

Synthesis and characterization of fluorinated copolyetherimides with $-\text{CH}_2-\text{C}_6\text{F}_{13}$ side chains based on the ULTEMTM structure

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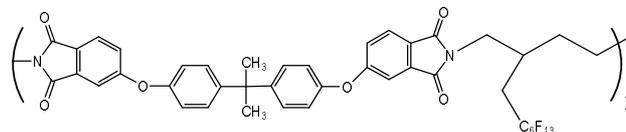
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The hydrophobicity and the thermal properties of soft non-porous films are studied.



Synthesis and characterization of fluorinated copolyetherimides with $-\text{CH}_2-\text{C}_6\text{F}_{13}$ side chains based on the ULTEM™ structure

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Abstract

Step polymerization of Bisphenol-A diphthalic anhydride (BAPA) with various mixtures from m-phenylene diamine (m-PDA) and 2-(perfluorohexylmethyl)butan-1,4-diamine (TFD) led to hydrophobic copolyetherimides bearing $R_F = -\text{CH}_2-\text{C}_6\text{F}_{13}$ side chains that were characterized by NMR, elementary analysis, DSC, TGA and surface energy analysis. By increasing the TFD unit %, the glass transition temperature (T_g) decreases according to the Fox equation from 217 °C (m-PDA 100 % and TFD 0% like in ULTEM™ 1000) to 113 °C (m-PDA 0% and TFD 100 %). Similarly the surface energy (γ_s) decreases from 45.3 mJ m⁻² to 27.4 mJ m⁻². The thermal decomposition temperature (T_d for 5% weight loss under argon) is slightly affected by introducing TFD units compared with T_d for ULTEM™ and it is close to 400 °C. The best compromise between thermal stability, hydrophobic and organophilic properties as well as the ability to form a soft non-porous film by the cast-evaporating method led us to select the copolyetherimide with m-PDA 25% and TFD 75% for which $T_g = 121$ °C, $T_d = 400$ °C and $\gamma_s = 30.8$ mJ m⁻².

Keywords : Fluorinated polyetherimide; Hydrophobic non-porous films; Cast membrane

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1. Introduction

The thermal stability, hydrolytic resistance and solubility in organic solvents of aromatic polyetherimides can be enhanced by fluorinated groups judiciously fixed on the appropriate sites of the polymer backbone. Resins from fluorinated polyetherimides showing such structural properties combined with more specific properties have very important applications in microelectronics [1] and composite materials.

The fluorinated groups are usually introduced into the macromolecular chain via a fluorinated dianhydride monomer or/and a fluorinated diamine monomer in the case of the most common step-polymerization [2,3]. For example the fluorinated polyetherimide prepared from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2'-bis[4-(4-aminophenoxy)diphenyl]hexafluoropropane (BDAF) exhibits a glass transition temperature (T_g) of 270 °C, a long-term thermo-oxidative stability and a reduced water absorption relative to non-fluorinated samples [4]. In spite of the flexibility brought from the ether linkage in the macromolecular chain, some fluorinated polyetherimides have a structural rigidity that leads to a delicate processability and a great fragility of the final materials. This special feature imposes a limitation on the use of these polymers for some applications, notably for the spin-coating technique and the deposition of a thin-protective layer or a specific-property layer. By introducing in the chain aliphatic carbon segments associated with the ether linkage, of course the softness of the final material increases but a negative effect is the decrease of T_g that leads to a possible reduction in thermal stability. To optimize the properties of the polymer, the flexibility of the chain must be improved without a strong decrease of T_g .

Among all applications for which polyimides are good-candidate materials, a very high thermal stability as well as a high T_g are not required for applications such as membrane separation techniques particularly to elaborate non-porous membranes. In this field the fluorinated copolyetherimides are being more and more used. These materials are the subject of a major development because of its interesting hydrophobic and organophilic properties. They are particularly used for the separation of organic-organic liquid mixtures and for the extraction of volatile organic compounds (VOC) from water by the pervaporation process [5,6]. Nevertheless the flexibility of the chains is a necessary condition to swell the membrane and to possibly obtain good transfert properties. For that, new polymers and modified polymers obtained by crosslinking, grafting or blending are required in order to prepare easy processing materials, soft non-porous membranes as well as coatings. After modification of

the polymer structure, of course the hydrophobic character and the hydrolytic stability of the fluorinated polyetherimides are to be maintained.

The well-known polyetherimide ULTEMTM 1000 (manufactured and marketed by General Electric Plastic) obtained by step-polymerization of bisphenol-A diphthalic anhydride (BAPA) and m-phenylenediamine (m-PDA), is widely used in microelectronics and in membrane field for gas separation [7] and, more recently but to a lesser extent, for pervaporation [8]. Surprisingly ULTEMTM 1000 was the subject of few works in order to synthesize new ULTEM structure-based copolyetherimides and related non-porous membranes. The main experiments were about the increase of hydrophilicity by chemical surface functionalization as well as plasma treatment [9]. The increase of hydrophobicity was also studied for example by blending ULTEMTM 1000 with oligomeric fluoropolymers synthesized by polyurethane chemistry and tailored with fluorinated end groups [10].

The purpose of the present study is to prepare and characterize fluorinated copolyetherimides based on the ULTEMTM structure where m-PDA is gradually replaced by an aliphatic diamine bearing the long perfluorinated side chain $R_F = -CH_2-C_6F_{13}$. The effects of the composition of the copolymer on the hydrophobicity and the thermal properties are analyzed. A rough estimation of the softness of cast films is also made. We selected the copolymer showing the best combination between all these properties to elaborate non-porous membranes.

Shortly these materials will be tested as pervaporation membranes. By varying the number of the hydrophobic side chains in the copolymer, the physical properties of the membranes as well as its accessible volume to the permeated molecules, could be partly controlled. By this way, the flux and the selectivity of the VOC through the membrane, particularly the traces of chlorinated solvents from water, could be studied and related to the structure of the macromolecular chain.

2. Results and discussion

2.1. Synthesis and structural characterization of the fluorinated polyetherimides

It is well known that the long perfluoroalkyl chains R_F bring a strong contribution to the hydrophobicity, particularly by the terminal trifluoromethyl group. Only a few fluorinated aliphatic diamines with such side chains are available and can be used as starting monomers for the synthesis of polyimides. In previous articles we reported the synthesis of

2,3-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)butan-1,4-diamine and 2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)butan-1,4-diamine respectively called NFD and TFD.

The NFD diamine led to polyetherimide bearing two side chains $-\text{CH}_2\text{C}_4\text{F}_9$ [11] per monomer unit whereas the TFD diamine [12] that is the subject of this article, led to polyetherimide bearing one side chain $-\text{CH}_2\text{C}_6\text{F}_{13}$ per monomer unit. The scheme of the synthesis of fluorinated copolyetherimides by the step reaction of BAPA with various mixtures of m-PDA and TFD is shown in Fig.1.

The selected molar fractions of TFD in the mixture of diamine were 0, 0.10, 0.18, 0.25, 0.50, 0.75, 0.90 and 1. The polymer obtained from TFD/m-PDA in the ratio 0/1 was called UPEI, it shows the same structure as ULTEM™ 1000 developed by General Electric Plastics. It is used as a reference structure for doing a best comparison between non-fluorinated and fluorinated polyetherimides. So, all the materials have been prepared in our laboratory. The polymer obtained from TFD/m-PDA in the ratio 1/0 and the copolyetherimides obtained from the various mixtures were called FPEI and coFPEI respectively. All compositions from 0.10 to 0.90 led to the formation of copolymers that were characterized.

This article reports the structural results (NMR, DSC, GTA, elementary analysis) concerning the following molar fractions 0, 0.25, 0.50, 0.75 and 1 for that the same equipment was used and similar analysis were performed. All the values in the composition range are given for the wettability, the surface energy and the resistance-test of the films.

The ^1H NMR spectra of some samples reproduced in Fig.2 show that the molar fraction of fluorinated units (y in Tab.1) can be easily determined by the ratio of the intensity of both signals of methylene $-\text{CH}_2-\text{N}(\text{CO})_2$ and methyle $-\text{CH}_3$ groups, respectively $I_{\text{CH}_2-\text{N}(\text{CO})_2}$ and I_{CH_3} (equation 1).

$$y = 1/4 I_{\text{CH}_2-\text{N}(\text{CO})_2} / 1/6 I_{\text{CH}_3} \quad (1)$$

By this method we obtained approximate values of the contents in the copolymers, nevertheless the y value deduced is consistent with the initial composition of the m-PDA and TFD monomer mixtures for long reaction time. The similar composition of monomers mixtures and related copolymers suggests that the full amount of diamine was incorporated in the macromolecular chain in spite of the likely difference in reactivity between m-PDA and

TFD. Indeed the high yield, close to 96 %, obtained for the solid polyetherimide, confirmed the almost complete incorporation of dianhydride and both diamines in the copolymer, nevertheless the molecular weights (Tab.1) seem to show that TFD is not as reactive as m-PDA under these experimental conditions. The weight fraction of fluorinated units (w in Tab.1) then the fluorine weight percentage (Fluorine wt %) were deduced from y considering the molecular weight of the non-fluorinated (M_{m-PDA} with $C_{37}H_{24}O_6N_2 = 592$) and fluorinated (M_{TFD} with $C_{42}H_{29}F_{13}O_6N_2 = 904$) units.

The following equations (2 and 3) were used:

$$w = M_{TFD} y / M_{TFD} y + M_{m-PDA} (1 - y) \quad (2)$$

$$F\% = 100 (19 \times 13) y / M_{TFD} y + M_{m-PDA} (1 - y) \quad (3)$$

The comparison of the Fluorine wt % resulting from NMR by this way and from elementary analysis (Tab.1^c and 1^d respectively) show slightly lower values for elementary analysis determination. The difference in values between the two techniques can be generally explained by an incomplete combustion of the fluorinated samples during the analysis that leads to a lower Fluorine % estimation.

The ¹⁹F NMR spectrum of coFPEI 75/25 (Fig.3) showed the characteristic peaks of the R_F chain at δ (ppm) -81.0 (CF₃), -112.9, -121.9, -123.0, -123.7, -126.4 (5 CF₂) that were very close for coPEI and FPEI.

2.2. Influence of the fluorinated unit content on the thermal properties of the polyetherimides

T_g decreases from UPEI to FPEI depending on the increase of the molar fraction of the fluorinated units (Tab.1). The easier mobility of the polymer chain at low temperature is attributable to the aliphatic segments -(CH₂)₄- of TFD units incorporated in the main chain as well as to the bulky -CH₂-C₆F₁₃ side chains. The gradual effect of the TFD weight fraction on the T_g value is shown in Fig.4. Experimental T_g have a good correlation with the predicted T_g

according to the Fox and Couchman methods [13,14]. Based on the average values of the depicted straight lines, a fall of 1 °C for T_g is approximately due to a supplementary incorporation of 0.01 TFD unit weight fraction in the copolymer.

In Tab.2 and Fig.5a, are reported the thermogravimetric characteristics and TG curves of polyetherimides obtained under argon. As shown, the fluorinated polyetherimides start decomposing at a lower temperature than UPEI (T_d 5% = 400 °C and 500 °C respectively) (Fig.5a). In fact for this comparison, the temperature corresponding to a 5% weight loss was considered (T_d 5%). It is significant that T_d 5% increases with the fluorine weight % (T_d 5% = 460 °C for FPEI). The maximum rate of decomposition of UPEI for the T_{max} temperature is followed by a less marked decomposition step; similar behaviour is not so obvious for coFPEI for which only one decomposition step clearly appears (DTG not shown). For FPEI, the DTG curve shows the maximum rate of decomposition at $T_{max} = 508$ °C and a weak shoulder at 440 °C. At 800 °C a charred residue was left in the 13-48 w% range for all polymers. The 13% residue was left by FPEI.

In Fig.5b, TG curves were obtained under air. These results are different when they are compared to the results under argon atmosphere. A slight decrease of T_d 5% and T_{max} was noticed as well as two decomposition steps for all polyetherimides. Moreover no residue was left at 750 °C, this is due to a more complete and quick combustion of the polymers in air.

Under argon and air, the weight loss at 200-300 °C range is related to the elimination of traces of the NMP solvent anyway present in the polymers in spite of the fact that the samples were carefully dried. The strong interactions between the polymer and the solvent impose to reach a higher temperature than the boiling point of the solvent (T_{eb} NMP = 202 °C) to entirely burn it away. For coFPEI, more particularly for coFPEI 25/75 (curves b in Fig.5), the weight loss close to 6% at 200 °C can be partly attributed to the decomposition of NMP solvent as well as to the decomposition of unreacted starting molecules possibly present in this analyzed sample. We cannot exclude the possibility that a complete imidization of the amic-acid intermediate in these conditions is achieved.

The combination of mass spectrometry with thermogravimetric analysis (MS-TGA) allowed more information to be obtained about the gas compounds produced during the temperature upward run. The MS-TGA coupling technique was performed for the analysis of the degradative process under argon. Only the higher mass loss for UPEI and FPEI were analyzed.

As indicated above two decomposition steps were identified for UPEI under argon at $T_{\max 1} = 533\text{ }^{\circ}\text{C}$ and $T_{\max 2} = 585\text{ }^{\circ}\text{C}$ with the maximum decomposition rates of $7\% / \text{min}$ and $1.8\% / \text{min}$ respectively.

The evolution profiles of the main emitted gas from UPEI at $533\text{ }^{\circ}\text{C}$ under argon (Fig.6 a₁) show the extraction of phenol and benzonitrile that present a similar fragmentation and the most intense peaks following : $m/z = 94, 66, 65, 63, 51, 50$. The presence of CO_2 and CO ($m/z = 44, 28$); CH_4 ($m/z = 16, 15, 14$) and H_2O ($m/z = 18, 17$) was also detected. $\text{CO}_2 + \text{CO}$ were attributed to a degradation involving an initial hydrolysis of the imid group in first step due to traces of absorbed water. An intermediate amic-acid structure could be also formed besides the non-hydrolyzed imid ring that breaks with heat in subsequent step [15]. The amic-acid structure uncompletely imidized at the end of the polymerization could also participate to the formation of water. It was shown that the simultaneous cleavage of ether linkage and isopropylidene group led to the formation of water, also available for catalyzing the hydrolysis of the imid group [16]. The initial hydrolysis led to the appearance of $\text{CO} + \text{CO}_2$ at a temperature less high than the temperature of all products from pyrolysis at about $400\text{ }^{\circ}\text{C}$ (Fig.6 a₃, a₅). Phenol ($m/z = 94, 66$) and benzene ($m/z = 78, 77, 52, 51, 50$) begin to appear at about $460\text{ }^{\circ}\text{C}$ (Fig.6 a₄) and reach the maximum amount at about $580\text{ }^{\circ}\text{C}$ indicating that these pyrolysis products were formed in second step [16]. After decarboxylation the intermediate amic-acid structure could be done imino forms leading to nitrile group by dehydration [15].

Two decomposition steps were also identified for FPEI under argon at $T_{\max 1} = 440\text{ }^{\circ}\text{C}$ (weak shoulder) and $T_{\max 2} = 508\text{ }^{\circ}\text{C}$ with the maximum decomposition rates of $3\% / \text{min}$ and $13.2\% / \text{min}$ respectively. At $508\text{ }^{\circ}\text{C}$ a comparison with UPEI leads to a similar assignments of the main peaks related to the formation of phenol and benzonitrile ($m/z = 94$ (weak), $66, 65, 51$), $\text{CO}_2 + \text{CO}$ ($m/z = 44, 28$), methane ($m/z = 16, 15, 14, 13$) then H_2O ($m/z = 18$) (Fig.7 b₁). Fig.7 b₂ clearly shows the appearance of CO_2 . New peaks seems to be attributable to the aliphatic chain of the backbone structure consequently assigned to the fragments CH_2NH_2 ($m/z = 30$), C_2H_5 ($m/z = 29, 28, 27, 26$) (Fig.7 b₃) as well as to the perfluorinated side chain cleavage characterized by the typical fragments following: CF_3 ($m/z = 69$) (Fig.7 b₄) and CF ($m/z = 31$) (Fig.7 b₃). This behaviour can be supported by a similar interpretation as UPEI by considering the existence of amic-acid and imino structures.

The scheme of a possible mechanism of the thermal degradation of FPEI is summarized in Fig.8.

2.3. Influence of the fluorinated unit content on the wettability and surface energy of the polyetherimides

The difference in contact angles and surface energy values [17] for ULTEM™ and UPEI films (Tab.3) are certainly due to different surface states arising from their respective preparation methods, that is to say extrusion for ULTEM™ film and cast-evaporating for UPEI film. The wettability measurements are particularly sensitive to the rugosity and surface density of the fil; it is important to compare the surface properties of coFPEI and FPEI samples with those of UPEI obtained by the same way.

As the TFD monomer units increase in the polymer, $\theta_{\text{H}_2\text{O}}$ increases from 88° to 92° showing a minimal value for coFPEI 25/75 and 50/50 whereas $\theta_{\text{I}_2\text{CH}_2}$ increases regularly. Such evolution of contact angles with the copolymer composition could be related with the possible reorientation of polar groups at the top surface. Further investigations are necessary to study in-depth and possibly to confirm this interpretation. However the evolution of $\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{I}_2\text{CH}_2}$ results in a regular decrease of γ_s from 45.3 mJ m⁻² for UPEI ($\gamma_{s \text{ UPEI}}$) to 27.4 mJ m⁻² for FPEI ($\gamma_{s \text{ FPEI}}$). This hydrophobic behaviour can be mainly related to the strong decrease of γ_s^d slightly compensated by the increase of γ_s^p (Tab. 3).

To try to find a better correlation between the experimental γ_s value and the composition of the copolymers, we plotted the predicted curve obtained from the equation similar to the previous Fox equation. In the following equation (equation 4):

$$1 / \gamma_s = z / \gamma_{s \text{ FPEI}} + (1-z) / \gamma_{s \text{ UPEI}} \quad (4)$$

γ_s replaces T_g and z represents an undefined percentage value from 0 % to 100 %. The curve a) in Fig. 9 shows γ_s versus z . Then we plotted the γ_s values versus experimental y and w TFD unit fractions in order to conclude the best correlation.

A non linear curve fitting method gave a correlation coefficient better for $z = y$ ($r = 0.99515$) than for $z = w$ ($r = 0.98887$). Although the r values are close, it seems that the y experimental values are in better agreement with the predicted curve. So, the surface energy will be better analyzed in this polymer series by considering the TFD unit molar fractions incorporated in the copolymer.

Based on the additivity principle we can suggest that a fall of 1 mJ m^{-2} is approximately due to a supplementary incorporation of 0.05 TFD unit molar fraction, this result coming from the calculation of the average slope of the curve. The additivity principle means that a large number of properties, including surface energy [18], when expressed per mole of a substance, may be calculated by summation of either atomic, group or bond contributions.

3. Conclusions

Fluorinated copolyetherimides based on the ULTEMTM structure have been synthesized by incorporating increasingly TFD units in the main chain from an original diamine bearing a long side chain $R_F = -\text{CH}_2-\text{C}_6\text{F}_{13}$. The combination of the ether linkage with the aliphatic chain segment and the R_F side chain led to an increase in polymer flexibility that was estimated by taking into account the decrease in T_g from $217 \text{ }^\circ\text{C}$ to $113 \text{ }^\circ\text{C}$ for UPEI and FPEI respectively. The thermal stability seems to be slightly weaker in the case of coFPEI however it remains enough for working these polymers in the membrane field. As the TFD units increase, γ_s decreases and consequently the hydrophobicity is steadily enhanced, furthermore these polymers are slowly soluble at ambient temperature in tetrahydrofuran and chloroform that is a good indication about their organophilic properties. The cast-evaporating method carried out in the case of coFPEI gave films with practical softness and mechanical strength enough to endure the pervaporation tests, typically 2-50 h transfer time, $25\text{-}50 \text{ }^\circ\text{C}$ temperature and 2-4 mm Hg pressure. So, after staying in contact with water under these experimental conditions no damage, crack or hole were detected on the samples up to 0.75 molar fraction of TFD unit. On the opposite coFPEI with molar fraction higher than 0.75 and FPEI led to brittle and unusable films. The compromise between the chain mobility, thermal stability, hydrophobicity and material softness allows us to conclude that coFPEI with 0.75 TFD molar unit seems to be the optimized film ($T_g = 121 \text{ }^\circ\text{C}$, $T_d 5\% = 400 \text{ }^\circ\text{C}$, $\gamma_s = 30.8 \text{ mJ m}^{-2}$). All things considered, the properties of these polymer series allows it to be evaluated as non-porous membranes for the extraction of traces of organic compounds from water.

4. Experimental

4.1. Materials

Diphthalic anhydride BAPA was kindly supplied by General Electric Plastics. m-phenylene diamine (m-PDA from Aldrich) and the solvent N-methylpyrrolidone (NMP from Aldrich) were used as received.

4.2 Synthesis of the fluorinated diamine monomer

The synthesis of the aliphatic diamine 2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)butan-1,4-diamine with $R_F = -CH_2-C_6F_{13}$ side chain called TFD in an abridged manner, has been already described in a detailed way elsewhere [12]. In brief, TFD was prepared from itaconic acid dimethyl ester (I) via the addition of perfluorohexyl iodide leading to the fluorinated diester (II) followed by the gradual transformation of ester groups in amino groups.

4.3. Synthesis of copolyetherimides

Fluorinated polyetherimide and copolyetherimides were prepared in NMP under argon atmosphere by heating at 120 °C for 48 h a stoichiometric amount of BAPA and a diamine mixture made up of various molar fractions of m-PDA and TFD freshly synthesized. A partially imidized poly(ether amic acid) intermediate and the expected polyetherimide were first obtained. The mixture was precipitated in EtOH/H₂O mixture. To improve the imidization state of the viscous copolymer mixture, the samples were dried in a vacuum oven at 140 °C for 12 h. However the complete imidization was difficult to prove. The dehydration resulting from the reaction between the residual carboxylic acid and the amide groups led to the solid polyetherimides after solvent being eliminated (Tab.1).

4.4. Films preparation and preliminary resistance-test

The cast-evaporating technique was carried out using a 20 % weight polymer solution in NMP for UPEI and in tetrahydrofuran or chloroform for coFPEI and FPEI. The slow-stirred solution at 80 °C for 4 h was cast on a glass plate and dried at 120 °C under vacuum for 24 h. Preliminary tests to evaluate the resistance of the films obtained from all compositions were achieved using a pervaporation cell with a total volume of 100 ml. The cell was filled with water, the pressure downstream from the film was 2-4 mm Hg and the tests were carried out at 25-50 °C for 50 h. Thus, we tried to find films showing practical softness and mechanical strength enough to endure the next pervaporation experiments.

4.5. Analysis and equipment

^1H (400 MHz, CDCl_3) and ^{19}F (235 MHz in CDCl_3) NMR spectra were recorded with a Bruker AC instrument. Tetramethylsilane (TMS) and trichlorofluoromethane were used as internal reference for ^1H and ^{19}F NMR spectra respectively. Molecular weights were determined by gel permeation chromatography (GPC) on a Waters instrument equipped with a differential refractometer, and the system was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) data were taken on a Mettler DSC 30 instrument under an atmosphere of nitrogen, taking two scans at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. T_g were predicted using the Fox [13] and Couchman [14] methods (equations 5,6):

$$1 / T_g = w_A / T_{gA} + w_B / T_{gB} \quad (5)$$

$$\ln T_g = (w_A \Delta C_{pA} \ln T_{gA} + w_B \Delta C_{pB} \ln T_{gB}) / (w_A \Delta C_{pA} + w_B \Delta C_{pB}) \quad (6)$$

where T_{gA} , T_{gB} and w_A , w_B are the glass transition temperatures and the weigh fractions of the two components, respectively. ΔC_{pA} and ΔC_{pB} are the magnitudes of the incremental increase in heat capacity at T_g of the pure components polymers.

Thermogravimetric analysis (TGA) was recorded with a Netzsch STA 409 thermobalance coupled with a mass spectrometer Baltzers QMG 421. This assembly allows to analyse the gas or volatile compounds released during the pyrolysis in the range 1-100 m/z. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves (DTG curves are not shown in the article) were recorded from 2 mg samples at a heating rate of $10\text{ }^\circ\text{C/min}$ up to $900\text{ }^\circ\text{C}$ under argon or air at a flow rate of 60 mL/min .

Static measurements of contact angles with water ($\theta_{\text{H}_2\text{O}}$) and diiodomethane ($\theta_{\text{I}_2\text{CH}_2}$), were made using a Kruss G1 apparatus. The 10 %w solution of polymers in THF was spread on a metal support, a smooth-thin film was obtained after the solvent evaporation. The accepted contact angles are the average of 6 measurements made on about 5 s after the liquid drop was

deposited on the film surface. The surface energy (γ_s), the polar (γ_s^p) and dispersive (γ_s^d) components were obtained from the Owens and Wendt method [17] (equation 7):

$$(1 + \cos\theta) \gamma_L = 2(\gamma_s^d - \gamma_L^d)^{1/2} - 2(\gamma_s^p - \gamma_L^p)^{1/2} \quad (7)$$

where γ_L is the interfacial tension of the liquid ($\gamma_{LH_2O} = 72.8 \text{ mJ m}^{-2}$, $\gamma_{LH_2O}^p = 51 \text{ mJ m}^{-2}$, $\gamma_{LH_2O}^d = 21.8 \text{ mJ m}^{-2}$ and $\gamma_{LCH_2I_2} = 50.8 \text{ mJ m}^{-2}$, $\gamma_{LCH_2I_2}^p = 1.3 \text{ mJ m}^{-2}$, $\gamma_{LCH_2I_2}^d = 49.5 \text{ mJ m}^{-2}$).

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