Synthesis, characterization and surface properties of fluorinated methacrylic polymers for the protection and conservation of stone

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Abstract

Physicochemical properties of two fluorinated methacrylic homopolymers (PTFEMA and PHFIMA) were studied by Inverse Gas Chromatography (IGC) and the Contact Angle method. The dispersive component of the polymers’ surface energy was calculated by both methods, while the total surface energy by the contact angle method. Moreover the polymer-solvents interactions were investigated by IGC. The results revealed that both polymers are hydrophobic and insoluble in many organic solvents.

Introduction

Perfluoroalkyl methacrylic polymers exhibit low surface energy and good stability towards degradation compared to their unfluorinated analogs. Moreover, the introduction of fluorine atoms into methacrylic polymers' structure results in good adhesion and film-forming properties[1,2]. The above mentioned merits qualify these polymers as promising materials for stone protection. The goal of the present work was to study the effects of the fluorine group contained in the polymer chain on the surface properties of the material. The following homopolymers were included in the study: poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) and poly(1,1,1,3,3,3 hexafluoroisopropyl methacrylate) (PHFIMA). The polymers were synthesized by free radical polymerization using AIBN as initiator in tetrahydrofuran. Supercritical carbon dioxide was also used as an alternative, “green” polymerization medium for the synthesis of all polymers. Polymer surface properties were studied with Inverse Gas Chromatography (IGC) and with the Contact Angle Method. In most polymers the dispersive component is the main contributor to the surface energy. The dispersive component is a very valuable indication about the polymers’ hydrophobicity. It is well known that polymers with low surface energy are hydrophobic.

Theory

Contact angle method

The Young contact angle, θ, between a liquid drop and a solid is provided by the following equation[3]:

$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{L}} \cos\theta + \gamma_{\mathrm{SL}} \quad (1)$$

Where γ_s, γ_L and γ_{sL} are the surface energy of the solid, the surface energy of the liquid and the interfacial energy between the solid and liquid, respectively.

Fowkes suggested that the surface energy of a solid or a liquid consists of two components, the dispersive and polar.

$$\gamma^{\mathrm{T}} = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}} \quad (2)$$

Where γ^T is the total surface energy, γ^d is the dispersive component and γ^p the polar component of surface energy. The polar component of surface energy γ_p can be expressed as:

$$\gamma^{\mathrm{p}} = 2(\gamma^{-}\gamma^{+})^{\frac{1}{2}} \quad (3)$$

Where γ^+ and γ^- are representing the electron-acceptor and electron-donor parameters of γ, respectively.

According to Van Oss[3] $\gamma^{\mathrm{SL}} = \gamma_{\mathrm{S}} + \gamma_{\mathrm{L}} - 2[(\gamma_{\mathrm{L}}{}^{\mathrm{d}}\gamma_{\mathrm{S}}{}^{\mathrm{d}})^{\frac{1}{2}} + (\gamma_{\mathrm{S}}{}^{-}\gamma_{\mathrm{L}}{}^{+})^{\frac{1}{2}} + (\gamma_{\mathrm{S}}{}^{+}\gamma_{\mathrm{L}}{}^{-})^{\frac{1}{2}}]$ (4)

Equation (1) in conjunction with equation (4) gives

$$\gamma_{\mathrm{L}}(1+\cos\theta) = 2[(\gamma_{\mathrm{S}}{}^{\mathrm{d}}\gamma_{\mathrm{L}}{}^{\mathrm{d}})^{\frac{1}{2}} + (\gamma_{\mathrm{S}}{}^{-}\gamma_{\mathrm{L}}{}^{+})^{\frac{1}{2}} + (\gamma_{\mathrm{S}}{}^{+}\gamma_{\mathrm{L}}{}^{-})^{\frac{1}{2}}] \quad (5)$$

The calculation of all components of the surface energy of a polymer ($\gamma_S{}^d$,$\gamma_S{}^+$, $\gamma_S{}^-$) is possible when equation 5 is applied for three liquids with known values of $\gamma_L{}^d$, $\gamma_L{}^+$, $\gamma_L{}^-$. The liquids are usually two polar and an apolar (γ_L= $\gamma^d{}_L$). In this study, water, diiodomethane and formamide were employed.

Inverse gas chromatography (IGC)

IGC is a useful and reliable technique to characterize the surface and thermodynamic properties of polymers. The dispersive component of polymers' surface energy and their solubility parameters can be evaluated by the use of IGC.

The term inverse implies that the material under study is the stationary phase and probes of known properties are injected at infinite dilution. When the measurements are carried out at infinite dilution the probe–probe interactions are negligible and stationary phase–probe interactions are the governing ones.

The keynote measurement in IGC experiments is the net retention volume V_N. The retention volume of a probe is the volume of the carrier gas required to sweep out an injected probe from the column. The specific retention volume (V_g) can be used for the calculation of thermodynamic properties [4,5] is: $V_g = \dfrac{273V_N}{W_S T} = \dfrac{273}{W_S T_F} \cdot j \cdot F_M \cdot \left(1 - \dfrac{p_W}{P^{'}}\right) \cdot \left(t_R - t_M\right)$ (6)

Where Ws is the polymer's mass, F_M is the uncorrected flow rate of the carrier gas measured by bubble flow meter, t_R is the retention time of the probe, t_M is the retention time of non adsorbing marker (methane). T and T_F are the column and flow meter temperatures, respectively. p_W is the vapor pressure of water at T_F and P' is the pressure at the flow meter.

The free energy of adsorption is expressed as the standard free energy of transferring 1 mole of molecules from the standard gaseous state to a standard adsorption state and it is related to the retention volume Vn according to: $\Delta \mathrm{G}^{\mathrm{ads}} = -\cdot \mathrm{R} \cdot \mathrm{T} \cdot \ln\left(\mathrm{V_N}\right) + \mathrm{C}$ (7)

Where R is the gas constant, T is the column temperature and C is a constant depending on the reference state and on the total surface area of the solid contained in the column. From the slope of the plot of $R \cdot T \cdot \ln V_N$ versus $\alpha\left(\gamma_L^d\right)^{1/2}$ the dispersive component of the surface free energy can be calculated.

Another way to calculate the dispersive component of the surface free energy of a polymer is through the use of Dorris and Gray equation:

$$\gamma_s^d = \left(\frac{1}{4 \cdot \gamma_{CH_2}}\right) \cdot \left(\frac{-\Delta G^{CH_2}}{N \cdot \alpha_{CH_2}}\right) n \quad (8)$$

Where α_{CH_2} is the area occupied by a -CH$_2$- group (0.06 nm^2), and γ_{CH_2} is the surface tension of a surface consisting of CH$_2$ groups. $\gamma_{CH_2} = 36.8 - 0.058 \cdot T$ (9)

ΔG^{CH_2} can be calculated by the slope of a straight line obtained from the plot of ΔG^{ads} of n-alkanes versus their number of carbon atoms.

The weight fraction activity coefficient of the solvent at infinite dilution, Ω_1^∞, is given by the following equation;

$$\Omega^\infty = \frac{273,15 \cdot R}{V_g P_1^0 M_1 \exp\left(\frac{-P_1^0\left(B_{11} - V_1\right)}{RT}\right)} \quad (10)$$

Where R is the universal gas constant, T is the column temperature, M_1 is the molecular weight of the solute, B_{11} is the second virial coefficient of the solute, V_1 molar volume and P_1 is the vapor pressure of the solute. All constants are known[6].

The weight fraction activity coefficient of the solvent at infinite dilution, Ω_1^∞, gives an idea of the polymer–solvent compatibility indicating that; $\Omega_1^\infty < 5$ for good solvents, $5 < \Omega_1^\infty < 10$ for moderate solvents and $\Omega_1^\infty > 10$ for bad solvents.

Experimental Section

Materials

Solvents: Tetrahydrofuran (THF) (Aldrich) was dried over molecular sieves before polymerization. Carbon dioxide (purity >99.98%) and nitrogen (purity >99.999%) were purchased from Air Liquide Mediterranee. All solvents were of the highest purity available (Aldrich).

Initiator: 2, 2'-azobisisobutyrronitrile (AIBN) was purchased from Acros Organics and was recrystallized twice from ethanol.

Monomers: 2,2,2-trifluoroethyl methacrylate (TFEMA), 1,1,1,3,3,3 hexafluoroisopropyl methacrylate (HFIMA) were purchased from Acros Organics. All monomers were used as received without further purification.

Polymerization using THF as the polymerization medium

The polymerization reactions were carried out in glass test tubes with a narrow neck. The first step was to insert the monomer in the tube and then the polymerization solvent. AIBN was then added to the solution at 0.3 wt % ratio with respect to the monomers mass. The mixture was emerged in an ice-bath and purged with nitrogen gas for 10 min in order to remove oxygen and create inert atmosphere. Afterwards, the glass tube was carefully sealed and placed in a water bath at 65°C. The polymerization time was 24 hours. The resulting polymers were recovered as precipitate after the addition of methanol. The polymer was washed with excess volume of methanol in order to remove any unreacted monomer, filtered and dried under vacuum overnight[7]. The yield was 73% and 57% for PTFEMA and PHFIMA, respectively.

Polymerization using carbon dioxide as the polymerization medium

Polymerizations were conducted in a 15 ml high pressure cell. The mixture (monomer and AIBN 0.3 wt% of monomer) was added in the reactor and purged with nitrogen. Carbon dioxide was charged in the reactor at room temperature. The initial pressure was 73 bar. Then it was placed in a furnace and heated at 65°C. The pressure after heating was 78 bar. 24 hours after the cell left to cool at room temperature and then carbon dioxide was depressurized slowly through a glass trap filled with methanol. At the end of reaction pressure became 91 bar. Pressure variations can be attributed to the changes of the monomer volume while being converted to polymer. Both polymers showed the same trend as far as pressure changes are concerned. The resulting polymer was recovered by the procedure previously described. The apparatus consists of a high pressure cell, an autoclave valve, a pressure gauge, a thermocouple, a temperature indicator, a back-pressure regulator and a glass trap[8,9]. The yield was 85% and 79% for PTFEMA and PHFIMA, respectively.

Polymer characterization

Fourier transform infrared measurements were performed on a Bio-Rad FTS 175 FTIR spectrophotometer. The dominant carbonyl group absorption appears at circa 1760 cm^{-1}. SEC Analysis was carried out using a PLGPC210 + Viscometer system equipped with a refractive index detector, model PL-210, a viscometry detector, Viscotek Model 210R and 2x PLgel 10um mixed B columns. Chloroform was used as the eluent. All polymers had high molecular weight and low polydispersity index. Differential scanning calorimetry measurements were performed using a Shimadzu DSC-50Q analyzer. Glass transition temperatures were 74°C and 69°C for PTFEMA and PHFIMA, respectively. TGA measurements were performed with a Shimadzu TGA-50 thermogravimetric analyzer. The onset of the first decomposition step (10% weight loss) occurs at around 250°C.

Contact angle measurements

Polymers' solutions of 5% wt in THF were spin coated on silicon wafers for 30 seconds at a spin rate of 6000 rpm. Tetrahydrofuran was left to be evaporated overnight. Measurements preformed in a Kruss DSA 100 goniometer. An average volume of 5 μl drop of each test liquid was deposited on the surface under study. Up to ten measurements of each liquid were made for the calculation of the surface energy. The liquids used were water, formamide and diiodomethane.

Inverse gas chromatography (IGC)

Polymer solutions 2%wt were coated on Chromosorb W HP (80/100 mesh) from Supelco. Polymers' loading on Chromosorb was 14.5%. Chromosorb was carefully packed with mechanical vibration in stainless steel columns with O.D 1/8 inch and 65 cm length. The ends of the columns were closed with glass wool. Inverse gas chromatography measurements were conducted using a Shimadzu GC14-A gas chromatograph ecquiped with a flame ionization detector (FID). The carrier gas was helium at a flow rate of 20 ml/min. Flow rates were measured with a calibrated soap bubble flowmeter. The injector and detector temperatures were set at 150 and 200°C, respectively. All columns were conditioned overnight at the working temperature. The temperature under study was 50°C. Methane was used as the non-interacting reference marker to determine the dead volume of the column. Four injections for each probe were made manually with a Hamilton 1μl syringe.

Results and Discussion

Contact angle measurements

The measured contact angles and the calculated components of the surface energy of each polymer are shown in tables 1 and 2, respectively.

Table 1. Contact angles of various liquids on polymer's surface.

Polymer	Contact angles θ (^{0})		
	Water	Diiodomethane	Formamide
PTFEMA	97	77	80
PHFIMA	103	88	95

Table 2. Components of surface energy

Polymer	Components of surface energy (mJ/m^2)				
	γ^d	γ^+	γ^-	γ^P	γ^T
PTFEMA	19,1800	0,4119	2,7471	2,1	21,3
PHFIMA	13,4039	0,0046	4,5008	0,3	13,7

Water contact angles are larger than 90° for both polymers, indicating thus the hydrophobic nature of the tested materials. The latter may be therefore further studied for stone protection. The surface energies of the tested materials at 25°C follow the same trend with their contact angles. PHFIMA exhibits very low dispersive surface energy with respect to PTFEMA. That can be attributed to the fact that PHFIMA has a higher fluorine content than PTFEMA.
The contribution of the polar part to the total surface energy appears to be small in both cases.

Inverse gas chromatography (IGC)

All measurements were conducted at 50°C. The apolar probes used for the determination of the dispersive component of surface energy were n-alkanes. Figures and show the plot of $RT\ln V_N$ versus the number of carbon atoms of alkanes, from n-hexane to n-decane. For both polymers the above function was linear and the regression coefficient was 0.999.

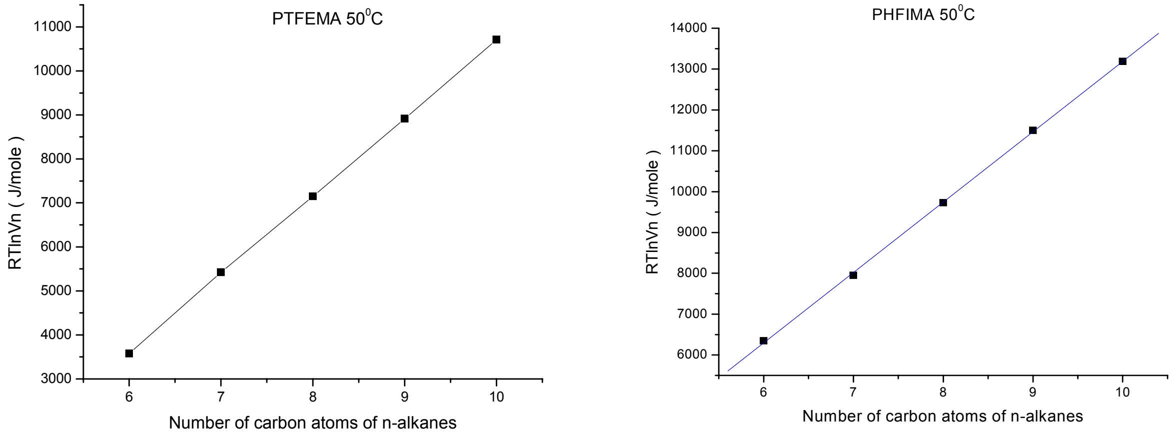

Figure 1. Adsorption free energy versus the number of carbon atoms of n-alkanes

Table 3. Dispersive component of surface energy

Polymer	γ^d (mJ/m^2)
PTFEMA	17,78
PHFIMA	16,74

Comparing the values of the dispersive component of surface energy γ^d obtained by the contact angle method (Table 5) with that obtained by IGC (Table 6), we see a difference between results of the two methods. The value of γ^d of PTFEMA seems to decrease from 19,18 mJ/m^2 at 25°C (contact angle method) to 17,78 mJ/m^2 at 50°C (IGC). That seems to be normal according to the fact that the surface free energy decreases linearly with an increase of temperature. In the case of PHFIMA the value of γ^d decreases with the increase of temperature. The results derived from the two methods are not uniform due to the fact that IGC measures the surface energy by means of zero coverage adsorption, whereas a multilayer adsorption is utilized in contact angle measurement[10]. The weight fraction activity coefficient of a solvent at infinite dilution, Ω_1^{∞} was calculated for both polymers at 50°C. The solvents under study, apart from n-alkanes, were: Acetonitrile, ethanol, 1- propanol, n-butanol, terrahydrofuran, nitropropane, chloroform, 2-butanone and pyridine.

Solvents	V_g (cm^3/g)		Ω_1^∞	
	PTFEMA	PHFIMA	PTFEMA	PHFIMA
n-Hexane	13,63	37,85	36,86	13,27
n-Heptane	27,07	68,69	45,27	17,84
n-Octane	51,49	133,07	58,13	22,49
n-Nonane	99,37	257,16	73,95	28,57
n-Decane	194,11	477,99	94,32	38,30
Acetonitrile	50,67	36,70	33,61	46,40
Chloroform	37,45	30,33	7,51	9,28
2-Butanone	67,45	71,01	13,31	12,64
THF	49,94	94,67	11,01	5,81
Ethanol	19,75	18,90	85,94	89,80
2-Propanol	37,08	40,55	43,15	39,46
n-Butanol	82,04	77,18	81,29	86,41
Pyridine	230,14	206,59	13,11	14,61
Nitropropane	261,51	181,30	19,46	21,35

Table 4 Retention volumes and activity coefficients of various solvents.

The weight fraction activity coefficient of the examined range of solvents for PTFEMA and PHFIMA reveals the fact that they are insoluble in many organic solvents[10]. The results in table 4 s how that only chloroform is a good solvent for both polymers[7]. Moreover tetrahydrofuran[1,8] is nearly moderate solvent for PTFEMA and good solvent for PTFEMA. The second solvent that could be considered as a moderate solvent for PTFEMA and PHFIMA, is 2-butanone[11].

Conclusions

The fluorinated methacrylic polymers PTFEMA and PHFIMA were synthesized by two free radical polymerization processes. Apart from using an organic solvent as the polymerization medium, carbon dioxide substituted THF successfully.

The surface properties of two polymers with different fluorine content were investigated by means of the contact angle method and inverse gas chromatography. The study indicates that both polymers are hydrophobic but the polymer with the highest fluorine content, PHFIMA, is more hydrophobic than PTFEMA. The results of the dispersive component of surface energy calculated with both methods are inconsistent due to the fact that IGC mainly evaluates high-energy sites, whereas contact angle measurement represents mainly low-energy regions of a surface. In terms of polymer-solvent compatibility, IGC provided valuable information. The solubility of the polymers in various solvents was established experimentally for the first time through the use of IGC.

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