Investigation of Thermodynamic Properties of Hyperbranched Poly(ester amide) by Inverse Gas Chromatography

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ABSTRACT: Thermodynamic properties of the hyperbranched poly (ester amide) (Hybrane® 1200) were investigated by inverse gas chromatography (IGC) using 19 different solvents as the probes at infinite dilution. Retention data of probes were used for an extensive characterization of the polymer, which includes the determination of the Flory-Huggins interaction parameter, the weight fraction activity coefficient, the total, partial, and additive solubility parameters. The analysis of the results indicated that the additive value of the solubility parameter is lower than the value obtained from a standard procedure. Furthermore, the solubility parameter decreases with increase of temperature. © 2008 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 46: 2166–2172, 2008
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INTRODUCTION

During the last decade, dendritic macromolecules such as dendrimers and hyperbranched polymers have attracted considerable scientific attention. They present a well-defined globular macromolecular architecture and a large number of functional groups. Because of their structure, they present many unique properties,[1] and they can be used in a wide range of applications, which include oil industry, polymer and composite materials, rheology modifiers, paper coatings, and biomaterials for controlled drug delivery.[2–6] However, despite the great variety of their applications, there is a lack of data for many thermodynamic properties of these materials.

Inverse gas chromatography (IGC) is a useful and very versatile method for materials' characterization because it can provide information on thermodynamic properties over a wide temperature range. The term "inverse" indicates that the stationary phase of the chromatographic column is of interest, in contrast to conventional gas chromatography. The chromatographic column contains the material under study. The method is simple, fast, and efficient. It has been used for the characterization of hyperbranched polymers,[7] block copolymers,[8] polymer blends,[9,10] nanocomposites,[11] fillers,[12,13] cement pastes,[14] fibers,[15] and crude oils.[16]

The interaction between probes and a polymer is usually represented by the values of Flory-Huggins interaction parameter and analyzed by the solubility parameters of the probes and polymers.[17] Determination of solubility parameters is very important for a number of relevant

applications where the solubilization properties of systems involving polymers is crucial, like in drug delivery,[18] in nanoparticle preparation,[19] and in coatings applications.[20]

In this study, IGC was applied to investigate thermodynamic and surface properties of a hyperbranched poly(ester amide), Hybrane®.[2] The molar heat sorption, the partial molar heats of mixing, the weight fraction activity coefficient, the Flory-Huggins interaction parameter, the total, the partial, and the additive solubility parameters were calculated.

INVERSE GAS CHROMATOGRAPHY-INFINITE DILUTION THEORY

Thermodynamics of IGC

In IGC, molecular probes are injected at infinite dilution to exclude lateral probe–probe interactions. Therefore, their retention on the solid surface is governed only by solid-probe interactions. The specific retention volume (V_g) or the net retention volume (V_N) used to describe the elution behavior of probes can be calculated according to the following relationship[21]:

$$V_g = \frac{273 V_N}{W_S T} = \frac{273}{T_F W_S} J F_M \left(1 - \frac{p_w}{p'}\right)(t_R - t_M) \quad (1)$$

where, t_R, t_M are the probe's and marker's retention times, respectively, F_M is the carrier gas flow rate measured at the column outlet at ambient pressure, p' and temperature, T_F. Also, T is the column temperature, p_w is the vapor pressure of water at T_F and J is the James and Martin factor used to correct for the gas carrier compressibility, defined as follows:

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

where, P_i and P_o are the inlet and outlet pressures, respectively.

The specific retention volume (V_g) can be used for the calculation of thermodynamic properties. The molar heat (enthalpy) of probe's absorption in the polymer (ΔH_1^s), the molar heat of mixing (ΔH_1^∞), and the weight fraction activity coefficient at infinite dilution (Ω_1^∞) of the probe can be calculated as follows[21]:

$$\Delta H_1^s = -\frac{R\partial \ln V_g}{\partial(1/T)} \quad (3)$$

$$\Omega^\infty = -\frac{273.15R}{V_g P_1^o M_1}\exp\left(\frac{-P_1^o(B_{11} - V_1)}{RT}\right) \quad (4)$$

$$\Delta H_1^\infty = -\frac{R\partial \ln \Omega^\infty}{\partial(1/T)} \quad (5)$$

The Flory-Huggins parameter (χ_{12}^∞), which points out the strength of the interaction between the polymer and the probe, can be calculated from the relationship as follows[21,22]:

$$\chi_{12}^\infty = \ln\left(\frac{273.15 R v_2}{V_g P_1^o V_1}\right) - 1 - \frac{P_1^o(B_{11} - V_1)}{RT} \quad (6)$$

where P_1^o, M_1, V_1, and B_{11}, are the vapor pressure, molecular weight, molar volume, and the second virial coefficient, respectively, of the probe. R and v_2 are the gas constant and the specific volume of the polymer, respectively.

Furthermore, heats of vaporization of the probes are calculated through the equation:

$$\Delta H_v = \Delta H_1^\infty - \Delta H_1^s \quad (7)$$

The solubility parameter of the probe (δ_1) is calculated through the well-known equation:

$$\delta_1 = \left(\frac{\Delta H_v - RT}{V_1}\right)^{1/2} \quad (8)$$

where ΔH_v is the molar enthalpy of vaporization.

Additionally, according to Guillet and Dipaola-Baranyi[23] and Guillet,[24] the solubility parameter of the polymer (δ_2) can be calculated using the ensuing equation:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{12}^\infty}{V_1}\right) = \frac{2\delta_2}{RT}\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi s}{V_1}\right) \quad (9)$$

where χ^S is the entropy term of the interaction parameter, χ_{12}^∞. Plotting the left hand side of this equation versus (δ_1) the solubility parameter (δ_2) of the investigated material is calculated from the slope of the straight line.

Voelkel and Janas[25] proposed a method for the estimation of Hansen's partial solubility parameters. These are related to the total solubility parameter by the equation:

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (10)$$

where δ_T is the total additive solubility parameter, whereas δ_d, δ_p and δ_h are the partial solubility
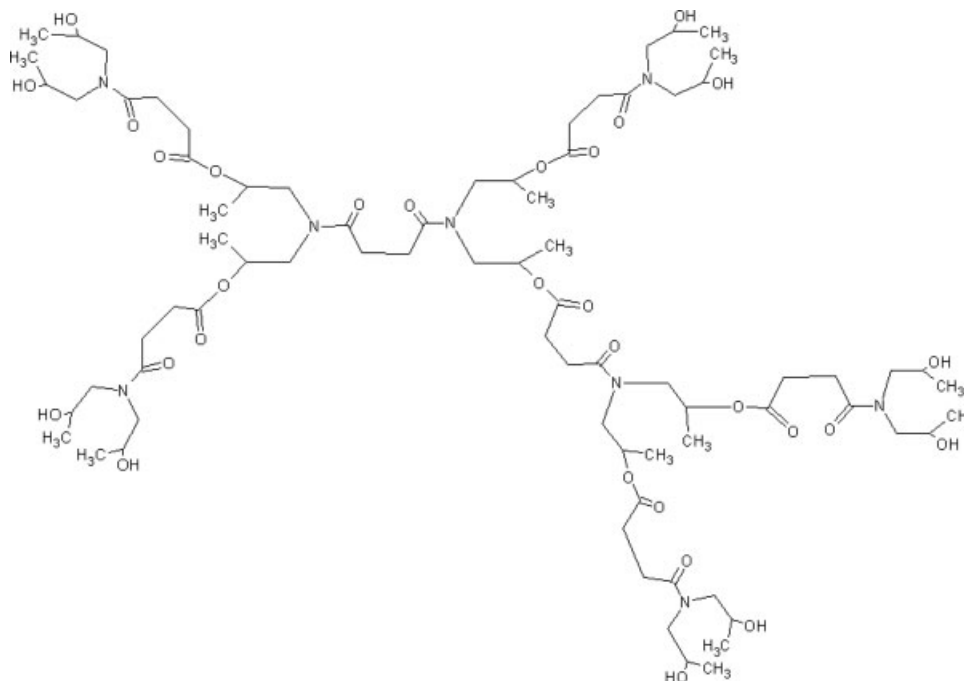
Figure 1. Chemical structure of the hyperbranched polyesteramide used in the present investigation.

parameters due to dispersive, polar, and hydrogen bonding interactions, respectively. The partial parameters are calculated from the slope of the corresponding straight lines, defined by the following equations:

$$\delta_{\rm d} = \frac{m_{n\text{-alkanes}} RT}{2}$$
$$\delta_{\rm p} = \frac{(m_1 - m_{n\text{-alkanes}})RT}{2} \qquad (11)$$
$$\delta_{\rm hb} = \frac{(m_2 - m_{n\text{-alkanes}})RT}{2}$$

where, $m_{n\text{-alkanes}}$ is the value of the slope using $n(6–10)$ alkanes as (nonpolar probes), m_1 the value of the slope using 2-butanone, 2-pentanone, acetonitrile, and toluene (polar probes), and m_2 is the value of the slope for ethanol, 2-propanol, n-butanol, 1,4 dioxane, and pyridine (hydrogen bonding fluids).

EXPERIMENTAL

Materials

Hyperbranched poly (ester amide) Hybrane 1200 (see Fig. 1) was obtained from DSM with a num-

ber–average molecular weight ($M_{\rm n}$) of 1200 g/mol. The column solid support was Chromosorb W HP (80/100 mesh) from Supelco.

Nineteen solvents (n-hexane, n-heptane, n-octane, n-nonane, n-decane, benzene, dichloromethane, ethyl acetate, acetonitrile, toluene, chloroform, 2-butanone, 2-pentanone, tetrahydrofuran, 1,4 dioxane, ethanol, 2-propanol, n-butanol, and pyridine) of analytical grade were used as the probes and were purchased from Aldrich.

Inverse Gas Chromatography Apparatus and Conditions

A Hewlett–Packard HP 5890 gas chromatograph, equipped with a flame ionization detector, was used. The flow rate is determined using soap bubble flow meter at room temperature. Column specifications and conditions of the measurements are listed in Table 1. Methane was used as noninteracting marker. A small amount of the solvent (0.1 μL) was injected manually with a 1-μL Hamilton syringe. Five injections were made for each probe. Because the eluted peaks had a small asymmetrical profile, the retention times were determined via the first moment of the concentration distribution.[21]

Table 1. Column Specifications and Chromatograph Conditions

	Hybrane
Loading (%)	10
Mass coated (g)	0.064
Column length (cm)	65
Column i.d. (in)	0.0625
Column temperature (°C)	75, 85, 95
Injector temperature (°C)	150
Detector temperature (°C)	200
Carrier gas	Helium
Flow (mL/min)	25

RESULTS AND DISCUSSION

Initially, the specific retention volume for all the probes was estimated from the elution profile. Next, given the values of (V_g) the molar heat sorption and the partial molar heats of mixing were calculated. Following, the weight fraction activity coefficient, the Flory-Huggins interaction parameter, and the solubility parameters were also determined. A detailed account of the procedures followed for the determination of the above quantities is provided in the next sections.

Specific Retention Volumes and Interaction Parameters

Specific retention volumes (V_g) of 19 probes were obtained at three different temperatures, 348.15, 358.15, and 368.15 K, which are higher than the glass transition temperature of Hybrane (313 K as measured by DSC). Three different groups of probes were used to determine the thermodynamic properties of Hybrane: normal alkanes from hexane to decane; polar nonhydrogen bonding aromatic hydrocarbons, ketones, acetonitrile; and hydrogen bonding probes, alcohols, 1,4-dioxane and pyridine. Table 2 shows the specific retention volumes of probes on Hybrane at different temperatures. The reported V_g values refer to the average of at least four measurements. In all cases, the standard deviation was lower than 2.5% of the reported value.

The specific retention volume (V_g) of the probes decreases as the temperature increases. Furthermore, the weight fraction activity coefficient and the Flory-Huggins parameter decreases as the temperature increases. Consequently, the solubil-

ity of the Hybrane in these probes increases as the temperature increases.

In addition, the specific retention volume of the alkanes increases with the length of the chain. In Table 3, data for the molar heat of sorption are presented. The exothermic molar heat of sorption of the alkanes increases as the chain length increases. Also, the weight fraction activity coefficient decreases as the chain length increases. In other words, the longer the alkane chain length, the stronger its interaction with polymer chains.

A comparison of data presented in Tables 2 and 3 reveals that the specific retention volume and the molar heat of sorption of polar probes are higher than the corresponding values of the nonpolar probes with comparable boiling points. This should be attributed to the combination of hydrogen bonding, dipole–dipole, and dispersive interactions.

Furthermore, as presented in Table 3, the heats of vaporization (ΔH_v) for all probes are comparable with the literature values,[26] indicating that the experimental values of ΔH_1^s and ΔH_1^∞ were amenable to thermodynamic analysis.

The experimental values of the weight fraction activity coefficient (Ω_1^∞) and of the Flory-Huggins parameter (χ_{12}^∞) are reported in Tables 4 and 5, respectively. The values of the specific volume were obtained from fully atomistic molecular

Table 2. Specific Retention Volumes, V_g ($cm^3 g^{-1}$) of Probes at 348.15, 358.15, and 368.15 K

Probes	348.15	358.15	368.15
n-Hexane	38.60	33.07	28.68
n-Heptane	92.10	70.80	56.15
n-Octane	208.95	157.01	120.41
n-Nonane	499.05	357.24	260.25
n-Decane	1106.14	757.47	531.29
Benzene	118.17	95.15	76.48
Dichloromethane	61.10	49.46	40.00
Ethylacetate	71.15	57.23	47.40
Acetonitrile	119.60	93.22	73.54
Toluene	262.07	200.72	159.16
Chloroform	116.56	95.21	76.82
2-Butanone	81.51	63.59	50.07
2-Pentanone	146.62	118.29	95.51
Tetrahydrofuran	88.99	73.67	60.09
1,4 Dioxane	207.90	173.53	143.94
Ethanol	131.83	93.04	69.81
2-Propanol	115.31	88.17	65.55
n-Butanol	417.76	301.23	213.55
Pyridine	562.87	419.10	311.25

Table 3.   The Molar Heat of Sorption, (ΔH_1^s), the Partial Molar Heat of Mixing (ΔH_1^∞) of Probes on Hybrane, and the Heats of Vaporizations (ΔH_v) of Probes at 348.15–368.15 K

Probes	ΔH_1^s	ΔH_1^∞	ΔH_v	$\Delta H_v{}^a$
n-Hexane	-16.45 ± 0.28	13.01 ± 0.28	29.46 ± 0.56	27.65
n-Heptane	-27.43 ± 0.06	7.18 ± 0.54	34.61 ± 0.60	32.80
n-Octane	-30.51 ± 0.50	8.75 ± 0.15	39.26 ± 0.65	37.65
n-Nonane	-36.04 ± 0.78	7.93 ± 0.05	43.97 ± 0.83	42.32
n-Decane	-40.64 ± 0.80	8.03 ± 0.08	48.67 ± 0.88	46.83
Benzene	-24.07 ± 1.60	8.11 ± 0.39	32.17 ± 1.99	30.46
Dichloromethane	-23.46 ± 0.90	3.56 ± 0.44	27.02 ± 1.34	25.50
Ethylacetate	-22.50 ± 0.10	10.89 ± 0.64	33.39 ± 0.74	31.65
Acetonitrile	-26.91 ± 0.65	5.43 ± 0.05	32.34 ± 0.70	30.01
Toluene	-27.65 ± 0.06	8.78 ± 0.69	36.44 ± 0.75	35.03
Chloroform	-23.06 ± 1.30	6.46 ± 0.78	29.51 ± 2.08	28.20
2-Butanone	-26.96 ± 0.68	5.88 ± 0.16	32.84 ± 0.84	31.22
2-Pentanone	-23.74 ± 0.88	12.75 ± 0.21	36.49 ± 1.09	34.65
Tetrahydrofuran	-21.73 ± 1.31	8.89 ± 0.75	30.62 ± 2.06	28.77
1,4 Dioxane	-20.35 ± 0.98	15.97 ± 0.28	36.32 ± 1.26	35.34
Ethanol	-35.21 ± 0.60	5.55 ± 1.33	40.76 ± 1.93	38.10
2-Propanol	-31.23 ± 2.06	10.58 ± 1.45	41.81 ± 3.51	39.11
n-Butanol	-37.11 ± 1.97	11.74 ± 1.18	48.84 ± 3.15	46.91
Pyridine	-32.75 ± 1.32	5.84 ± 0.64	38.60 ± 1.96	37.01

[a] Experimental values from ref. 26.

dynamic simulations.[27] These parameters characterize the ability of a solvent to dissolve the investigated polymer. Theoretically, if χ_{12}^∞ is smaller than 0.5 and Ω_1^∞ is smaller than 5 the probe is characterized as "good solvent" for the polymer. Subsequently, as shown in Tables 4 and 5, in the investigated temperature range, alkanes and acetonitrile can be characterized as moderate solvents, whereas the other probes as good solvents.

Table 4.   Weight Fraction Activity Coefficient (Ω_1^∞) of Probes on Hybrane at 348.15, 358.15, and 368.15 K, respectively

Probes	348.15	358.15	368.15
n-Hexane	5.90	5.23	4.67
n-Heptane	5.28	4.97	4.64
n-Octane	5.03	4.64	4.30
n-Nonane	4.56	4.22	3.95
n-Decane	4.53	4.20	3.92
Benzene	2.94	2.71	2.55
Dichloromethane	1.54	1.47	1.44
Ethylacetate	4.02	3.66	3.30
Acetonitrile	6.07	5.76	5.51
Toluene	2.95	2.74	2.51
Chloroform	1.10	1.02	0.98
2-Butanone	4.59	4.32	4.13
2-Pentanone	4.46	3.93	3.55
Tetrahydrofuran	2.73	2.48	2.33
1,4 Dioxane	3.01	2.57	2.26
Ethanol	4.36	4.22	3.94
2-Propanol	4.52	3.99	3.74
n-Butanol	4.30	3.77	3.48
Pyridine	1.93	1.80	1.74

Table 5.   The Flory-Huggins Parameter (χ_{12}^∞) of Probes on Hybrane at 348.15, 358.15 and 368.15 K

Probes	348.15	358.15	368.15
n-Hexane	0.15	0.02	-0.10
n-Heptane	0.09	0.02	-0.06
n-Octane	0.07	-0.02	-0.10
n-Nonane	0.00	-0.08	-0.16
n-Decane	0.01	-0.07	-0.14
Benzene	-0.24	-0.34	-0.40
Dichloromethane	-0.50	-0.55	-0.59
Ethylacetate	0.08	-0.02	-0.14
Acetonitrile	0.35	0.29	0.23
Toluene	-0.25	-0.33	-0.42
Chloroform	-0.71	-0.79	-0.84
2-Butanone	0.10	0.03	-0.03
2-Pentanone	0.09	-0.05	-0.16
Tetrahydrofuran	-0.31	-0.42	-0.49
1,4 Dioxane	-0.05	-0.22	-0.35
Ethanol	0.04	0.00	-0.08
2-Propanol	0.07	-0.06	-0.14
n-Butanol	0.06	-0.07	-0.16
Pyridine	-0.55	-0.62	-0.66

Table 6. Hybrane Solubility Parameters (δ_2) $(MPa)^{1/2}$, Calculated from eq (9) at 348.15, 358.15, and 368.15 K, respectively

Temperature	Slope	δ_2 from slope
348.15	0.01259 ± 2.84E-04	18.22 ± 0.41
358.15	0.01207 ± 2.64E-04	17.97 ± 0.39
368.15	0.01156 ± 2.58E-04	17.69 ± 0.39

Chloroform presents significantly low values of χ_{12}^{∞} and Ω_1^{∞} indicating that this is the best solvent between all of the examined probes.

Solubility Parameters

The solubility parameter (δ_2) of Hybrane can be determined from the slope of eq 9. The experimental data at three different temperatures are shown in Table 6 along with the maximum error. In all cases, the correlation coefficients were relatively high (>0.99). A small decrease of the solubility parameters with increase in temperature can be observed.

The experimental values of the additive solubility parameter δ_T and its components δ_d, δ_p, δ_h are presented in Figures 2 and 3. In all cases, the correlation coefficient was high (>0.994). The values of the total additive solubility parameters δ_T are lower than those calculated from eq 9 (see Table 6), in agreement with the statements of Voelkel et al.[25] In addition, the values for δ_T are in good agreement with preliminary results from fully atomistic molecular dynamic simulations.[27]
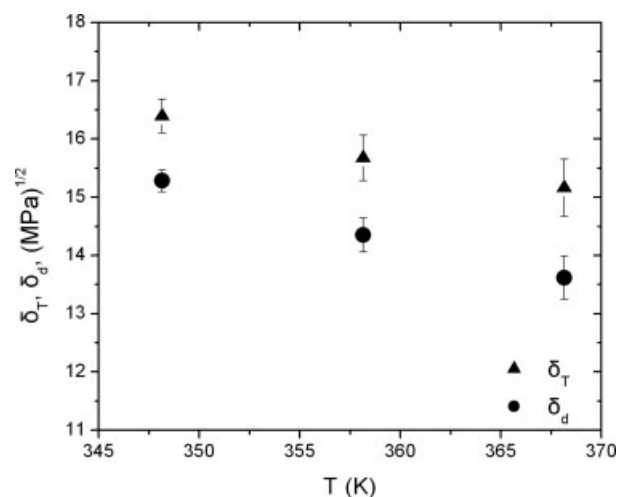
Figure 2. Influence of temperature on the total and dispersive component of the solubility parameter.
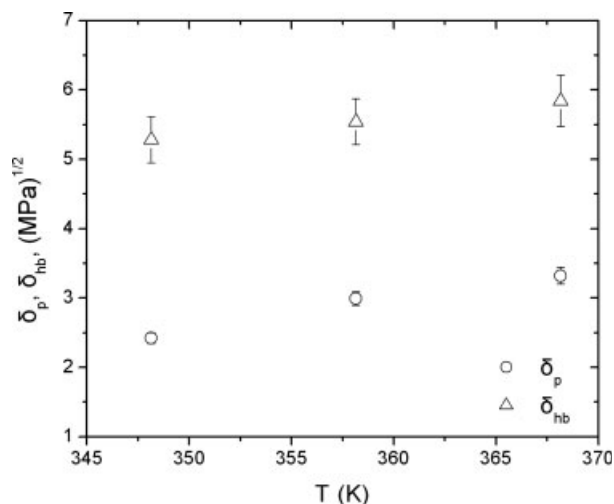
Figure 3. Influence of temperature on the polar and hydrogen bonding component of the solubility parameter.

It is clear that the dispersive component decreases linearly with increase in temperature. On the other hand, the polar component increases, in a linear fashion, with increase in temperature. The influence of temperature on the hydrogen bonding component appears to be weak. The net effect of the influence of temperature on the partial solubility parameters is a linear decrease of the total solubility parameter (δ_T) with increase in temperature.

CONCLUSIONS

In this work, we have presented for the first time a detailed account of thermodynamic properties of a hyperbranched poyesteramide (Hybrane), by means of IGC. The main results from this study can be summarized as follows:

1. IGC proved a versatile technique for the characterization of the thermodynamic and surface properties of Hybrane.
2. The values of the Flory-Huggins parameter and the weight fraction activity coefficient indicate that chloroform is the best solvent between all the investigated probes.
3. The additive solubility parameter and the dispersive component were found to decrease linearly with increase in temperature.
4. The adsorption of polar probes on Hybrane depends on the acidic or basic character of the probes.

In view of the level of accuracy afforded by IGC to the characterization of the studied system, we believe it can be successfully applied to the study of other polymers of technological importance bearing a hyperbranched architecture.

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