



Investigation of thermodynamic properties of hyperbranched aliphatic polyesters by inverse gas chromatography

G.S. Dritsas, K. Karatasos, C. Panayiotou*

Laboratory of Physical Chemistry, Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

ARTICLE INFO

Article history:

Received 18 August 2009
Received in revised form 13 October 2009
Accepted 14 October 2009
Available online 22 October 2009

Keywords:

Hyperbranched polymers
Polyesters
Inverse gas chromatography
Thermodynamic properties

ABSTRACT

Thermodynamic properties of a series of commercial hyperbranched aliphatic polyesters (Boltorn® H20, H30 and H40) were examined for the first time by inverse gas chromatography (IGC) using 13 different solvents at infinite dilution as probes. Retention data of probes were utilized for an extensive characterization of polymers, which includes the determination of the Flory–Huggins interaction parameter, the weight fraction activity coefficient as well as the total and partial solubility parameters. Analysis of the results indicated that the total and partial solubility parameters decrease with increase of temperature. Furthermore, upon increase of the molecular weight, while the hydrogen bonding component decreases, no influence on the total solubility parameter is noticed within the experimental error margins. Results from the present study while providing new insight to the thermodynamic characteristics of the examined systems, they are also expected to reflect more general aspects of the behavior of hyperbranched polymers bearing similar end-groups.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

During the last decade, dendritic macromolecules such as dendrimers and hyperbranched polymers have attracted considerable scientific interest. They are characterized by a well defined globular macromolecular architecture with nanosized dimensions and a large number of functional groups. Due to their structure, they present a number of unique properties [1] which render them appropriate candidates for a wide variety of applications [2–4]. While dendritic molecules with perfectly symmetric structure (i.e., dendrimers) are only available through laborious multistep procedures, synthetic procedures of hyperbranched analogues with non-regular topological features, remain much cheaper. Due to their multifunctional characteristics and their cost-effective synthesis hyperbranched polymers have recently become the focus of intense academic and industrial research. A characteristic example of such hyperbranched molecules which can now be produced on an industrial scale, belong to the aliphatic polyester family bearing the commercial name Boltorn®. Due to their commercial availability and their unique properties, these molecules have been used as basic constituents for several practical purposes [5–7]. However, despite the great variety of their applications, there is still a lack

of data concerning some of the key thermodynamic properties of these materials.

Inverse gas chromatography is a useful and quite versatile technique 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 [8], block copolymers [9], polymer blends [10], nanocomposites [11], fillers [12], cement pastes [13], fibers [14], and crude oils [15].

The interactions between one probe and the polymer are usually characterized by the values of Flory–Huggins interaction parameter, while, in this direction, the pure compound solubility parameters are also quite useful [16]. The knowledge of solubility parameters is very important for a number of relevant applications, where the solubilization properties of systems involving polymers are of great importance, such as drug delivery [17], nanoparticle fabrication [18], and coating applications [19].

In the present study, inverse gas chromatography was applied to investigate thermodynamic properties of hyperbranched aliphatic polyesters, bearing the commercial names Boltorn® H20, H30 and H40. The molar heat of sorption, the partial molar heats of mixing, the weight fraction activity coefficient, the Flory–Huggins interaction parameter, the total and the partial solubility parameters were calculated. In addition, the influence of molecular weight and

* Corresponding author at: Aristotle University of Thessaloniki, Faculty of Chemical Engineering, University Campus, Thessaloniki, Greece. Tel.: +30 2310 996223; fax: +30 2310 996232.

E-mail address: cpanayio@auth.gr (C. Panayiotou).

temperature on the solubility parameters of the hyperbranched systems was examined.

2. Inverse gas chromatography-infinite dilution theory

2.1. Thermodynamics of IGC

In inverse gas chromatography, molecular probes are injected at the infinite dilution limit in order to avoid 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 [20]:

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

where t_R , t_M are the probe's and marker's retention times, respectively, W_S is the mass of the polymeric stationary phase, 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:

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

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 at infinite dilution, ΔH_1^∞ , and the weight fraction activity coefficient at infinite dilution of the probe, Ω_1^∞ , can be calculated as follows [20]:

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

$$\Omega_1^\infty = \frac{273.15R}{V_g P_1^o M_1} \exp \left(\frac{-P_1^o (B_{11} - V_1)}{RT} \right) \quad (4)$$

$$\Delta H_1^\infty = \frac{R \partial \ln \Omega_1^\infty}{\partial (1/T)} \quad (5)$$

The Flory–Huggins parameter, χ_{12}^∞ , which reflects the strength of the interaction between the polymer and the probe, can be calculated from the relation [20,21]:

$$\chi_{12}^\infty = \ln \left(\frac{273.15Rv_2}{V_g P_1^o V_1} \right) - 1 - \frac{P_1^o (B_{11} - V_1)}{RT} \quad (6)$$

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 [20]:

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

The solubility parameter of the probe, δ_1 , is calculated through the well known equation [22]:

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

where ΔH_v is the molar enthalpy of vaporization.

Based on a set of $\chi_{(1,2)j}^\infty$ and δ_{1i} values for the respective test solutes, one may calculate the slope of the linear relationship

between the left hand-side of Eq. (9) versus δ_{1i} :

$$\left(\frac{\delta_{1i}^2}{RT} - \frac{\chi_{(1,2)j}^\infty}{V_1} \right) = \frac{2\delta_2}{RT} \delta_{1i} - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{V_1} \right) \quad (9)$$

where χ_s^∞ is the entropy term of interaction parameter, χ_{12}^∞ . The slope ($2\delta_2/RT$) is proportional to the solubility parameter of the examined material, δ_2 , [23–26].

Voelkel and Janas [27] proposed a method for the estimation of Hansen's partial solubility parameters. These are related to the total solubility parameter, δ_T , by the equation [28]:

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

where δ_d , δ_p and δ_h , are the partial solubility parameters due to dispersive, polar, and hydrogen bonding interactions, respectively. The partial parameters are calculated from the slope of Eq. (9), when this is used separately for three groups of probes (i) n-alkanes, (ii) polar non-hydrogen bonding and (iii) hydrogen bonding, which are defined by the following equations:

$$\delta_d = \frac{m_{n\text{-alkanes}} RT}{2}$$

$$\delta_p = \frac{(m_1 - m_{n\text{-alkanes}}) RT}{2} \quad (11)$$

$$\delta_{hb} = \frac{(m_2 - m_{n\text{-alkanes}}) RT}{2}$$

where $m_{n\text{-alkanes}}$ is the value of the slope of Eq. (9) using C8–C11 n-alkanes as (non-polar probes), m_1 is the value of the slope of Eq. (9) using 2-butanone, 2-pentanone, acetonitrile, cyclopentanone and nitropropane (polar probes) and m_2 is the value of the slope of Eq. (9) for ethanol, n-propanol, n-butanol and 1,4-dioxane (hydrogen bonding fluids).

3. Experimental

3.1. Materials

Hyperbranched aliphatic polyesters Boltorn H20, H30 and H40 (see Fig. 1) were obtained from Perstorp with a weight–average molecular weight (M_w) of 2100, 3500, and 5100 g/mol, respectively. The column solid support was Chromosorb W HP (80/100 mesh) from Supelco.

Thirteen solvents (n-octane, n-nonane, n-decane, n-undecane, acetonitrile, 2-butanone, 2-pentanone, nitropropane, cyclopentanone, 1,4-dioxane, ethanol, 2-propanol and n-butanol) of analytical grade were used as the probes and were purchased from Aldrich.

3.2. Inverse gas chromatography apparatus and conditions

A Hewlett Packard HP 5890 gas chromatograph, equipped with a flame ionization detector (FID), was used. The flow rate was determined using soap bubble flow meter at room temperature. Commonly, either methane or air [20,29] can be used as non-interacting marker for the determination of the column dead time. In this case methane was used as non-interacting marker. A small amount of the solvent (0.1 μ l) was injected manually with a 1 μ l 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 [20]. The columns were made from stainless steel and washed with acetone prior to use. Each hyperbranched aliphatic polyester was dissolved in a proper solvent (methanol). In this study, in order to have better control of the amount of polymer coated on Chromosorb, the coating method proposed by Al-Saigh and Munk [21] was adopted for the preparation of the stationary

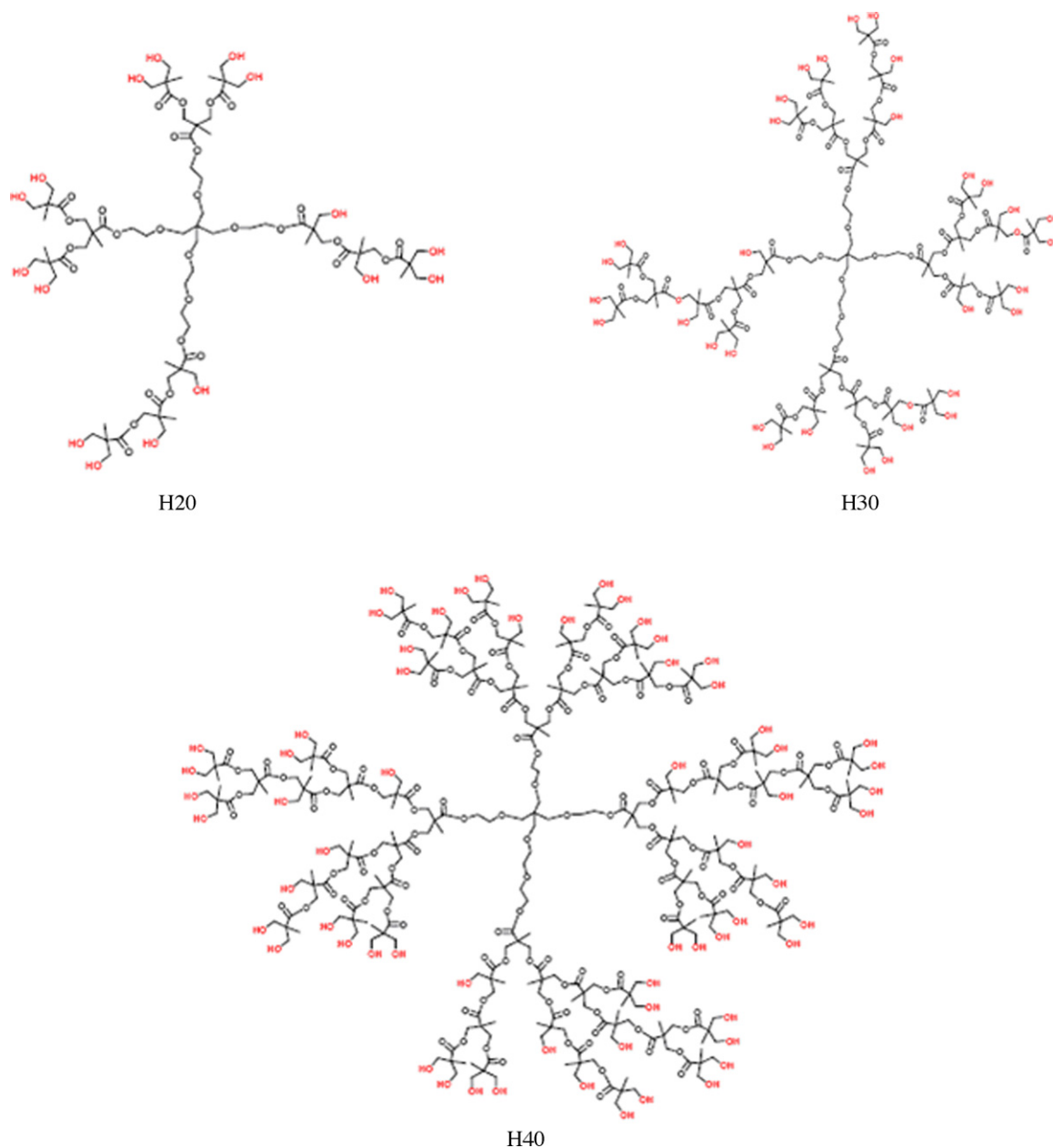


Fig. 1. Theoretical chemical structures of the hyperbranched aliphatic polyesters Boltorn H20, H30 and H40 used in the present investigation.

phase. The loading of the column was made by the aid of a mechanical vibrator and a vacuum pump. After packing, the column was capped by glass wool. Column specifications and conditions of the measurements are presented in Table 1.

4. Results and discussion

Initially, the specific retention volume for each probe was estimated from the elution profile for all the examined systems. Next, given the values of V_g , the molar heat of sorption and the partial molar heats of mixing were calculated for the Boltorn® H20 sample. Following, the values of the weight fraction activity coefficient and the Flory–Huggins interaction parameter were estimated. Finally, the influence of molecular weight and temperature on solubility parameters was also determined. More details on the procedures followed for the determination of the aforementioned quantities are provided in the next sections.

4.1. Specific retention volumes and interaction parameters

Specific retention volumes, V_g , of 13 probes were obtained for the Boltorn H20 at three different temperatures, 343.15, 353.15 and 363.15 K and for Boltorn H30 and H40 at 353.15 and

Table 1
Column specifications and chromatograph conditions.

	Boltorn H20	Boltorn H30	Boltorn H40
Loading (%)	16	15.5	16
Mass coated (g)	0.0882	0.0866	0.0889
Column length (cm)	65	65	65
Column i.d. (in)	0.0625	0.0625	0.0625
Column temperature (°C)	70, 80, 90	80	90
Injector temperature (°C)	200	200	200
Detector temperature (°C)	200	200	200
Carrier gas	Helium	Helium	Helium
Flow (ml/min)	12.8	12.8	12.8

Table 2Specific retention volumes, V_g ($\text{cm}^3 \text{g}^{-1}$) of probes on Boltorn H20 at 343.15, 353.15 and 363.15 K, on Boltorn H30 at 353.15 K and on Boltorn H40 at 363.15 K.

Probes	Boltorn H20			Boltorn H30	Boltorn H40
	343.15	353.15	363.15	353.15	363.15
n-Octane	22.16	19.22	16.91	20.40	11.49
n-Nonane	39.64	33.04	29.32	34.60	20.27
n-Decane	71.35	56.74	46.30	60.18	33.85
n-Undecane	110.04	90.46	75.93	108.85	55.12
Acetonitrile	117.27	92.48	71.23	82.89	67.67
Cyclopentanone	471.50	360.92	267.20	348.93	249.15
Nitropropane	266.78	194.61	148.54	188.97	136.17
2-Butanone	67.22	53.51	43.84	54.40	39.23
2-Pentanone	100.82	78.00	61.11	75.28	59.45
1,4-Dioxane	206.59	160.04	125.24	147.79	107.28
Ethanol	124.43	88.57	65.83	86.91	63.05
n-Propanol	206.50	139.18	100.58	133.15	91.98
n-Butanol	369.22	243.95	164.64	230.23	146.98

Table 3The molar heat of sorption, ΔH_1^s , the partial molar heat of mixing, ΔH_1^∞ of probes on Boltorn H20, and the heats of vaporizations, ΔH_V of probes at 343.15–363.15 K.

Probes	ΔH_1^s	ΔH_1^∞	ΔH_V	ΔH_V^a
n-Octane	-14.03 ± 0.42	24.04 ± 0.36	38.07 ± 0.78	37.99
n-Nonane	-15.65 ± 1.59	26.99 ± 0.72	42.64 ± 2.31	42.66
n-Decane	-22.41 ± 1.11	24.75 ± 0.15	47.16 ± 1.26	47.19
n-Undecane	-22.60 ± 2.55	29.38 ± 1.44	51.98 ± 3.99	52.14
Acetonitrile	-25.80 ± 0.72	5.49 ± 1.32	31.30 ± 2.04	30.28
Cyclopentanone	-29.39 ± 1.02	9.89 ± 1.77	39.28 ± 2.79	39.09
Nitropropane	-30.34 ± 1.35	9.71 ± 0.57	40.05 ± 1.92	40.39
2-Butanone	-22.14 ± 0.87	9.72 ± 0.24	31.87 ± 1.11	31.53
2-Pentanone	-25.93 ± 0.36	9.43 ± 0.36	35.36 ± 0.72	34.98
1,4-Dioxane	-25.92 ± 0.33	9.17 ± 0.39	35.08 ± 0.72	35.63
Ethanol	-32.99 ± 1.29	6.56 ± 0.45	39.55 ± 1.74	38.51
n-Propanol	-37.28 ± 2.07	6.38 ± 1.14	43.66 ± 3.21	41.70
n-Butanol	-41.83 ± 0.63	5.64 ± 0.39	47.47 ± 1.02	47.44

^a Experimental values from Ref. [25].

363.15 K, respectively. The temperatures are higher than the corresponding glass transition temperatures of Boltorn H20, H30 and H40 (303.15, 308.15 and 313.15 K, respectively, as measured by Differential Scanning Calorimetry). Three different groups of probes were used to determine the thermodynamic properties of the systems: normal alkanes from octane to undecane; polar non-hydrogen bonding probes such as ketones, acetonitrile, nitropropane, cyclopentanone; and hydrogen bonding probes such as alcohols and 1,4-dioxane. Table 2 shows the specific retention volumes of probes on the hyperbranched polymers 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% of the reported value.

For the Boltorn H20 sample, the specific retention volume, V_g , of the probes decreases as the temperature increases. Furthermore, the weight fraction activity coefficient and the Flory–Huggins interaction parameter decrease as the temperature increases. Also interactions between groups such as CH_2 , OH, O and COO of Boltorn H20 and groups such as CH_2 , OH and CO of probes, are expected to increase with temperature. This can be understood, since an increase in temperature leads to an increase of the kinetic energy of the polymer and the probes, enhancing thus the probability of these groups to be in the proper position for an efficient interaction between them to take place. Consequently, the solubility of the Boltorn H20 in these probes increases as the temperature rises.

A comparison of the 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 non-polar probes with comparable boiling points. This should be attributed to the fact that non-polar probes, like n-alkanes, interact with polymers only with dispersion forces in contrast to polar probes which

in addition interact with dipole–dipole (or dipole–quadrupole, etc.) interactions with their OH, COO and O groups.

In addition, the weight fraction activity coefficient and the Flory–Huggins parameter of the alkanes, ketones, and alcohols increase as the chain length of the probe increases. This could be due to the fact that penetration of probes inside the polymeric structure becomes more difficult as the chain length of the probe increases. In other words, the longer the alkanes, ketones and alcohols chain lengths, the weaker their interactions with the examined polymers.

Furthermore, as presented in Table 3, the heats of vaporization, ΔH_V , for all probes are comparable with literature values [30], 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. These parameters are related to the ability of a solvent to dissolve the investigated polymer. Theoretically, if χ_{12}^∞ is smaller than 0.5 or Ω_1^∞ is smaller than 5, the probe is characterized as “good solvent” for the polymer, whereas if $5 < \Omega_1^\infty < 10$, the probe is characterized as “moderate solvent”.

Subsequently, as shown in Tables 4 and 5, in the investigated temperature range, alkanes can be characterized as poor solvents, while all the hydrogen bonding probes as good ones. From the polar probes, cyclopentanone, 2-butanone, 2-pentanone, and acetonitrile can be considered as good solvents, whereas nitropropane as a moderate solvent. 1,4-Dioxane, because of the strong hydrogen bonding interaction between O group and OH groups of hyperbranched polymers shows significantly low values of χ_{12}^∞ and Ω_1^∞ indicating that this is the best solvent amongst all examined probes. This behavior appears to be independent from the molecular weight of the hyperbranched polymers.

Table 4

Weight fraction activity coefficient, Ω_1^∞ of probes on Boltorn H20 at 343.15, 353.15 and 363.15 K, on Boltorn H30 at 353.15 K and on Boltorn H40 at 363.15 K.

Probes	Boltorn H20			Boltorn H30	Boltorn H40
	343.15	353.15	363.15	353.15	363.15
n-Octane	57.58	45.37	36.20	42.74	53.25
n-Nonane	71.32	55.86	42.33	53.34	61.23
n-Decane	89.31	70.09	55.38	66.08	75.74
n-Undecane	142.59	103.14	75.80	85.72	104.43
Acetonitrile	7.26	6.74	5.42	7.52	6.88
Cyclopentanone	4.40	3.88	3.64	4.02	3.90
Nitropropane	7.83	7.19	6.49	7.41	7.08
2-Butanone	6.54	5.98	5.42	5.88	6.06
2-Pentanone	7.77	7.05	6.48	7.31	6.66
1,4-Dioxane	3.61	3.29	3.03	3.56	3.54
Ethanol	5.65	5.34	4.97	5.44	5.19
n-Propanol	5.71	5.47	5.05	5.72	5.52
n-Butanol	6.20	5.83	5.56	6.18	6.23

Table 5

The Flory–Huggins parameter, χ_{12}^∞ of probes on Boltorn H20 at 343.15, 353.15 and 363.15 K, on Boltorn H30 at 353.15 K and on Boltorn H40 at 363.15 K.

Probes	Boltorn H20			Boltorn H30	Boltorn H40
	343.15	353.15	363.15	353.15	363.15
n-Octane	2.43	2.18	1.95	2.13	2.33
n-Nonane	2.67	2.41	2.13	2.37	2.50
n-Decane	2.91	2.66	2.42	2.60	2.73
n-Undecane	3.30	2.97	2.66	2.79	2.98
Acetonitrile	0.45	0.37	0.32	0.50	0.37
Cyclopentanone	0.16	0.03	-0.04	0.07	0.03
Nitropropane	0.79	0.70	0.59	0.73	0.67
2-Butanone	0.37	0.27	0.16	0.27	0.27
2-Pentanone	0.56	0.45	0.36	0.50	0.39
1,4-Dioxane	0.05	-0.05	-0.14	0.03	0.01
Ethanol	0.22	0.16	0.07	0.19	0.12
n-Propanol	0.25	0.20	0.11	0.25	0.20
n-Butanol	0.34	0.28	0.22	0.34	0.34

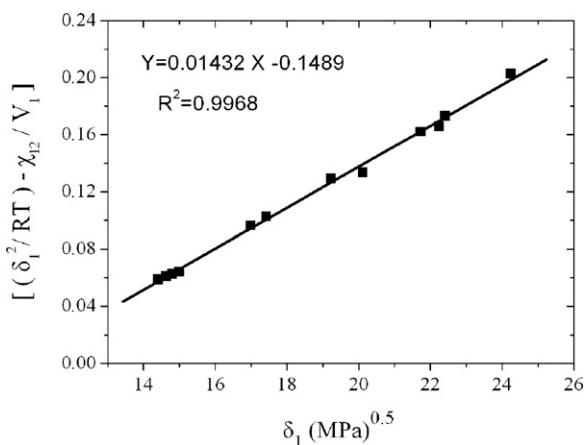


Fig. 2. Variation of δ_1 against $[(\delta_1^2/RT) - \chi_{12}/V_1]$ on Boltorn H20 at 343.15 K.

4.2. Solubility parameters

The solubility parameter, δ_2 , of the polymeric samples can be determined from the slope of Eq. (9) (Fig. 2). The experimental data for the so-calculated solubility parameters together with the maximum error, are shown in Table 6 for Boltorn H20 and in Table 7 for Boltorn H30 and H40. In all cases, the correlation coefficients were relatively high (>0.996). A small decrease of the solubility parameter of Boltorn H20 with increase of temperature can be observed. Moreover, no influence of the molecular weight on the solubility parameter can be noticed.

Table 6

Boltorn H20 solubility parameters, δ_2 (MPa)^{1/2}, calculated from Eq. (9) at 343.15, 353.15 and 363.15 K.

Temperature	Slope	δ_2 from slope
343.15	0.01432 ± 2.53E-04	20.42 ± 0.36
353.15	0.01369 ± 2.5E-04	20.09 ± 0.37
363.15	0.01309 ± 2.53E-04	19.76 ± 0.38

Table 7

Boltorn H30 and Boltorn H40 solubility parameters, δ_2 (MPa)^{1/2}, calculated from Eq. (9) at 353.15 and 363.15 K respectively.

	Temperature	Slope	δ_2 from slope
Boltorn H30	353.15	0.01353 ± 2.66E-04	19.86 ± 0.39
Boltorn H40	363.15	0.01318 ± 2.54E-04	19.89 ± 0.38

The total solubility parameter δ_T and its components δ_d , δ_p , δ_h , were determined by using Eqs. (10) and (11). The experimental values for the examined polymers at all temperatures, are presented in Figs. 3–6. In all cases, the correlation coefficients remained high (>0.992). The values of the total solubility parameters δ_T which were calculated from Eq. (10) are lower than those calculated from Eq. (9) (see Table 6), in agreement with the behavior noticed by Voelkel and Janas [27] for linear polymer systems.

A small decrease of the total, dispersive, polar, and hydrogen bonding components of the solubility parameter of Boltorn H20 with increase of temperature can be observed in Figs. 3 and 4.

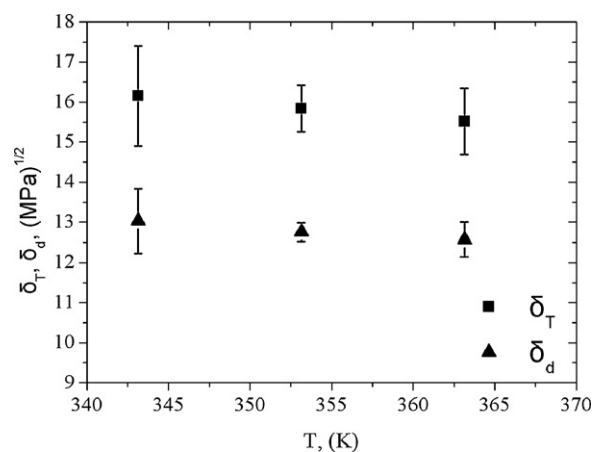


Fig. 3. The total and dispersive components of the solubility parameters in Boltorn H20 as a function of temperature.

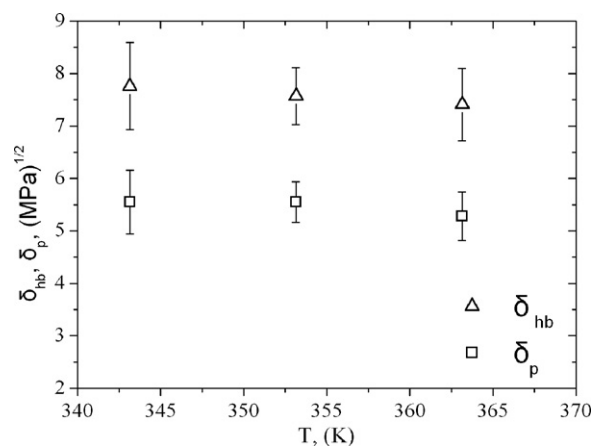


Fig. 4. Effect of temperature on the hydrogen bonding and polar components of the solubility parameters in Boltorn H20.

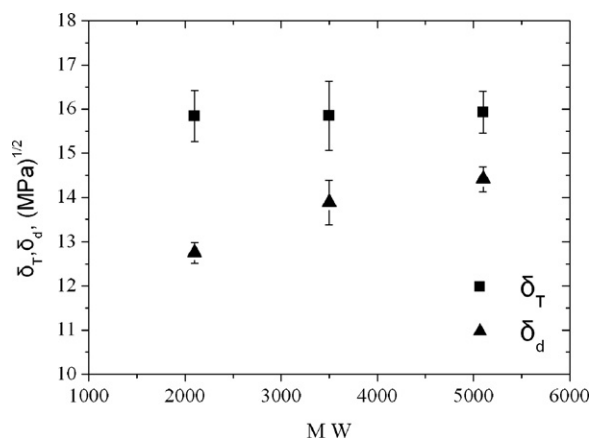


Fig. 5. Molecular weight dependence of the total and dispersive components of the solubility parameters.

In order to investigate the influence of molecular weight on the solubility parameter and its partial components, it is reasonable to keep the difference between the examined temperature and glass transition temperature of each sample the same. The H20 and H30 systems are characterized by almost the same glass transition temperature, while that of the third generation sample (i.e., H40) is approximately ten degrees higher compared to those of the lower molecular weight systems. Taking this into account, as shown in Fig. 5, the molecular weight does not seem to influence the total solubility parameter.

It is also evident from Fig. 6 that the hydrogen bonding component decreases with increase of molecular weight. This behavior might be accounted for by the expected differences in the geometrical features between the smallest in size and the higher generation molecules; the star-like structure of the H20 molecule (Fig. 1) could allow for a higher accessibility of the probes to almost all the molecular sites, and, thus, increase the probability of hydrogen bond formation. On the other hand, the dispersive component increases with increase of the molecular weight (see Fig. 5). The effect of molecular weight on the polar component appears to be analogous to the one observed for the hydrogen bonding component, as depicted in Fig. 6. This might be associated with the fact that a significant percentage of the polar interactions involve polymeric sites capable of hydrogen bond formation (e.g., hydroxyl and carbonyl groups) and, thus, may bear analogous to hydrogen-bonding characteristics.

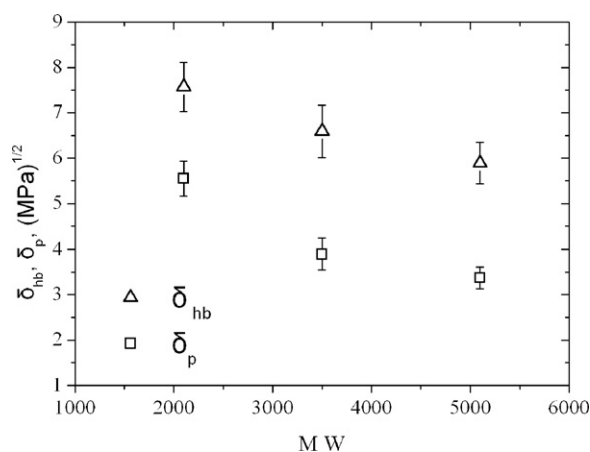


Fig. 6. Influence of molecular weight on the hydrogen bonding and polar components of the solubility parameters.

5. Conclusions

In this work we have presented a detailed study of thermodynamic properties of a series of hyperbranched aliphatic polyesters (Boltorn H20, H30 and H40) by means of inverse gas chromatography.

Based on the detailed level of the analysis that could be performed from the collected data, it appears that IGC can be used as a particularly sensitive technique for the characterization of the thermodynamic properties of such molecules.

More specifically, calculation of the values of the Flory–Huggins parameter and the weight fraction activity coefficient, allowed the classification of the probes regarding their quality as solvents for the hyperbranched molecules: the non-polar probes were found to behave as poor solvents, whereas the hydrogen bonding probes as good solvents for the examined systems. In particular, 1,4-dioxane was found to be the best solvent amongst the examined probes.

For the calculation of the total solubility parameter, both, Guillet [23] and Voelkel [27] methods were applied. The values of the total solubility parameter, which were calculated from Voelkel and Jannas method, were found lower than those calculated from the Guillet method, in line with the observations of Voelkel and Janas [27] for linear polymer systems. However, the behavior of the total solubility parameter as a function of molecular weight and temperature was found to be unaffected by the chosen method of analysis.

Increase of molecular weight does not seem to incur any significant change in the total solubility parameter, while elevation of temperature imparts only a small decrease on the δ_T values. The hydrogen bonding and polar components decrease upon increase of molecular weight and temperature. The dispersive component, on the other hand, while decreasing as temperature rises, it appears to increase with increase of molecular weight.

In view of the successful application of IGC in the studied systems, we believe that it can be a particularly useful tool in the study of other polymers of technological importance bearing a hyperbranched architecture as well.

Acknowledgements

This research project is co-financed by E.U.-European Social Fund (75%) and the Greek Ministry of Development-GSRT (25%), under the EU/GSRT PENED 2003 Grant No 03E Δ 716.

References

- [1] S. Svenson, D.A. Tomalia, *Adv. Drug Deliv. Rev.* 57 (2005) 2106.
- [2] O.A. Matthews, A.N. Shipway, J.F. Stoddart, *Prog. Polym. Sci.* 23 (1998) 1.
- [3] M. Prabaharan, J.J. Graier, S. Pilla, D.A. Steeber, S. Gong, *Biomaterials* 30 (2009) 3009.
- [4] S.E. Stiriba, H. Frey, R. Haag, *Angew. Chem. Int. Ed.* 41 (2002) 1329.
- [5] S. Chen, X.Z. Zhang, S.X. Cheng, R.X. Zhuo, Z.W. Gu, *Biomacromolecules* 9 (2008) 2578.
- [6] M. Seiler, *Fluid Phase Equilib.* 241 (2006) 155.
- [7] J.H. Zou, Y.B. Zhao, W.F. Shi, *J. Phys. Chem. B* 110 (2006) 2638.
- [8] G.S. Dritsas, K. Karatasos, C. Panayiotou, *J. Polym. Sci., Part B: Polym. Phys.* 46 (2008) 2166.
- [9] Q.C. Zou, S.L. Zhang, S.M. Wang, L.M. Wu, *J. Chromatogr. A* 1129 (2006) 255.
- [10] A. Al-Ghamdi, Z.Y. Al-Saigh, *J. Polym. Sci., Part B: Polym. Phys.* 38 (2000) 1155.
- [11] K. Boukerma, J.Y. Piquemal, M.M. Chehimi, M. Mravcakova, M. Omastova, P. Beaunier, *Polymer* 47 (2006) 569.
- [12] K. Milczewska, A. Voelkel, *J. Chromatogr. A* 969 (2002) 255.
- [13] V. Oliva, B. Mrabet, M.I.B. Neves, M.M. Chehimi, K. Benzarti, *J. Chromatogr. A* 969 (2002) 261.
- [14] A. van Asten, N. van Veenendaal, S. Koster, *J. Chromatogr. A* 888 (2000) 175.
- [15] F. Mutelet, G. Ekulu, M. Rogalski, *J. Chromatogr. A* 969 (2002) 207.
- [16] J.E. Guillet, J.H. Purnel, *Advances in Analytical Chemistry and Instrumentation Gas Chromatography*, Wiley, New York, 1973.
- [17] U. Bertram, R. Bodmeier, *Eur. J. Pharm. Biopharm.* 63 (2006) 310.
- [18] C. Duclairioir, E. Nakache, H. Marchais, A.M. Orecchioni, *Colloid Polym. Sci.* 276 (1998) 321.
- [19] C.M. Hansen, *Prog. Org. Coat.* 51 (2004) 77.

- [20] J.R. Conder, C.L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, Chichester, 1979.
- [21] Z.Y. Al-Saigh, P. Munk, *Macromolecules* 17 (1984) 803.
- [22] J. Hildebrand, R.L. Scott, *Regular Solution*, Prentice-Hall, Englewood Cliffs, NJ, 1962.
- [23] G. Dipaola-Baranyi, J.E. Guillet, *Macromolecules* 11 (1978) 228.
- [24] J.E. Guillet, *J. Macromol. Sci. Chem. A* 4 (1970) 1669.
- [25] A. Voelkel, J. Janas, *J. Chromatogr. A* 669 (1994) 89.
- [26] W. Wasiak, A. Voelkel, I. Rykowska, *J. Chromatogr. A* 690 (1995) 83.
- [27] A. Voelkel, J. Janas, *J. Chromatogr.* 645 (1993) 141.
- [28] C.M. Hansen, *Hansen Solubility Parameter*, CRC Press, Boca Raton, FL, 2000.
- [29] A. Voelkel, B. Strzemiescka, K. Adamska, K. Milczewska, *J. Chromatogr. A* 1216 (2009) 1551.
- [30] T.E. Daubert, R.P. Danner, *Data Compilation Tables of Properties of Pure Compounds*; AIChE Symp Ser. No. 203, American Institute of Chemical Engineers, New York, 1985.