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Fluorination of poly(*p*-phenylene) using TbF_4 as fluorinating agent

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Abstract

The fluorination using TbF_4 as fluorinating agent was successfully performed on poly(*p*-phenylene). The method allows the fluorine content of the polymer to be controlled and the formation of structural defects, such as dangling bonds, to be significantly decreased by comparison with the direct fluorination using pure F_2 gas. The aromatic character of the phenyl ring is partly maintained through the fluorination contrary to the direct fluorination (using pure F_2 gas), for which a quasi-perfluorination and a partial decomposition of the polymer occur. Complementary analytical techniques have been used, such as ^{19}F and ^{13}C solid state NMR, FT-IR and EPR to compare the samples as a function of the reaction conditions.

Keywords: Fluorination; Poly(*p*-phenylene); Polymer; Fluorinating agent; Terbium tetrafluoride

1. Introduction

Fluorinated polymers exhibit many desirable physicochemical properties, such as high thermal and chemical stability, hydrophobicity, optical transmittance, i.e. transparency in visible and UV, good friction coefficient, gas separation properties, low surface energy when compared to their non fluorinated analogs, wettability [1–3]. Their application range is large, including the uses as polymer electrolyte membrane in fuel cell systems, as polymeric membranes for gas separation, as membranes and separators for chloro alkali cell and batteries, as coatings and containers for handling aggressive products due to their exceptional thermal stability, chemical resistance and dielectric properties and as catalyst supports for use under severe reaction conditions due to the improvement in thermal stability and hydrophobicity [4].

Direct fluorination using F_2 gas of polymers was successfully performed to reduce the refractive index [5], the friction coefficient [6], to improve their optical transparency [1] and their hydrophobicity to render the surface impermeable to the hydrocarbon fuels [1], to modify the wettability [7]. Many commercial polymers were fluorinated in this way: polyethylene, polypropylene, polystyrene, sulfonated polystyrene, poly(ethylene terephtalate), polyamide, and so on [8,9]. Two distinct ways are ordinarily used for the fluorination of the polymers. Firstly, the direct gas–solid reaction of the polymer with fluorine gas, either pure or diluted atmosphere, [1,2,6,8,10,11]. Nevertheless, the exceptional reactivity of F_2 can limit this way when the polymer contains easily breakable bonds because the degradation through the fragmentation of the polymer chain can occur [12]. Direct fluorination sometimes requires special conditions such as dilution with N_2 or He or low reaction temperature. An alternative way using fluorinating agents can also be used due to their thermal decomposition which produces $F^{\bullet}$ radical and/or F_2 molecules. This makes possible the release of a definite quantity and thus to control the fluorine content. Various inorganic fluorides are convenient as fluorinating agents in various physical states: gaseous such as NF_3, SiF_4, BF_3, SF_6 [13], SF_4/HF [14], CF_4 plasma [15,16]; non-volatile fluorides, CoF_3 [17].

This tuneable process is suitable to the fluorination of polymers. For comparison, this way was often used to fluorinate fullerene using K_2PtF_6, MnF_3 (alone or involved in binary or ternary mixtures), CoF_3 with alkali metal fluorides and MnF_2 [18], silver(I) or silver(II) fluorides [19], or lead fluorides (PbF_2, PbF_4, Pb_2F_6) and their complexes with alkali metal and alkali earth metal fluorides (M_2PbF_6, M_3PbF_6 and $MPbF_6$). This particular example shows the varying nature of the fluorinating agents. The fluorination was applied to poly(*p*-phenylene), PPP, of chemical formula $(C_6H_4)_n$, a conjugated polymer which consists of phenyl rings connected exclusively in para position. Although a π delocalization along the chain,

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which increases its chemical and thermal stabilities, PPP strongly reacts with fluorine gas even at room temperature [6,20]. The quasi-perfluorination is easily obtained in pure F_2 stream with duration lower than 1 h [6,20]. Nevertheless, for such conditions, some phenyl rings are broken, resulting in the formation of defects within the polymer chain such as CF_3 groups. When the fluorination is prolonged, a weight loss is noted due to the formation of volatile CF_4 and C_2F_6 species [6,20]. A recent study revealed that the annealing at 400 °C under dynamic vacuum of the pristine polymer improves its crystalline order, the chain length and increases the grain size of the powder [20]. These changes of the pristine polymer lead to a decrease of the reactivity with respect to F_2 gas.

In the present study, the process using a fluorinating agent was applied to the more reactive PPP, i.e. the polymer which was obtained by the Kovacic method without annealing, in order to check this fluorination method. The new fluorinated polymers obtained by this method will be compared to the samples fluorinated using molecular F_2 gas (direct fluorination). Our choice of the fluorinating agent was terbium tetrafluoride TbF_4. Chilingarov et al. [21] studied its thermal decomposition highlighting that its decomposition generates mainly atomic fluorine $F^\bullet$ rather than fluorine F_2. Moreover, the partial pressure of atomic fluorine is much higher than that corresponding to the equilibrium $2F^\bullet \Leftrightarrow F_2$. So TbF_4 constitutes an excellent fluorine generator. The major advantage of TbF_4 is that its temperature of decomposition is relatively low (300–400 °C). Moreover, after the process, the produced TbF_3 can be easily regenerated into TbF_4 in F_2 gas at 500 °C [22].

2. Results and discussion

Prior to the fluorination, the polymer was heated at 150 °C for 2 h in order to remove traces of adsorbed water molecules, which could form HF in the presence of F_2 and/or $F^\bullet$.

After the polymer cooling until room temperature, the temperature of the oven part containing TbF_4 was then increased with 5 °C min^{-1} to reach the required temperature (350 or 500 °C). Even if the fluorinated product was not washed before characterization, the content of HF molecules is low and HF is not detected by ^{19}F NMR (^{19}F chemical shift is expected at ~ -153 ppm/$CFCl_3$). It must be noted that the products were conserved in a dried atmosphere in order to avoid the reaction with moisture.

The fluorine content x in C_6F_x, after fluorination, obtained by weight uptake method is summarized in Fig. 1 and Table 1. For comparison, data for PPP fluorinated in F_2 gas (0.33 and 14 h) are added. These values were obtained by weight uptake assuming that the linking of one fluorine atom with PPP results in an increase of either 18 g/mol when x in C_6F_x is lower than 4 (substitution of hydrogen by fluorine) or 19 g/mol for $x > 4$ (fluorine addition). These data display the fluorination level rather than the chemical composition, which must be given as $C_6F_xH_y$. Amongst the different samples prepared using the fluorinating agent, the highly fluorinated polymer was obtained with a decomposition temperature of 500 °C under vacuum for TbF_4. As expected, the fluorination is limited using TbF_4 instead of F_2.

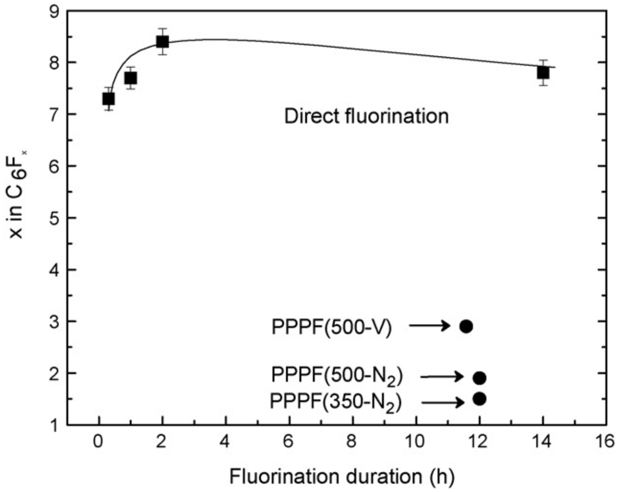


Fig. 1. Evolution of the fluorine content x in C_6F_x into fluorinated PPP. Data of the direct fluorination are extracted from [20].

2.1. FT-IR

The vibrational modes of the virgin PPP, shown in Fig. 2, are observed in the 697–860 cm^{-1} range; these are related to C–C and C–H vibrations of monosubstituted and parasubstituted phenyl rings [6,23–25]. The strong band at 1200 cm^{-1}, which is observed whatever the fluorinated sample, is assigned to covalent C–F bonds in fluorinated carbons [26]. In agreement with the fluorination level evolution, infrared spectroscopy data (Fig. 2) show that the highest intensity of the 1200 cm^{-1} band, i.e. the highest amount of C–F bonds, is observed when TbF_4 is heated at 500 °C under vacuum. Contrary to the direct fluorination, even for 20 min, the peaks, which are characteristic of the raw PPP, are still present. Their intensities decrease when compared to the C–F bonds lines with the fluorination duration. As expected, the higher the fluorine content, the lower these intensities. Moreover, the bands at 850 and 980 cm^{-1} assigned to CF_3 groups [27,28] do not appear for PPP fluorinated with TbF_4 contrary to the direct fluorination. Using F_2 gas, some highly fluorinated rings are broken resulting in the formation of both CF_3 groups and –$(CF_2)_n$–CF_3 ($n \leq 4$) linear part (amongst the various possible reactions, one is shown in Eq. (1)). This one could then be

Table 1
Experimental conditions and fluorine content of the various fluorinated PPP

Temperature (°C)		Initial atmosphere	Duration (h)	Sample	Fluorination level
PPP	TbF_4				
25	350	N_2	12	PPPF(350-N_2)	$C_6F_{1.5}$
25	500	N_2	12	PPPF(500-N_2)	$C_6F_{1.9}$
25	500	Vacuum	12	PPPF(500-V)	$C_6F_{2.9}$
25	–	F_2	0.33	PPPF(F_2-0.33)	$C_6F_{7.3}$
25	–	F_2	14	PPPF(F_2-14)	$C_6F_{7.8}$

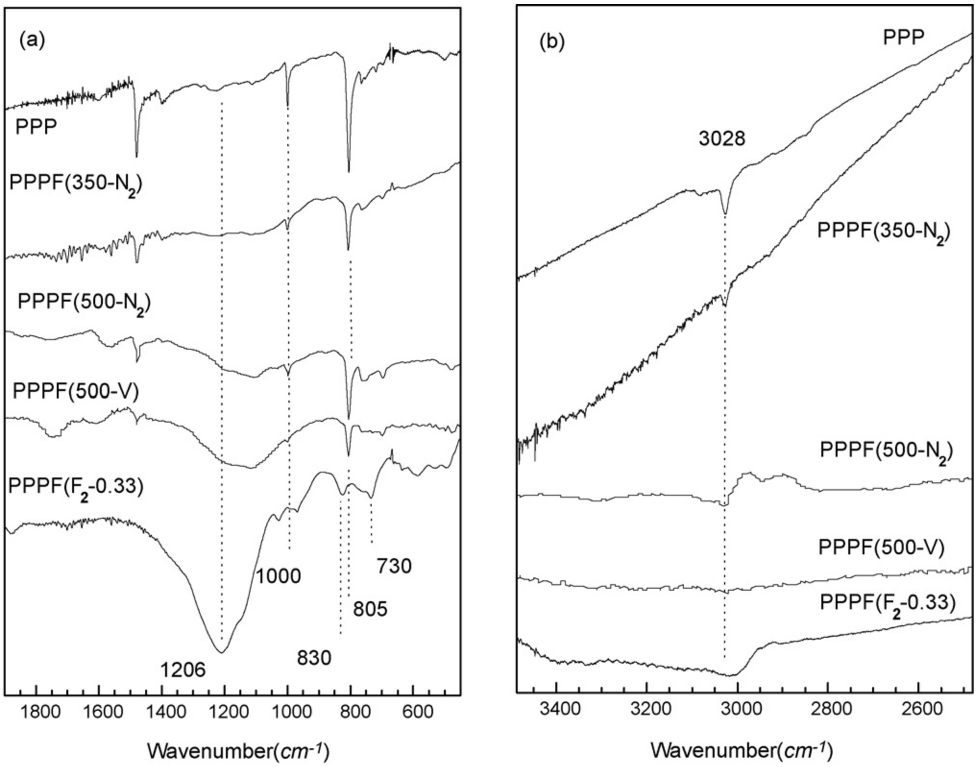
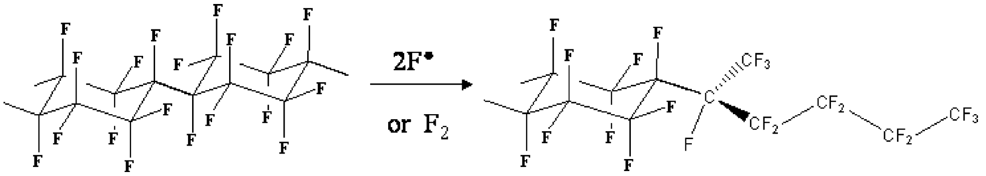


Fig. 2. FT-IR spectra of the pristine and fluorinated PPP in two ranges: (a) 450–1750 cm^{-1} and (b) 2500–3500 cm^{-1}.

decomposed in the presence of fluorine to form CF_4 and/or C_2F_6 volatile species. The CF_3 groups reveal then a degradation of the fluorinated polymer.



(1)

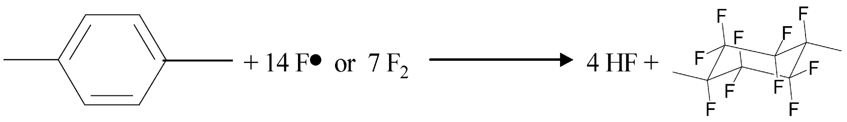
These results indicate that the fluorination can be limited using a fluorinating agent. The progressive nature of the fluorination using TbF_4 is also highlighted in the 2500–3500 cm^{-1} region. The content of the C–H bonds, which exhibit vibrational modes near 3000 cm^{-1}, decreases progressively during the fluorination using TbF_4, contrary to the direct fluorination, even for the shortest duration (Fig. 2b).

The efficiency of the process can be tuned according to the experimental condition: a decrease of the temperature applied to TbF_4 combined with a N_2 atmosphere instead of vacuum results in a decrease of x in C_6F_x. Nevertheless, FTIR data are only qualitative because the broad line at 1200 cm^{-1} is in fact a superimposition of various C–F contributions. The nature of the fluorinated polymer, and in particular, the maintaining of the aromaticity cannot be deduced. Complementary characterizations are necessary, such as ^{13}C and ^{19}F NMR, which allow the various C–F contributions to be differentiated.

2.2. NMR

By considering the results concerning the direct fluorination [6,20], the criteria which must be taken into account are:

The area ratio of the two ^{19}F resonance lines C–F and CF_2. The existence of CF_2 groups indicates a loss of the aromatic character according to the idealized reaction (Eq. (2)):



(2)

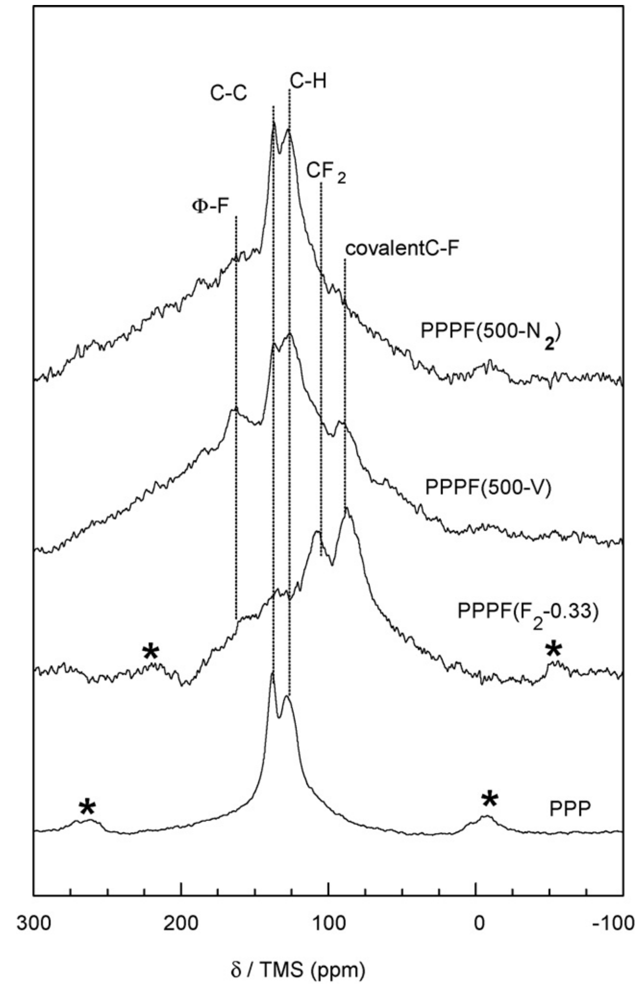


Fig. 3. ^{13}C MAS-NMR spectra of virgin and fluorinated PPP. The spinning speed is of 10 kHz (*marks off the spinning sidebands).

As discussed before, the presence of CF_3 groups suggests an opening of the phenyl ring. The chemical shifts δ for ^{19}F NMR experiment of the various groups, C–F (−170 to −200 ppm/$CFCl_3$), CF_2 (−100 to −140 ppm) and CF_3 (−50 to −90 ppm), are sufficiently different to be distinguished. ^{13}C NMR allows also investigation of the non-fluorinated polymer.

The partial conservation of the pristine polymer is confirmed by ^{13}C NMR (Fig. 3), because the two resonance peaks, centered at +128 and +139 ppm, are still present whatever the operating conditions using a fluorinating agent, contrary to the direct fluorination. These two peaks are assigned, respectively, to carbon atoms linked to hydrogen atoms and carbon atoms which ensure the connection between the rings, i.e. non-hydrogenated carbons, respectively [6,29–31].

For the sample fluorinated under vacuum (PPPF(500-V)), additional peaks appear; the first one at +88 ppm/TMS, is assigned to C–F groups and the second one, a shoulder, at +110 ppm, is related to the presence of CF_2 groups. The last one is observed at +160 ppm. This ^{19}F chemical shift indicates strong interaction between sp^2 hybridized carbon and fluorine atoms. Whereas a non-fluorinated carbon atom of a phenyl ring exhibits a chemical shift close to +139 ppm, the δ value of +160 ppm results from the interaction with fluorine atoms. By analogy with graphite fluorides [29,32], this interaction can be either a covalent bond or a hyperconjugation between non-fluorinated sp^2 carbon atoms and fluorine atoms in neighboring C–F bond. This line is denoted Φ-F as in a previous paper concerning the direct fluorination of PPP [6]. This latter reveals the conservation of the π delocalization for a part of the phenyl rings after fluorination.

^{19}F NMR spectra confirm the conservation of some phenyl rings, their fluorination leads to a line at −200 ppm. This shift is different from that of semi-covalent C–F bonds located at −180 ppm [29–31]. These two types of the C–F bonds coexist in PPPF(500-N_2) and PPPF(500-V) for which the NMR spectra exhibit the lines at −183 and −230 ppm as shown in Fig. 4.

For the same scan number, the signal/noise ratio is lower for PPPF(500-N_2) compared to PPPF(500-V), in agreement with the F:C ratio in the sample and with the ^{13}C NMR spectrum on which the intensity of the lines assigned to C–F and CF_2 groups are low for PPPF(500-N_2). When the fluorination is performed with F_2 gas or with TbF_4, C–F bonds are formed in –C–F, $>CF_2$, –CF_3 or Φ-F groups. Only their relative amounts change. In order to estimate the percentage of each kind of groups, the simulation of the ^{19}F NMR spectra was performed (Table 2 and

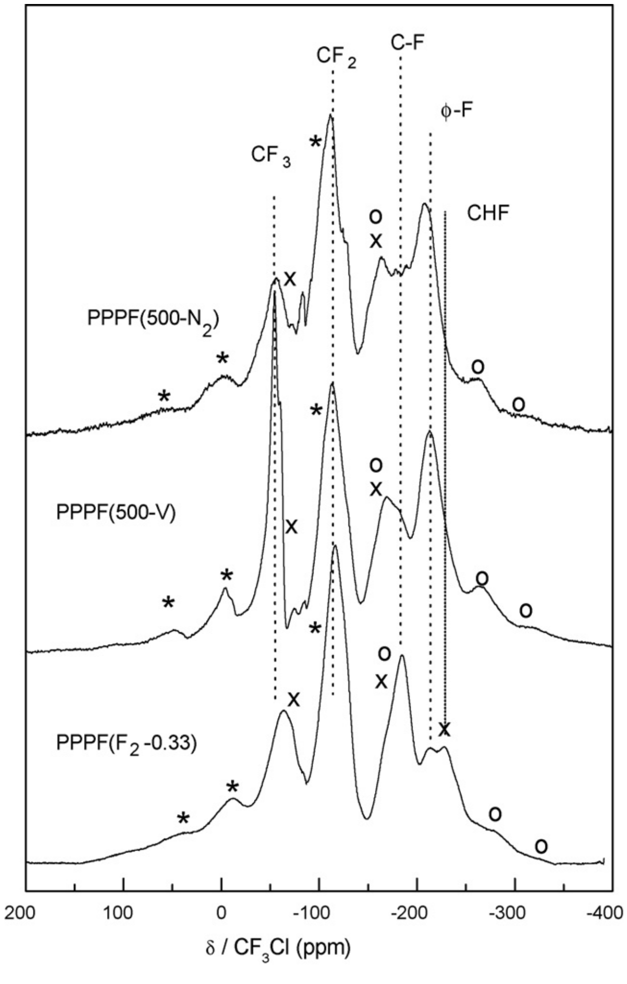


Fig. 4. ^{19}F MAS-NMR spectra of fluorinated PPP (spinning speed is of 14 kHz; the location of the spinning sidebands for each isotropic line are calculated and marked with *, x, o for CF_3, CF_2 and Φ-F, respectively.

Table 2
Characteristic area ratio of some ^{19}F NMR lines

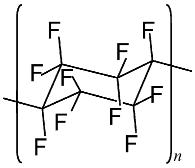
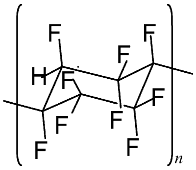
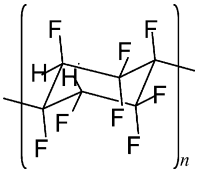
Samples	S_{CF_2}/S_{C-F}	$S_{\Phi\text{-}F}/S_{C-F}$	Fluorine level
PPPF(500-N_2)	3.5	3.4	$C_6F_{1.9}$
PPPF(500-V)	1.7	2.6	$C_6F_{2.9}$
PPPF(F_2-0.33)	1.6	0.6	$C_6F_{7.3}$
PPPF(F_2-14)	1.6	0.7	$C_6F_{7.8}$
	4	0	C_6F_{10}
	3	0	$C_6F_9H_1$
	2	0	$C_6F_8H_2$

Fig. 5a). The main difficulty is the broadness of the line, which is due to strong ^{19}F–^{19}F homonuclear coupling. A spinning frequency of 14 kHz is not sufficient to suppress this interaction into the NMR spectra. The lines remain broad even with high spinning frequency and the presence of the spinning sidebands hinders the simulation. This latter was carried out by considering the spinning sidebands on both sides of the isotropic line. The linewidths of these sidebands were fixed equal to the one of the corresponding isotropic line (Fig. 5a). Four isotropic lines were considered: CF_3 ($\delta \sim -55$ ppm), CF_2 ($\delta \sim -115$ ppm), C–F ($\delta \sim -183$ ppm) and Φ-F ($\delta \sim -200$ ppm). It must be noted that fluorine atom in $\rangle$CHF exhibits ^{19}F chemical shift of −236 and −226 ppm in C_7HF_{13} and $C_6H_4F_6$ molecules, respectively [33,34]; the line of this $\rangle$CHF group unambiguously appears only for PPP fluorinated using F_2. Nevertheless, it cannot be excluded that this line is also present for the other samples but with low intensity.

The ^{19}F spectra of the samples obtained with direct fluorination (0.33 and 14 h) were also simulated. The relative amount of the fluorine atoms involved into Φ-F is significantly higher for the sample obtained using the fluorinating agent. This amount, close to 38% and 36% for PPPF(500-N_2) and PPPF(500-V), respectively, is twice the value for PPP fluorinated with F_2 (Fig. 5b). Surprisingly, the amount of CF_3 is high for PPPF(500-V) suggesting a degradation of the polymer chain. This process, which could occur on the grain surface, is lowered when a N_2 atmosphere is initially applied instead of vacuum.

The simulation of the ^{19}F NMR spectra shows that the area ratio S_{CF_2}/S_{C-F} of the C–F ($S_{C\text{–}F}$) and CF_2 (S_{CF_2}) lines, is close to 1.6 whatever the sample except for PPPF(500-N_2) (Table 2). Such a value is lower than the one expected for a perfluorinated phenyl ring, i.e. –(C_6F_{10})–. In this case, the ratio S_{CF_2}/S_{C-F} must be theoretically equal to 4. Rather than be perfluorinated, the ring still contains CHF groups in accordance with the fluorine content e.g. $C_6F_{7.3}$ for PPPF(F_2-0.33). If one or two hydrogen atoms per ring are conserved after fluorination, the S_{CF_2}/S_{C-F} ratio is equal to 3 or 2, respectively (Table 2).

It is also interesting to compare the area ratio for the two types of carbon-fluorine bond, denoted C–F and Φ-F. This $S_{\Phi\text{-}F}/S_{C-F}$ ratio is equal to 2.6 and 0.6–0.7 for PPP fluorinated with TbF_4 (vacuum) or with F_2 respectively. The case of PPPF(500-N_2) is particular as evidenced by the ratio $S_{CF_2}/S_{C-F} = 3.5$ and $S_{\Phi\text{-}F}/S_{C-F} = 3.4$. The progressive fluorination forms a few CF_3 groups and maintains the π character in a large part of the polymer. When the aromatic character is lost, the rings are quasi-perfluorinated (as C_6F_{10}) because the S_{CF_2}/S_{C-F} is closer to the theoretical value of 4 for C_6F_{10}. These results show that the fluorination with TbF_4 allows the conservation of the π character in spite of the fluorination. This maintaining does not concern the overall sample but only

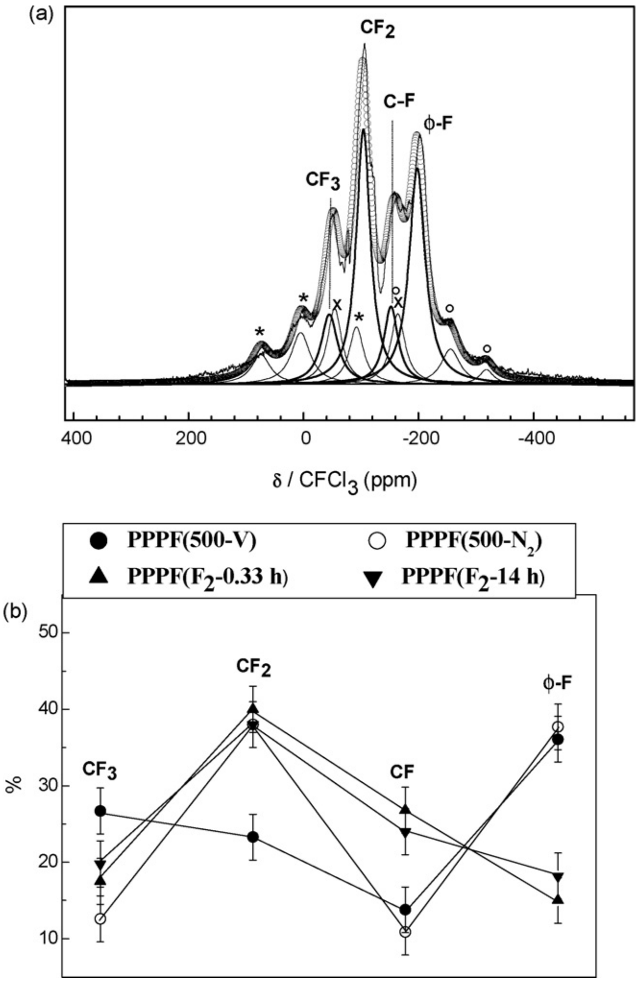
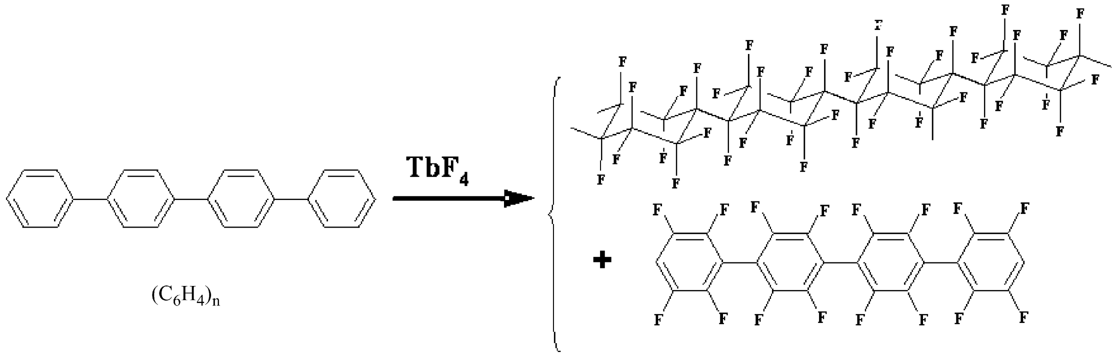


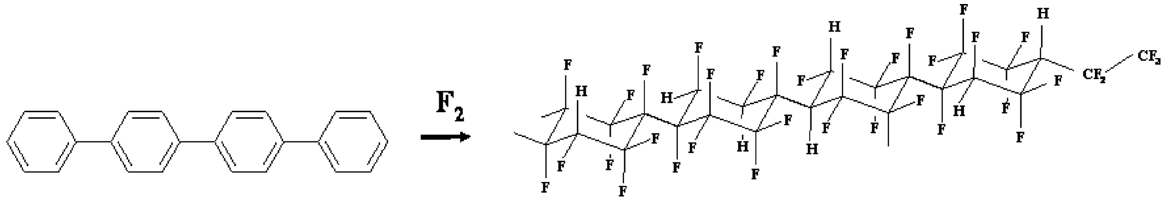
Fig. 5. (a) Simulation of the ^{19}F NMR spectrum of PPP fluorinated with TbF_4 under vacuum at 500 °C and (b) proportion of the various groups. Bold lines on (a) show the isotropic lines and o, x, * mark off the spinning sidebands of Φ-F, CF_2 and CF_3 groups. Lines on (b) are eye guides.

limited parts. The other chains are highly fluorinated forming CF_2 and CHF groups.

The following equations summarize the idealized fluorination processes owing to the two fluorination routes: using TbF_4 as fluorinating agent, the π character of some phenyl rings is partly maintained in addition to perfluorinated part (Eq. (3)). On the contrary, using F_2 gas some hydrogen atoms are conserved (Eq. (4)):



(3)



(4)

2.3. EPR

The EPR spectrum of the virgin PPP (Fig. 6) is symmetrical and consists of a single Lorentzian line (peak-to-peak linewidth ΔH_{pp} is equal to 2.9 G, $g = 2.0030 \pm 0.0005$). EPR signals are assigned either to connection defects of the phenyl rings, i.e. cross-linking, or to residual radicals resulting from the synthesis which are trapped in the polymer bulk and are sterically inaccessible to air atmosphere [35]. After the treatment by a fluorinating agent, the EPR line decreases in intensity but the linewidth does not change. According to FTIR and ^{13}C NMR, residual non-fluorinated polymer still remains. These parts could be responsible of the single EPR line. The direct fluorination of PPP results in a high density of dangling bonds (DB), which are formed by the cleavage of C–C or C–H bonds. The superhyperfine interaction of these DB with the neighboring fluorine nuclei (nuclear spin number $I = 1/2$) explains the broadness of the EPR line ($\Delta H_{pp} \sim 80$ G). Moreover, the line of the pristine polymer is no longer present after 20 min of direct fluorination. The absence of the broadness line assigned to DB when fluorinating agent is used means that this method generates very few defects in spite of the high fluorine content. For comparison, for PPP fluorinated for 20 min using F_2, the spin density D_s is of 57.0×10^{18} spin g^{-1} whereas for PPPF(500-N_2) and PPPF(500-V), D_s is equal to 0.3×10^{18} and 0.2×10^{18} spin g^{-1}, respectively. The pristine polymer exhibits a value of 0.8×10^{18} spin g^{-1}.

The fluorination seems to occur on the surface rather than in the bulk. This explains that the EPR signal of the pristine polymer is still conserved after the fluorination. The radical species are included in the bulk. The grain size of the polymer is a major parameter of the fluorination [20]; it is included between 3.6 and 145 μm (this values have been estimated by laser granulometry [20]). Larger grain size requires an increase of the fluorination duration, allowing the fluorination to progress into the bulk. In our experimental conditions, the overall bulk may be not fluorinated.

3. Conclusion

Using a fluorinating agent, terbium tetrafluoride, the fluorination of poly(*p*-phenylene) was controlled. The thermal decomposition of TbF_4 released a defined amount of fluorine atoms ($F^{\bullet}$ or F_2); this allows the process to be more progressive than the direct fluorination in pure F_2 gas. In this latter case, even for 20 min treatment, the polymer is quasi-perfluorinated. On the other hand, when a fluorinating agent is used, the π character of some polymer parts is maintained although the fluorination. The presence of sp^2 carbon atoms in interaction with fluorine (denoted Φ-F), i.e. bonded to fluorine, is underlined by both ^{13}C and ^{19}F NMR. Residual non-fluorinated polymer is also present with this method contrary to the direct fluorination. The fluorine content and the amount of this Φ-F depend on the experimental conditions. When the reaction is performed under vacuum, undesirable CF_3 groups are formed by the breaking of the phenyl rings. This side reaction is

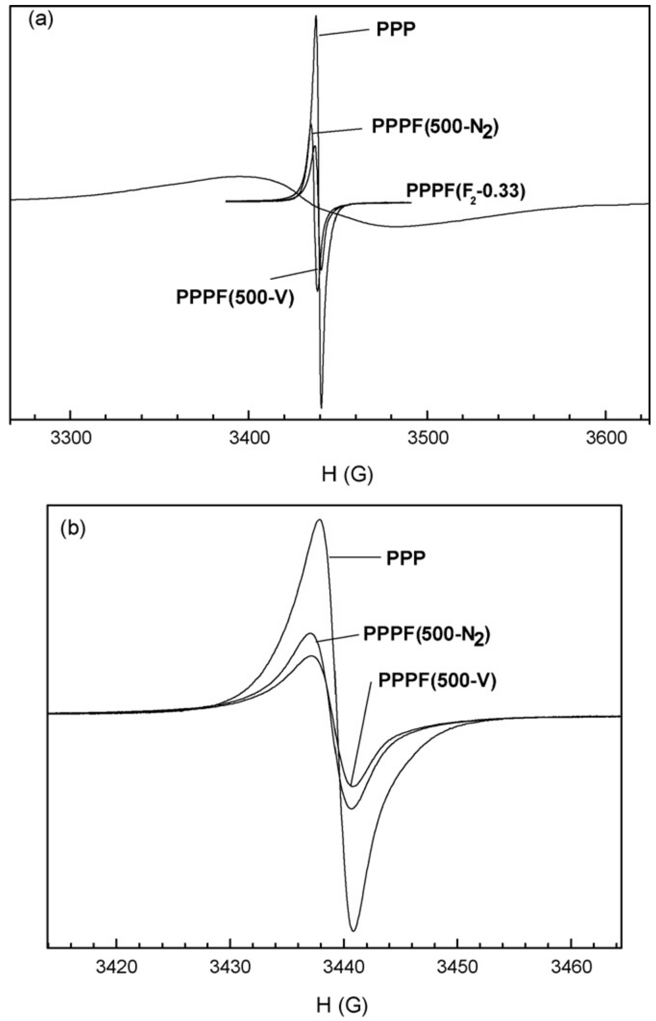


Fig. 6. EPR spectra of fluorinated PPP according to the fluorination methods.

lowered at the same decomposition temperature of TbF_4, i.e. 500 °C, under initial N_2 atmosphere. These conditions appear to be optimal for this polymer. The fluorinated polymer obtained using a fluorinating agent exhibits few structural defects, such as dangling bonds, contrary to the direct fluorination.

4. Experimental

4.1. Polymer synthesis

Kovacic's synthesis was carried out [24]; it consisted of a polymerization of benzene in the presence of a catalyst, aluminum chloride ($AlCl_3$), and an oxidant, copper(II) chloride ($CuCl_2$). The powder obtained exhibited a brown color. The sample was used as-synthesized.

The characterization of the pristine polymer was extensively described in a previous paper, in which the fluorination with F_2 gas was discussed as a function of several parameters, such as powder grain size, surface properties, cristallinity and chain length [20]. Using FT-IR and ^{13}C NMR, the chain length of the as-synthesized polymer is estimated and 11–12 phenyl rings per chain was found; the cristallinity is close to 30% and the specific surface area is 55 $m^2\ g^{-1}$.

4.2. Fluorination

Several methods were used. For all the cases, contrary to the direct fluorination which is performed with a F_2 stream, the experiments were carried out in a closed reactor in order to preserve the defined fluorine amount, which is delivered by TbF_4 decomposition. A two temperature oven was used: the part containing TbF_4 was heated whereas PPP was maintained at room temperature (the cooling was ensured by an external water circuit).

The fluorination duration was 12 h; the thermal decomposition of TbF_4 was obtained between 350 and 500 °C (Table 1); the reaction was carried out either under initial nitrogen gas (one atmosphere), or under primary vacuum ($\sim 10^{-3}$ atm). Considering the ideal case for which each hydrogen atom is replaced by a fluorine atom, the theoretical reaction is Eq. (5):

$$(C_6H_4)_n + 8nF^{\bullet}\ \mathrm{ou}\ 4nF_2 \rightarrow (C_6H_4)_n + 4nHF \qquad (5)$$

Due to the chain length (11–12 phenyl rings per PPP chain [20]), the hydrogen or chlorine atoms on chain edges have been neglected. As Kovacic's method consists of a polymerization with $AlCl_3$ and $CuCl_2$, chlorine atoms remain in low amounts probably on chain edges (1.1% Cl, 0.4% Al and 0.1% Cu w/w using chemical analysis).

Terbium tetrafluoride was obtained in pure F_2 gas at 500 °C starting from TbF_3 (Aldrich, 99.9%). Prior to the use as fluorinating agent, the purity of TbF_4 and the absence of TbF_3 were systematically checked by X ray diffraction. The thermogravimetric analysis (TGA) of TbF_4, realized until 350 °C, indicated that exactly one mole of $F^{\bullet}$ was released per mole of TbF_4 between 100 and 300 °C. This experiment was carried out under argon flow in order to avoid the formation of oxyfluoride.

$(n_{TbF_4})_{Th}$ is the molar amount of TbF_4 necessary for the reaction. An excess of TbF_4 (denoted n_{TbF_4}) was used in each case according to the molar ratio $(n_{TbF_4})/(n_{TbF_4})_{Th} = 1.5$; the mass were of 0.100 and 1.855 g for PPP and TbF_4, respectively. The total conversion of TbF_4 into TbF_3 was systematically checked by both the mass loss and X-ray diffraction analysis.

Direct fluorination was carried out under a pure fluorine gas flow (14 ml min^{-1}) at room temperature under normal pressure. Fluorine gas (Solvay FLUOR GmbH) contained no trace of oxygen. So, the formation of C=O containing groups (e.g. –C(=O)F) into the fluorinated PPP did not occur. The sample was placed in a nickel boat inside a Monel reactor.

4.3. Physicochemical characterizations

NMR experiments were performed with Bruker Avance spectrometer, with working frequencies for ^{13}C and ^{19}F of 73.4 and 282.2 MHz, respectively. A Magic Angle Spinning probe (Bruker) operating with a 4 mm rotor was used. For MAS spectra, a simple sequence (τ-acquisition) was performed with a single π/2 pulse length of 4 and 3.5 μs for ^{19}F and ^{13}C, respectively. ^{13}C chemical shifts were externally referenced to tetramethylsilane (TMS). ^{19}F chemical shifts were referenced with respect to $CFCl_3$.

EPR spectra were carried out with a Bruker EMX digital X band ($\nu = 9.653$ GHz) spectrometer. Diphenylpicrylhydrazil (DPPH) was used as the calibration reference to determine both the resonance frequency and the spin carrier densities.

Fourier transform infrared spectroscopy (FT-IR) was performed using spectrometer THERMO NICOLET 5700; the spectra were recorded by transmission in a dry air atmosphere between 400 and 4000 cm^{-1} with 64 spectra accumulations.

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