Thermodynamic characterization of poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate) by inverse gas chromatography

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ABSTRACT

The thermodynamic characterization of a fluorinated methacrylic homopolymer was conducted by means of inverse gas chromatography (IGC) at infinite dilution. The polymer under study, poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate) (PHFIMA) was synthesized via a free radical polymerization reaction and was properly characterized prior to IGC measurements. The IGC characterization encompassed the calculation of the thermodynamic sorption parameters, the parameters of mixing at infinite dilution, the weight fraction activity coefficients and the Flory–Huggins interaction parameters of 15 probes. Moreover, the total and partial solubility parameters of the polymer were determined. The impact of the temperature and the chemical nature of the probes on the aforementioned thermodynamic parameters are discussed. Results demonstrate that PHFIMA is insoluble in almost every tested solvent, with the exception of chloroform, due to its proton donor character which is favorable for the formation of hydrogen bonds with the fluorine groups and the oxygen atoms of the carbonyl groups (proton acceptors) of the polymer. Furthermore, the total and dispersive solubility parameters descend in a linear manner with the increase of temperature, whereas the polar and hydrogen bonding solubility parameters increase when temperature rises, probably due to the conformational changes of the polymer on the solid support.

1. Introduction

Fluorinated methacrylic polymers exhibit attributes of both methacrylic and fluorine-containing polymers. The highly stable C–F covalent bonds endow this category of polymers with distinctive physicochemical traits, such as low surface energy, low refractive index, chemical inertness, excellent weatherability and stain resistance [1–4]. Therefore, fluorinated methacrylic polymers have been extensively studied or used as high performance coatings for a plethora of diverse applications ranging from textile finishes, protective coatings and surface modifiers to denture lining materials [1,5–7]. Nevertheless, the poor solubility of these polymers in most of the common organic solvents undermines their processability [5,6].

The knowledge of solubility parameters of the polymers used in the aforementioned technological applications is of vital importance [8]. Hildebrand and Hansen's solubility parameters are physicochemical parameters useful for the evaluation or prediction of the compatibility between various materials, such as polymers [8,9], fillers [8], drugs [10,11] and solvents. The interactions between polymers and solvents are often quantified by

the Flory–Huggins interaction parameters and the weight fraction activity coefficients, assisting thus in the selection of proper solvents for every application [9].

Inverse gas chromatography (IGC) is widely used for the measurement of surface and thermodynamic properties of various materials, over a wide temperature range [9,12–18]. The basic tenet of IGC is that the stationary phase of the chromatographic column is the object of investigation while probes of known physicochemical properties are injected [9]. IGC provides insight into the thermodynamic properties of both traditional and novel materials like green solvents [19] and dendritic polymers [20].

A fluorinated methacrylic homopolymer of particular interest in numerous applications is poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate) (PHFIMA). PHFIMA has been investigated as a homopolymer [21,22], as copolymer [23,24] and as a polymer blend [25,26]. It has been extensively studied as coating for the protection of stone-made monuments [1,27,28] and recently appears to be promising as a dental material [7] and as a lubricant for electrical contacts [29,30]. However, to the best of our knowledge, there is a paucity of information on the dissolution profile of PHFIMA, at least in thermodynamic terms. To this end, we report the first results of the thermodynamic characterization of PHFIMA by means of IGC at infinite dilution. In particular, the sorption thermodynamic parameters (molar heat, energy and entropy of sorption), the molar heats and energies of mixing at infinite dilution and the

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heats of vaporization of 15 probes were calculated. Additionally, the weight fraction activity coefficient, the Flory–Huggins interaction parameter of each test probe as well as the total and partial solubility parameters of the polymer were determined. Prior to reporting our experimental work, the basic theoretical background will be summarized in the next section.

2. Theory and calculations

IGC experiments can be conducted either at infinite dilution or at finite concentration. At infinite dilution, minor amounts of the probes are injected into the column so that the lateral probe–probe interactions are prevented and the retention is mainly governed by stationary phase–probe interactions [9].

The net retention volume of a solute, V_N, is the volume of the carrier gas necessary to elute the solute from the column and is calculated by [31]:

$$V_N = jF_M(t_R - t_M)\frac{T}{T_F}\left(1 - \frac{p_W}{P_o}\right) \tag{1}$$

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_o, and at room 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 the gas carrier compressibility, defined as [31]:

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

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

Many thermodynamic properties can be determined from the specific retention volume, V_g^0. It is characteristic of a particular solute, stationary phase and carrier gas [31]:

$$V_g^0 = \frac{273 V_N}{W_s T} \tag{3}$$

where W_s is the mass of the polymeric stationary phase.

The molar heat (enthalpy) of sorption, ΔH_1^s, and the molar free energy of sorption, ΔG_1^s, of the probe absorbed by the polymer are given by the following equations [31]:

$$\Delta H_1^s = -\frac{R\partial \ln V_g^0}{\partial(1/T)} \tag{4}$$

$$\Delta G_1^s = -RT \ln \left(\frac{M_1 V_g^0}{273.15 R}\right) \tag{5}$$

where T is the column temperature, M_1 is the molecular weight of the probe and R is the gas constant.

The calculation of the entropy of sorption, ΔS_1^s of the solutes was made by combining Eqs. (4) and (5) [15]:

$$\Delta G_1^s = \Delta H_1^s - T\Delta S_1^s \tag{6}$$

The weight fraction activity coefficient, Ω_1^∞, the molar heat of mixing at infinite dilution, ΔH_1^∞, and the molar free energy of mixing, ΔG_1^∞, of each probe can be calculated as follows [15,31]:

$$\Omega_1^\infty = \frac{273.15 R}{V_g^0 P_1^0 M_1} \exp \left(\frac{-P_1^0(B_{11} - V_1)}{RT}\right) \tag{7}$$

$$\Delta H_1^\infty = \frac{R\partial \ln \Omega_1^\infty}{\partial(I/T)} \tag{8}$$

$$\Delta G_1^\infty = RT \ln \Omega_1^\infty \tag{9}$$

where P_1^0 is the vapor pressure of the probe at temperature T and B_{11} its second virial coefficient.

The Flory–Huggins interaction parameter χ_{12}^∞ is used to describe the interaction between the polymer and the probe and is given by the following equation [15,31]:

$$\chi_{12}^\infty = \ln \left(\frac{273.15 R v_2}{V_g^0 P_1^0 V_1}\right) - 1 - \frac{P_1^0(B_{11} - V_1)}{RT} \tag{10}$$

where V_1 and v_2 are the probe's molar volume and the polymer specific volume, respectively.

The vapor pressures, the second virial coefficients, the molar volumes and the heats of vaporization of the probes were calculated from the literature data [32].

Experimental values of the heats of vaporization, ΔH_V, of the probes can be obtained from the heats of sorption and heats of mixing through the following equation [17]:

$$\Delta H_V = \Delta H_1^\infty - \Delta H_1^s \tag{11}$$

The solubility parameter of each probe, δ_1, is calculated from the following relation [33]:

$$\delta_I = \left(\frac{\Delta H_V - RT}{V_1}\right)^{1/2} \tag{12}$$

The solubility parameter of the polymer, δ_2, can be calculated from the following equation [9]:

$$\left(\frac{\delta_{1i}^2}{RT} - \frac{\chi_{(12)i}^\infty}{V_{1i}}\right) = \frac{2\delta_2}{RT}\delta_{1i} - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{V_{1i}}\right) \tag{13}$$

where χ_s is the entropy term of the Flory–Huggins interaction parameter.

By plotting the left hand side of this equation versus δ_{1i}, a straight line with slope of $2\delta_2/RT$ is obtained allowing for the determination of the δ_2 of the investigated material.

The total solubility parameter or Hildebrand solubility parameter, δ_T, is given by the following equation [9]:

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{14}$$

where δ_d, δ_p and δ_h are the partial solubility parameters due to dispersive, polar and hydrogen bonding interactions, respectively.

Voelkel and Janas [13] proposed the following procedure for the calculation of the partial solubility parameters of the investigated materials (the polymer in our case) via IGC experiments: Eq. (13) is applied separately for three groups of probes representing dispersive, polar and hydrogen bonding interactions, and the slopes obtained from the straight lines lead to the calculation of δ_d, δ_p and δ_h with the use of the following equations:

$$\begin{aligned}\delta_d &= \frac{m_{n\text{-alkanes}} RT}{2} \\ \delta_p &= \frac{m_1 - m_{n\text{-alkanes}} RT}{2} \\ \delta_{hb} &= \frac{m_2 - m_{n\text{-alkanes}} RT}{2}\end{aligned} \tag{15}$$

where $m_{n\text{-alkanes}}$ is the value of the slope for n-alkanes (non-polar probes), m_1 the value of the slope for aromatic hydrocarbons, ketones, acetonitrile, 1-nitropropane (polar probes) and m_2 is the value of the slope for alcohols, 1,4-dioxane, pyridine and chloroform (hydrogen bonding probes).

3. Experimental

3.1. Materials

The monomer 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFIMA) was purchased from Aldrich and was used as received. 2,2′-Azobis(2,4-dimethylvaleronitrile) (ABDV) (Neuss, Germany) was used as the free radical initiator and was recrystallized twice from methanol. Tetrahydrofuran of analytical grade was dried

over molecular sieves (Aldrich) prior to being used as the poly-merization solvent. For the IGC analysis, all solvents were of the highest available purity and were purchased from Aldrich. The probes used, were selected according to their ability to interact with three different types of interaction forces, namely, dispersive (*n*-octane, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane), polar (2-butanone, 2-pentanone, cyclopentanone, 1-nitropropane, toluene) and hydrogen bonding (1-propanol, *n*-butanol pyridine, 1,4-dioxane, chloroform). Chromosorb W HP (80/100) mesh (Supelco) was used as the solid support. All gases utilized were purchased from Air Liquide Mediterranee and were of high purity.

3.2. Homopolymerization of HFIMA

PHFIMA was prepared by the free radical polymerization of HFIMA. A degassed mixture of the monomer (2 g), the polymerization solvent (tetrahydrofuran) (5 ml) and the free radical initiator (ABDV) (1% wt of the monomer) was introduced in a glass tube with a narrow neck. The tube was then hermetically sealed and placed in a water bath at 40 °C, allowing the polymerization to proceed for 24 h. The polymer was collected by repeated precipitation into methanol and consequent centrifugation. The filtrate was then washed with a large volume of methanol and dried in a vacuum oven at 50 °C [17].

3.3. Characterization

The FTIR spectrum was obtained with a Bio-Rad FTIR (model FTS 175) spectrometer, with $2\,cm^{-1}$ resolution and 32 scans. The polymer was mixed with KBr in a mass proportion of ∼1/150 (polymer to KBr) and processed into pellets. Differential scanning calorimetry (DSC) measurements were performed on a Shimadzu DSC-50Q instrument, at scan rates of 20 °C/min on a 10 mg sample. The sample was heated from 20 to 200 °C. The glass transition temperature, T_g, was taken from the second heating scan as the midpoint of the curve inflection. Thermogravimetric analysis (TGA) was performed on a 10 mg sample, using a Shimadzu TGA-50 analyzer with a heating ramp of 10 °C/min up to 700 °C under a constant nitrogen flow of $20\,cm^3/min$. Size exclusion chromatographic (SEC) analysis was accomplished on a Polymer Laboratories PL-GPC210 system equipped with a differential refractometer PL-210 and a Viscotek Model 210R viscometer. Separations were made using two PLgel 10 μm MIXED-B columns. Chloroform was used as an eluting solvent with a flow rate of 1.0 ml/min at 35 °C. The molecular weight of the polymers was calibrated with 10 PMMA standards. The density of the polymer was measured at room temperature, using the buoyancy method (ASTM D-792) with ethylene glycol as the liquid of known density.

3.4. IGC setup

IGC measurements were carried on a Hewlett Packard HP 5890 gas chromatograph, equipped with a flame ionization detector (FID). High purity helium was used as the carrier gas. The flow rate of helium was measured with a soap bubble flowmeter, at room temperature. Methane was used as the non-interacting marker to determine the void volume of the column. IGC experimental conditions are presented in Table 1. Probes were injected manually with a 1 μl Hamilton syringe. The injection volume for each probe was 0.1 μl, in order to achieve infinite dilution. At least three injections were made for each probe and the average retention time, t_R, was used for the calculations. The standard deviation was less than 2% in all measurements. The retention times of the probes were determined after the calculation of the first-order moment of

Table 1
Chromatographic conditions and column specifications.

PHFIMA	
Injector temperature (°C)	200
Detector temperature (°C)	200
Column temperatures (°C)	120, 130, 140, 150
Column length (cm)	65
Column O.D. (inch)	1/8
Column I.D. (inch)	1/16
Mass coated (g)	0.08
Loading (%)	15
Flow rate (ml/min)	13.5

the concentration distribution. This was necessary due to the slight "tailing" exhibited by the elution profile of the probes [31].

3.5. Column preparation

A stainless steel column was used for the measurements and was washed with acetone prior to use. A 2% (w/v) solution of PHFIMA in tetrahydrofuran was used for the coating procedure. The stationary phase of the column was prepared with the coating method proposed by Al-Saigh and Munk [18], in order to better control the amount of the polymer coated on the solid support. The loading of the column was made by the aid of a mechanical vibrator and a vacuum pump. The end of the column was plugged with a small piece of glass wool and was connected to the vacuum pump. Mechanical vibration and manual tap ensured better packing of the stationary phase in the column. The column was shaped in a coiled form in order to be adjusted to the injector's and detector's ports. Prior to measurements, the column was conditioned overnight to the working conditions (temperature and helium flow rate) in order to remove any possible contaminants that could be eluted during measurements. The column characteristics are presented in Table 1.

4. Results

4.1. Characterization

The infrared spectrum of PHIMA (Fig. 1) exhibits a strong absorption due to carbonyl stretching (C=O) at $1775\,cm^{-1}$. The absorption in the region of $3000–2800\,cm^{-1}$ is indicative of the presence of aliphatic groups. Fluorinated carbonate groups absorb strongly at wavelengths between 1250 and $1110\,cm^{-1}$, while the absorptions at 690 and $730\,cm^{-1}$ can be attributed to the presence of CF_3 groups [12].
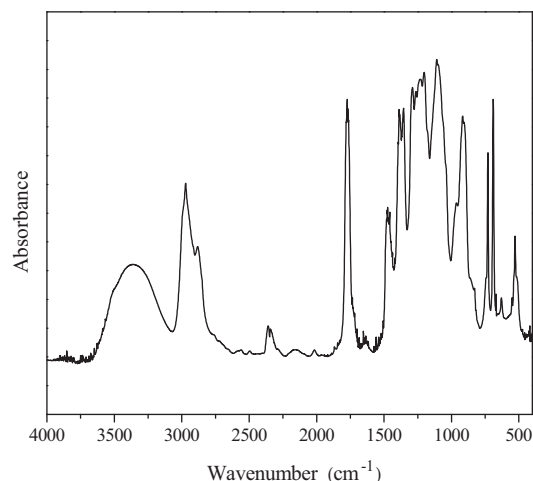

Fig. 1. IR spectrum of PHFIMA.

Table 2
Properties of PHFIMA.

Polymer	T_g (°C)	T_s (°C)	T_{10} (°C)	Density(g/cm³)	Mw	Mn	Mz	PDI
PHFIMA	81	190	249	1.10	181 800	141 100	222 500	1.29

The polymer's thermal properties are very important since they determine the working temperature range of the IGC measurements [9]. DSC analysis of PHFIMA showed that the only phase transition present is the glass transition. In the investigated temperature range, no crystallization or melting temperatures were observed.

The decomposition-starting temperature, T_s, and the temperature, T_{10}, which corresponds to 10% weight loss, were obtained from TGA. SEC analysis demonstrated that the polymer is of high molecular weight and of low polydispersity index. The results of the thermal characterization of the polymer, as well as the molecular weights are presented in Table 2.

4.2. IGC results

The thermodynamic characterization of PHFIMA was conducted at 120, 130, 140 and 150 °C. The selection of the temperature range was made bearing in mind, both, the glass transition temperature of PHFIMA, as well as its starting decomposition temperature (Table 2).

4.2.1. Specific retention volumes

Specific retention volumes of 15 probes, V_g^0, were obtained in the temperature range 120–150 °C. Their values were calculated according to Eq. (3) and are summarized in Table 3. The obtained V_g^0 values of the probes are temperature-dependent and decrease as the temperature increases. The specific retention volumes of probes with similar boiling points but with different functional groups are different. More specifically, n-octane presents lower V_g^0 values than n-butanol and cyclopentanone. This is commonly observed in the literature [17,34,35] and can be attributed to the fact that polar probes present additional interactions with the polymer when compared with the hydrocarbon interactions. The same trend is observed for the values of the molar heat of sorption of the probes, ΔH_1^s (Table 4) and will be further discussed in Section 4.2.2.

4.2.2. Thermodynamic sorption parameters

The molar enthalpies of sorption of the probes, ΔH_1^s, were calculated from the slopes of V_g^0 versus $1/T$, as described by Eq. (4). The values of ΔH_1^s are listed in Table 4. Generally, a good linear

Table 3
Specific retention volumes, V_g^0 (cm³/g) of various probes, on PHFIMA at 120, 130, 140 and 150 °C.

Probe	120 °C	130 °C	140 °C	150 °C
n-Octane	7.68	7.16	6.69	6.13
n-Nonane	12.41	11.16	10.20	9.06
n-Decane	19.78	17.44	15.62	13.51
n-Undecane	29.35	25.76	22.42	18.77
n-Dodecane	46.86	39.72	34.25	28.06
1-Propanol	5.43	5.02	4.87	4.68
n-Butanol	10.27	9.45	8.63	7.69
Pyridine	19.64	17.98	15.99	14.16
1,4-Dioxane	17.26	15.41	13.58	11.70
Chloroform	6.05	5.87	5.60	5.38
2-Butanone	8.69	8.10	7.45	6.75
2-Pentanone	12.73	11.67	10.60	9.40
Cyclopentanone	31.34	25.98	22.14	18.69
1-Nitropropane	22.36	19.93	16.64	14.38
Toluene	11.01	10.50	9.81	9.37

relationship was obtained for the probes, indicating that V_g^0 values were amenable to thermodynamic analysis. The linearity can be attributed to the establishment of equilibrium between the probe and the stationary phase [12,17,34,36–38].

The molar free energy of sorption and the entropy of sorption were calculated according to Eqs. (5) and (6), respectively. The sorption parameters ΔG_1^s and ΔS_1^s are given in Tables 5 and 6, respectively.

From the data reported in Tables 4–6 it can be seen that the molar heats of sorption are negative (exothermic), while the molar free energies of sorption are positive (unfavorable/endothermic). The values of the molar heats of sorption of the probes are strongly dependent on the type of probe and give useful information about their interaction with the material under study.

In the case of n-alkanes, their heats of sorption become more exothermic as their number of carbon atoms increases (Table 4 and Fig. 2). This can be attributed to the interaction between the methyl groups of n-alkanes and the methyl groups of PHFIMA, via dispersive forces. Probes with comparable boiling points, like n-octane, cyclopentanone and n-butanol exhibit different molar heats of sorption. The latter two presented more exothermic ΔH_1^s values as compared to the respective value of n-octane. This is attributed

Table 4
The molar heats of sorption, ΔH_1^s, the partial molar heats of mixing, ΔH_1^∞, of various probes on PHFIMA and the heats of vaporization, $\Delta H_v{}^a$, at 120–150 °C.

Probe	ΔH_1^s (kJ/mol)	ΔH_1^∞ (kJ/mol)	$\Delta H_v{}^a$ (kJ/mol)	$\Delta H_v{}^b$ (kJ/mol)
n-Octane	−10.28 ± 0.58	24.50 ± 0.75	34.78 ± 1.33	33.92
n-Nonane	−14.28 ± 0.66	24.74 ± 0.82	39.02 ± 1.48	38.62
n-Decane	−17.32 ± 0.85	25.96 ± 1.03	43.28 ± 1.88	43.01
n-Undecane	−20.43 ± 1.38	27.03 ± 1.62	47.46 ± 3.00	47.81
n-Dodecane	−23.29 ± 1.29	28.30 ± 1.52	51.59 ± 2.81	52.16
1-Propanol	−6.61 ± 1.03	31.95 ± 0.57	38.56 ± 1.60	37.85
n-Butanol	−13.23 ± 0.92	28.76 ± 1.26	41.99 ± 2.18	41.04
Pyridine	−15.17 ± 0.99	19.48 ± 1.15	34.65 ± 2.14	34.08
1,4-Dioxane	−17.85 ± 1.06	14.84 ± 1.20	32.69 ± 2.26	32.19
Chloroform	−5.51 ± 0.38	20.73 ± 0.48	26.24 ± 0.86	25.07
2-Butanone	−11.61 ± 0.80	17.31 ± 0.97	28.92 ± 1.77	27.76
2-Pentanone	−13.88 ± 0.95	18.51 ± 1.12	32.39 ± 2.07	30.99
Cyclopentanone	−23.70 ± 0.55	13.04 ± 0.46	36.74 ± 1.01	36.17
1-Nitropropane	−20.78 ± 1.40	16.44 ± 1.52	37.22 ± 2.92	37.33
Toluene	−7.63 ± 0.43	25.03 ± 0.48	32.66 ± 0.91	31.92

[a] Calculated according to Eq. (11).
[b] From Ref. [32].

Table 5
The molar free energies of sorption ΔG_1^s (kJ/mol), of various probes on PHFIMA at 120, 130, 140 and 150 °C.

Probe	120 °C	130 °C	140 °C	150 °C
n-Octane	10.59	11.09	11.60	12.19
n-Nonane	8.64	9.22	9.76	10.41
n-Decane	6.78	7.37	7.94	8.64
n-Undecane	5.18	5.75	6.37	7.15
n-Dodecane	3.37	4.01	4.62	5.43
1-Propanol	13.82	14.44	14.90	15.40
n-Butanol	11.05	11.61	12.21	12.91
Pyridine	8.72	9.24	9.87	10.54
1.4-Dioxane	8.79	9.40	10.06	10.83
Chloroform	11.23	11.61	12.06	12.49
2-Butanone	11.69	12.22	12.81	13.47
2-Pentanone	9.86	10.40	10.99	11.68
Cyclopentanone	6.99	7.80	8.54	9.35
1-Nitropropane	7.91	8.50	9.33	10.07
Toluene	10.12	10.53	11.03	11.45

Table 6
The entropies of sorption ΔS_1^s (J/mol K), of various probes on PHFIMA at 120, 130, 140 and 150 °C.

Probe	120 °C	130 °C	140 °C	150 °C
n-Octane	−53.07	−53.01	−52.95	−53.10
n-Nonane	−58.31	−58.29	−58.19	−58.35
n-Decane	−61.30	−61.25	−61.13	−61.35
n-Undecane	−65.14	−64.93	−64.86	−65.17
n-Dodecane	−67.82	−67.73	−67.56	−67.89
1-Propanol	−64.69	−64.62	−64.17	−63.84
n-Butanol	−63.43	−63.24	−63.16	−63.33
Pyridine	−82.48	−81.71	−81.27	−80.92
1.4-Dioxane	−75.21	−74.84	−74.65	−74.70
Chloroform	−47.96	−47.73	−47.66	−47.56
2-Butanone	−46.54	−46.71	−47.00	−47.45
2-Pentanone	−58.73	−58.62	−58.62	−58.87
Cyclopentanone	−56.36	−56.96	−57.38	−57.92
1-Nitropropane	−65.51	−65.34	−65.77	−65.97
Toluene	−39.75	−39.79	−40.03	−40.09

to the fact that ketones, like cyclopentanone, interact with the polymer via, both, dipole–dipole and dispersive forces. Specifically, the CH_2 groups of ketones interact with the CH_2 groups of PHFIMA (dispersive forces), whereas the C=O group of ketones interact with the C=O groups of PHFIMA (dipole–dipole forces). In the case of alcohols, in addition to the dispersive interaction, there is the hydrogen bonding interaction between the OH group of the alcohols with the C=O groups of the polymer [17,39–40].
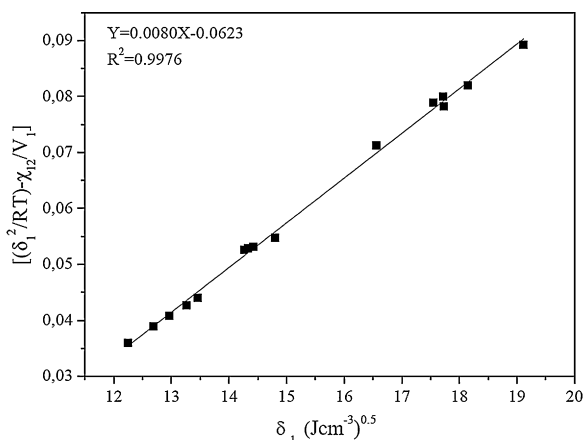

Fig. 2. Variation of δ_1 of various probes against $[(\delta_1^2/RT) - (\chi_{12}^\infty/V_1)]$, at 150 °C.

Table 7
Weight fraction activity coefficients, Ω_1^∞, of various probes at 120, 130, 140 and 150 °C.

Probe	120 °C	130 °C	140 °C	150 °C
n-Octane	31.61	25.93	21.58	18.63
n-Nonane	35.50	29.21	24.13	20.85
n-Decane	41.17	33.45	27.32	23.57
n-Undecane	50.62	40.00	32.63	28.28
n-Dodecane	58.29	46.20	36.92	31.79
1-Propanol	32.80	26.30	20.51	16.50
n-Butanol	28.52	22.36	18.08	15.32
Pyridine	13.02	10.89	9.54	8.52
1,4-Dioxane	9.29	8.09	7.25	6.75
Chloroform	7.01	5.91	5.12	4.46
2-Butanone	12.63	10.84	9.55	8.68
2-Pentanone	13.16	11.18	9.74	8.82
Cyclopentanone	11.83	10.77	9.70	8.96
1-Nitropropane	16.17	13.63	12.48	11.22
Toluene	17.92	14.61	12.36	10.37

4.2.3. Probe–polymer interaction parameters

The weight fraction activity coefficient, Ω_1^∞, and the Flory–Huggins interaction parameter, χ_{12}^∞, characterize the ability of a solvent to dissolve a polymer. It has been proposed that values of Ω_1^∞ lower than 5 and values of χ_{12}^∞ smaller than 0.5 are indicative of a good solvent for the polymer, while Ω_1^∞ values bigger than 10 and χ_{12}^∞ values greater than 0.5 represent unfavorable polymer–solvent interactions. When weight fraction activity coefficient values vary between 5 and 10, the solvent is characterized as moderate [17,39]. The values of the calculated parameters are given in Tables 7 and 8.

From the values reported in Tables 7 and 8, it is clear that, both, the interaction parameters as well as the weight fraction activity coefficients depend on temperature. The polymer–solvent interaction parameter χ is comprised of two terms, namely the enthalpic, χ_H and the entropic, χ_S [9]. Both terms are temperature-dependent. At low temperatures, enthalpic effects due to attractive forces are more pronounced than the entropic ones, whereas at high temperatures, the attractive forces weaken and the entropic effects arising from increased free volume differences are prevailing. In other words, χ_H decreases with the increase of temperature, while χ_S increases with the increase of temperature. The parabolic dependence of χ on temperature, together with the χ_H and χ_S temperature dependences gives the Upper and Lower Critical Solution Temperatures (UCST and LCST) characteristic of polymer solutions [41,42]. In the vicinity of the UCST, the polymer–solvent interaction parameter decreases with temperature, which is our case. The Ω_1^∞ and χ_{12}^∞ values decrease with increasing temperature. Moreover, the aforementioned parameter values increase as the

Table 8
Flory–Huggins interaction parameters, χ_{12}^∞, of various probes at 120, 130, 140 and 150 °C.

Probe	120 °C	130 °C	140 °C	150 °C
n-Octane	1.88	1.66	1.46	1.30
n-Nonane	2.02	1.81	1.61	1.45
n-Decane	2.19	1.97	1.76	1.60
n-Undecane	2.42	2.17	1.96	1.80
n-Dodecane	2.58	2.33	2.10	1.93
1-Propanol	2.05	1.81	1.55	1.31
n-Butanol	1.93	1.67	1.44	1.26
Pyridine	1.34	1.15	1.00	0.87
1.4-Dioxane	1.05	0.89	0.77	0.68
Chloroform	1.11	0.92	0.75	0.59
2-Butanone	1.06	0.89	0.74	0.62
2-Pentanone	1.13	0.95	0.79	0.68
Cyclopentanone	1.21	1.10	0.99	0.89
1-Nitropropane	1.57	1.39	1.28	1.16
Toluene	1.53	1.31	1.13	0.94

number of carbon atoms for the series of n-alkanes and ketones increases. This could be attributed to the fact that the penetration/approach and subsequently the interaction of the probes with the polymer become more difficult as the chain length of the probe increases. However, this is not applicable to the case of alcohols. In terms of reduction of χ_{12}^∞, the solubility of the polymer in alcohols becomes better as the number of carbon atoms of alcohols increases. Moreover, among the probes with similar boiling points, n-butanol presents the highest χ_{12}^∞ suggesting that it is less compatible with the polymer than n-octane and cyclopentanone. This is probably due to the high degree of self-association that alcohols exhibit here [35], since this interaction seems energetically favored over the OH- - -F–C cross-association.

As shown in Tables 7 and 8, in the investigated temperature range, n-alkanes are non-solvents for PHFIMA. Alcohols are also non-solvents for the polymer, as confirmed by the values of Ω_1^∞ and χ_{12}^∞. Pyridine, 1,4-dioxane, 2-butanone, 2-pentanone, cyclopentanone, 1-nitropropane and toluene are moderate solvents, as shown in Tables 7 and 8. The values of Ω_1^∞ and χ_{12}^∞ of chloroform are close to 5 and 0.5, respectively, suggesting that chloroform can be considered as good solvent for PHFIMA at high temperatures. The solubility of the polymer in the tested solvents can be elucidated when the proton donor/acceptor capability of the solutes in combination with the chemical structure of the polymer are taken into account. PHFIMA is rich in CF_3 groups which are functioning as proton acceptors. Among the tested solvents, n-propanol, n-butanol and chloroform act as proton donors able to form hydrogen bonds with the CF_3 and $C=O$ groups of the polymer. The incompatibility of PHFIMA with the alcohols could be attributed to their self-association, whereas the polymer's affinity to chloroform can be ascribed to the formation of cross-association hydrogen bonds between the hydrogen of chloroform and the fluorine atoms and the $C=O$ groups of the polymer (no competitive self-association here).

The observed incompatibility of the polymer with a wide range of solvents is in accordance with the literature. It is reported that the greater the fluorine content of a polymer is, the less soluble it becomes [22,43]. Previously published results further corroborate the aforementioned observation. More specifically, it was found that a less fluorinated methacrylic polymer than PHFIMA, namely poly(2,2,3,3,3-pentafluoropropyl methacrylate) (PPFPMA), is soluble in two ketones in the temperature range 80–120 °C [17], whereas PHIMA is insoluble almost in every tested solvent, even at higher temperatures.

4.2.4. Thermodynamic parameters of mixing

The molar heats of mixing at infinite dilution of the probes, ΔH_1^∞ were obtained from the slopes of Ω_1^∞ versus $1/T$ (Eq. (8)). The values of ΔH_1^∞ are presented in Table 4. The molar free energies of mixing, ΔG_1^∞, were calculated from Eq. (9) and the values are listed in Table 9.

From the data presented in Tables 4 and 9, regarding the molar heats and energies of mixing at infinite dilution of the probes, it is clear that the parameters of mixing are endothermic. Additionally, n-butanol presents higher molar heat of mixing and heat of vaporization than cyclopentanone and n-octane. This trend is in accordance with the literature [17,35].

Furthermore, the heats of vaporization, ΔH_V, of all probes (Table 4) are comparable with the literature values [32], suggesting that the values of ΔH_1^s and ΔH_1^∞ are amenable to thermodynamic analysis.

4.2.5. Solubility parameters

The solubility parameter, δ_2, of PHFIMA was calculated from the slope of a straight line obtained by plotting the left hand side of Eq. (13) versus δ_{1i}, as illustrated in Fig. 2.

Table 9
The molar free energies of mixing, ΔG_1^∞ (kJ/mol), of various probes on PHFIMA at 120, 130, 140 and 150 °C.

Probe	120 °C	130 °C	140 °C	150 °C
n-Octane	11.29	10.91	10.55	10.29
n-Nonane	11.67	11.31	10.93	10.69
n-Decane	12.15	11.76	11.36	11.12
n-Undecane	12.83	12.36	11.97	11.76
n-Dodecane	13.29	12.85	12.40	12.17
1-Propanol	11.41	10.96	10.38	9.86
n-Butanol	10.95	10.42	9.94	9.60
Pyridine	8.39	8.00	7.75	7.54
1.4-Dioxane	7.29	7.01	6.81	6.72
Chloroform	6.37	5.95	5.61	5.26
2-Butanone	8.29	7.99	7.75	7.60
2-Pentanone	8.42	8.09	7.82	7.66
Cyclopentanone	8.08	7.96	7.80	7.71
1-Nitropropane	9.10	8.75	8.67	8.51
Toluene	9.43	8.99	8.64	8.23

Table 10
Solubility parameters, δ_2, of PHFIMA, calculated from Eq. (13) at 120, 130, 140 and 150 °C.

T (°C)	Slope	δ_2 (J/cm^3)$^{0.5}$	R^2
120	0.0088	14.39 ± 0.26	0.9958
130	0.0085	14.31 ± 0.24	0.9965
140	0.0083	14.18 ± 0.21	0.9971
150	0.0080	14.05 ± 0.19	0.9976

The values of PHFIMA solubility parameters together with the maximum error are summarized in Table 10. In all cases, high regression coefficients were observed (>0.995). In the examined temperature range, it was found that δ_2 decreases with the increase of temperature. The variation of δ_2 with temperature is almost linear.

The total solubility parameter δ_r and its partial components δ_d, δ_p, δ_h were determined with the use of Eqs. (14) and (15). The temperature dependence of the solubility parameters is depicted in Figs. 3 and 4. The regression coefficients regarding the lines obtained from Eq. (15) were relatively high (>0.988).

The values of the total solubility parameters, δ_T, calculated from Eq. (14) (Fig. 3) are lower than those calculated from Eq. (13) (Table 10), an observation which is in accordance with the literature [14]. The difference between δ_1 and δ_2 ranges between 1 and 2 (J/cm^3)$^{0.5}$ and increases with the increase of temperature. The total and dispersive component of the solubility parameter decreases with the increase of temperature (Fig. 3). A linear decrease of the aforementioned properties with temperature is observed.
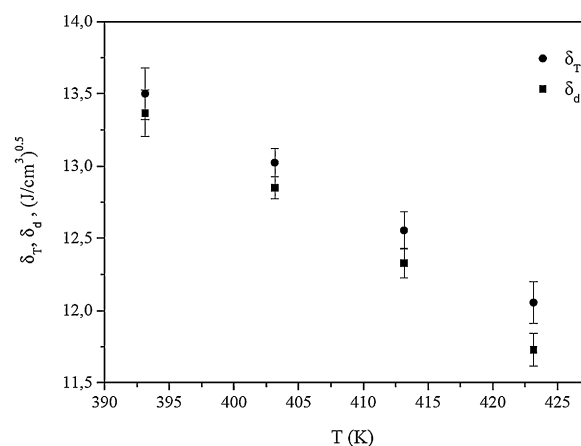

Fig. 3. The total and dispersive components of the solubility parameters of PHFIMA as a function of temperature.
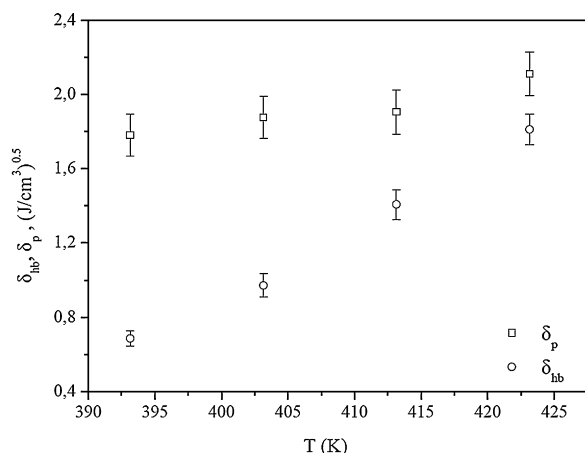
Fig. 4. The hydrogen-bonding and polar components of the solubility parameters of PHFIMA as a function of temperature.

On the contrary, the polar and hydrogen bonding components of the solubility parameter of PHFIMA increase with increasing temperature in a linear manner (Fig. 4). This behavior is often observed in the literature [13,14,16,44,45] and could probably be attributed to orientation, steric hindrance, or group exposure, which might be influenced by the conformational changes of the polymeric chain as it is spread and arranged on the solid support [14]. The influence of temperature on the polar component of the solubility parameter appears to be weaker than the one on the hydrogen bonding component (Fig. 4). Although the latter components of the solubility parameter increase with the increase of temperature, the total solubility parameter decreases with the increase of temperature, as stated earlier. The observed decrease in δ_T is attributed to the more pronounced decrease of its dispersive component with the increase of temperature.

5. Conclusions

The thermodynamic characterization of the fluorinated methacrylic polymer PHFIMA was conducted by means of IGC at infinite dilution. The molar heats of sorption of the probes on PHFIMA were found to be exothermic, while the molar free energies of sorption unfavorable or endothermic. The sorption parameters of the probes depend on their chemical nature which governs the various interactions with the polymer.

The determination of the Flory–Huggins interaction parameters and the weight fraction activity coefficients verify that PFHIMA is insoluble in most solvents, even at high temperatures. The values of the aforementioned parameters indicate that *n*-alkanes and alcohols are non-solvents for the polymer, polar solvents, pyridine and 1,4-dioxane are moderate solvents, whereas only chloroform can be considered as a good solvent for PHFIMA in the investigated temperature range. This can be further substantiated when taking into account the ability of chloroform to form cross-association hydrogen bonds the fluorine atoms and the oxygen atoms of the carbonyl group of the polymer.

The total and the dispersive component of the solubility parameter of PHFIMA exhibited a descending trend with the increase of temperature. However, the polar and hydrogen bonding components of the solubility parameter increased with the increase of temperature due to a combination of effects that include self-association and conformational or orientation changes of the polymer.

Based on the findings of this work, which is part of a series of similar work in our laboratory, it is shown that IGC can provide with an insightful understanding of the dissolution profile of PHFIMA and of other polymers of technological importance.

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