* **1994**, *265*, 1072−1074.

Haensler, J.; Szoka, F. C. Polyamidoamine Cascade Polymers Mediate Efficient Transfection of Cells in Culture. *Bioconjugate Chem.* **1993**, *4*, 372−379.

Heintz, A.; Lichtenthaler, R. N.; Prausnitz, J. M. Solubilites of Volatile Solvents in Polyvinyl Acetate, Polyvinyl Chloride and their Random Copolymers. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 926−928.

Israels, R.; Foster, D. P.; Balazs, A. C. Designing Optimal Comb Compatibilizers: AC and BC Combs at A/B Interface. *Macromolecules* **1995**, *28*, 218−224.

Jansen, J. F. G. A.; Meijer, E. W.; de Brabander-van den Berg, E. M. M. The Dendritic Box: Shape-Selective Liberation of Encapsulated Guests. *J. Am. Chem. Soc.* **1995**, *117*, 4417−4418.

Kikic, I. Modello di una Colonna Cromatografica in Gas-cromatografia Lineare. *Cron. Chim.* **1980**, *62*, 14−31.

Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. Homogeneous Catalysts based on Silane Dendrimers Functionalized with Arylnickel-(II) Complexes. *Nature* **1994**, *372*, 659−663.

Li, C.; Yu, X.; Somasundaran, P. Effect of a Comblike Amphiphilic Polymer on the Stability of Alumina Dispersions. *Colloids Surf.* **1992**, *69*, 155−158.

Lutz, P.; Rempp, P. New Developments in Star Polymer Synthesis. Star-shaped Polystyrenes and Star Block Copolymers. *Makromol. Chem.* **1988**, *189*, 1051−1056.

Merrill, E. W. Poly(ethylene oxide) Star Molecules: Synthesis, Characterization, and Applications in Medicine and Biology. *J. Biomater. Sci. Polymer Ed.* **1993**, *5*, 1−11.

Mio, C.; Jayachandran, K. N.; Prausnitz, J. M. Vapor-Liquid Equilibria for Binary Solutions of Some Comb Polymers Based on Poly(Styrene-*co*-Maleic Anhydride) in Acetone, Methanol and Cyclohexane. *Fluid Phase Equilib.* **1997**, *147*, 165−178.

Mio, C.; Kiritsov, S.; Thio, Y.; Brafman, R.; Hawker, C.; Malmstrom, E. E.; Prausnitz, J. M. Vapor-Liquid Equilibria for Solutions of Dendritic Polymers. *J. Chem. Eng. Data* **1998**, *43*, 541−550.

Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules. Concepts, Syntheses, Perspectives*; VHC: Weinheim, Germany, 1996.

Newman, R. D.; Prausnitz, J. M. Solvent Volatilities in Polymer Coatings from Chromatographic Meaurements. *J. Paint Technol.* **1973**, *45*, 33−45.

Romdhane, I. H.; Danner, R. P. Solvent Volatilities from Polymer Solutions by Gas−Liquid Chromatography. *J. Chem. Eng. Data* **1991**, *36*, 15−20.

Simms, A. J. Recent Advances in the Use of Star Polymers in Coatings. *Prog. Org. Coat.* **1993**, *22*, 367−377.

Smidsrød, O.; Guillet, J. E., Study of Polymer-Solute Interactions by Gas Chromatography. *Macromolecules* **1969**, *2*, 272−277.

Tomalia D. A.; Durst, H. D. Genealogically Directed Synthesis: Starburst/Cascade Dendrimers and Hyperbranched Structures. *Top. Curr. Chem.* **1993**, *165*, 193−260.

Wells, M.; Crooks, R. M. Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 10. Preparation and Properties of Chemically Sensitive Dendrimer Surfaces. *J. Am. Chem. Soc.* **1996**, *118*, 3988−3989.

Xu, Q.; Maltesh, C.; Somasundaran, P. Stability of Graphite Suspensions in the Presence of an Amphiphilic Comblike Polymer. *J. Dispersion Sci. Technol.* **1992**, *13(2)*, 195−200.

Yokoyama, H.; Takano, A.; Okada, M.; Nose T. Phase Diagram of Star-Shaped Polystyrene Cyclohexane System. Location of Critical Point and Profile of Coexistence Curve. *Polymer* **1991**, *32*, 3218−3224.

Received for review December 7, 1998. Accepted April 15, 1999. The financial support of NATO is gratefully acknowledged with reference to the Program CRG 971081 “Evaluation of Thermophysical Properties of Solutions Containing Hyperbranched Polymers”.

JE9803025