

# Polyfluorene Copolymer with a Multiply Blocked Rotaxane Architecture in the Main Chain: Synthesis and Characterization

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**ABSTRACT:** To improve the physical properties of polymer materials, a novel copolymer with a multiply blocked rotaxane architecture in the main chain was synthesized through Suzuki dehalogenative polycondensation from a 2,7-dibromofluorene/ $\gamma$ -cyclodextrin ( $\gamma$ -CD) inclusion complex and 9,9-dioctylfluorene-2,7-trimethylene diborate in the presence of a tetrakis(triphenylphosphine)palladium(0) catalyst. As demonstrated by computational calculations, the dioctyl groups were large enough to prevent the dethreading of  $\gamma$ -CD molecules. A copolymer polyrotaxane with a  $\gamma$ -CD/structural unit ratio as high as 1/1.4 and a bimodal molecular weight distribution was obtained, as proved by its <sup>1</sup>H-NMR spectrum and size exclusion chromatography curve, respectively. The polyrotaxane showed lower thermal stability and higher solubility in polar solvents in comparison with the noncomplexed homologue.

The fluorescence spectra of both the complexed and non-complexed copolymers exhibited typical well-resolved blue emission bands that arose from the fluorene chromophore units. In dimethylformamide solutions, the ratio of the intensities of the peaks of the emission spectra (emission spectra intensities<sub>413</sub> for the 0–0 band and emission spectra intensities<sub>437</sub> for the 0–1 band) was higher for the polyrotaxane than the noncomplexed copolymer, and this demonstrated a reduced quenching effect of the environment induced by the protection of the polymer chain by the macrocycle. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2384–2392, 2008

**Key words:** nanotechnology; NMR; polyaromatics; self-assembly; supramolecular structures

## INTRODUCTION

Nanometer-scaled supramolecular assemblies constructed through the simple inclusion complexation of cyclodextrins (CDs) with organic molecules represent a very active topic of science because of their potential applications. CDs and their chemically modified derivatives have been used as building blocks for the construction of the most diverse supramolecular architectures.<sup>1–7</sup> It is well known that CDs form inclusion complexes with a variety of compounds by including them in their cavities.<sup>8,9</sup> The synthesis of such structures is based on the molecular recognition principle and is a result of the cooperation of various noncovalent interactions. The major noncovalent interactions of the formation of CD inclusion compounds are hydrophobic and van der Waals interactions between the inner surface of

the CD ring and the hydrophobic sites on the guest.<sup>10</sup> The principle of molecular recognition can be exemplified through the formation of host–guest complexes. The role of hosts is played by cyclic molecules, such as crown ethers, cryptands, calixarenes, and CDs. The chemical nature of guests is extremely diverse: they include small molecules or polymers. Through the use of CDs as hosts in the synthesis of inclusion complexes, the reactions have usually been carried out in water as a result of their mode of binding through hydrophobic interactions between the interior of the molecular cavity and the insoluble or poorly soluble guest molecules.

Rotaxanes, pseudorotaxanes, and polyrotaxanes that incorporate CDs as ring components have been investigated by many groups, and the research in this area has been reviewed recently.<sup>1,4,6</sup> Depending on the location of the CD macrocycles on the polymer chain, different types of polyrotaxanes have been imagined, such as main-chain and side-chain structures.<sup>4</sup>

The first step in the preparation of a polyrotaxane is the threading of CD molecules onto polymer chains (an equilibrium process). A thermodynamically unstable inclusion complex called a *pseudorotaxane* is obtained. To avoid the dethreading of CD

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molecules, in a second step, a blocking reaction of both ends of the polymer chain with bulky groups is required.<sup>3,4,11</sup>

When the blocking reaction is a polycondensation of a pseudorotaxane with a bifunctional bulky agent, a novel type of polyrotaxane containing a multiply blocked rotaxane architecture in the main chain can be obtained. In this system, the macrocycle rings are fixed between two blocking groups. There have been only a few reports on this type of polyrotaxane.<sup>6,12,13</sup>

Recently, the encapsulation of conjugated polymers into CD cavities to improve their processability and to allow high-performance applications has received much attention.<sup>3,6</sup> Conjugated polymers are gaining commercial importance in light-emitting diodes, thin films for field-effect transistors, photovoltaic cells, and sensors.<sup>14–16</sup> By the encapsulation of the conjugated chains, the stability of the insulated molecular wire is increased. This approach allows a reduction of intermolecular interactions of polymer chains and of the concomitant quenching of the luminescence, while preserving the fundamental semiconducting properties of the conjugated system.

Special emphasis has been placed on polymers and copolymers based on fluorene. Polyfluorenes exhibit high luminescence efficiency, good charge-transport properties, excellent thermal and oxidative stability, and good solubility in common organic solvents.<sup>17</sup> They have been proposed as polymer thin films in light-emitting diodes and in the polarization of light emissions.<sup>18–20</sup> However, the practical use of such polymers is limited by their wide emission band during operation, which can be attributed to secondary reactions at the ninth position of the fluorene structural units resulting in fluorenone groups.<sup>17,21</sup>

We have already reported the preparation of fluorene copolymers with the ninth position of fluorene structural units protected by a persilylated  $\gamma$ -cyclodextrin ( $\gamma$ -CD) macrocycle.<sup>22</sup> The rotaxane copolymer showed good solubility in nonpolar solvents and ultraviolet–visible (UV–vis) absorption in the blue region.

The purpose of this work was to synthesize a conjugated polyrotaxane containing a multiply blocked rotaxane architecture in the main chain, based on a 2,7-fluorene-*alt*-2,7-9,9-dioctylfluorene alternating copolymer {poly[2,7-(9,9-dioctylfluorene)-*alt*-fluorene/ $\gamma$ -cyclodextrin] (PFc)} as the backbone and  $\gamma$ -CD, by Suzuki polycondensation and to evaluate its optical properties in comparison with the noncomplexed copolymer.

## EXPERIMENTAL

### Materials

$\gamma$ -CD was purchased from Wacker Chemie (Stuttgart, Germany) and used after drying *in vacuo* for 48 h at 100°C. 2,7-Dibromofluorene (**2**; 97%), 9,9-dioctyl-

fluorene-2,7-bis(trimethylene borate) (**1**; 97%), and tetrakis(triphenylphosphine)palladium(0) (99%) were purchased from Aldrich Chemical Co. (Steinheim, Germany) and were used as received. The solvents, dimethylformamide (DMF) and toluene, were carefully dried and freshly distilled before use. All other solvents were analytical-grade and were used without further purification.

### Synthesis of the 2,7-dibromofluorene/ $\gamma$ -CD inclusion complex (**2c**)

The general procedure was as follows: To a saturated aqueous solution of  $\gamma$ -CD (4.3231 g, 3.3 mmol) dissolved at room temperature in distilled water (18.6 mL), **2** (0.6501 g, 1.95 mmol) was added, and the mixture was stirred for 72 h at room temperature. The precipitate was filtered and washed thoroughly twice with water (10 mL) and acetone (5 mL). Finally, the white precipitate was dried *in vacuo* at 80°C for 24 h.

Yield: 61% (3.04 g). <sup>1</sup>H-NMR [dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>),  $\delta$ ]: 7.53–7.60 and 7.63–7.88 (m, 6H, Ar–H), 5.79 [16OH<sup>2+3</sup> (CD)], 4.88–4.89 [d, 8H<sup>1</sup> (CD)], 4.52–4.56 [t, 8OH<sup>6</sup> (CD)], 3.97 (s, 2H, CH<sub>2</sub>), 3.36–3.63 [48H<sup>2–6</sup> (CD)]. ANAL. Calcd for C<sub>61</sub>H<sub>88</sub>O<sub>40</sub>Br<sub>2</sub> (1621.13): C, 45.19%; H, 5.47%; Br, 9.85%. Found: C, 45.06%; H, 5.35%; Br, 9.72%.

### Synthesis of PFc

A flame-dried two-necked flask was charged with **1** (0.5756 g, 1 mmol), **2c** (1.6711 g, 1 mmol), and 12 mL of a 3/1 (v/v) toluene/DMF mixture under an argon stream. To the obtained heterogeneous solution, a 2-mL 2M sodium carbonate aqueous solution and tetrakis(triphenylphosphine)palladium(0) catalyst (2.38 mg, 2.06 mmol) were added. The mixture was protected in the dark under an argon atmosphere and was vigorously stirred at 90–95°C for 72 h. A bromobenzene end capper (1  $\mu$ L) was then added, and the reaction was continued for 10 h. After cooling, 50 mL of methanol was added to the mixture, and the obtained suspension was stirred at 60°C for 2 h. The insoluble fraction was filtered, washed with water and acetone, and dried. After extraction with methanol for 24 h in a Soxhlet apparatus to remove the oligomers and catalyst traces, the resulting polymer was dissolved in a 1/1 (v/v) toluene/DMF mixture under heating. A soluble part and an insoluble part were obtained. The insoluble part was proved to consist of the noncomplexed copolymer. The obtained solution was concentrated by vacuum evaporation of the solvents, and the complex was recovered by precipitation in water. The precipitate was filtered, washed with water, methanol, and acetone, and dried. Finally, 0.23 g (yield  $\approx$  28%) of the rotaxane copolymer was obtained as a yellow solid,

which was soluble in DMF, DMSO, and nonpolar/polar solvent mixtures. The copolymer was also soluble (ca. 12 wt %) in hot water.

$^1\text{H-NMR}$  [ $\text{DMSO-}d_6/\text{C}_6\text{D}_6$  (1/1 v/v), temperature =  $68^\circ\text{C}$ ,  $\delta$ ]: 7.53–7.85 (m, 12H), 5.53 and 5.64 [ $16\text{OH}^{2+3}$  ( $\gamma\text{-CD}$ )], 5.08–5.09 [d,  $8\text{H}^1$  ( $\gamma\text{-CD}$ )], 4.13 (s, 2H complexed fluorene units), 3.95–4.00 [t,  $8\text{OH}^6$  ( $\gamma\text{-CD}$ )], 3.51–3.91 [m,  $48\text{H}^{2-6}$  ( $\gamma\text{-CD}$ )], 3.70 (s, 2H non-complexed fluorene units), 2.11 (not resolved t, 4H), 0.82–1.29 (m, 24H), 0.64–0.71 (t, 6H). IR (KBr): 3370 (H-bonded OH), 2930 (OH), 1627 (OH), 1368 (OH), 1243 (OH), 1156 (COC and OH), 1079 and  $1032\text{ cm}^{-1}$  (COC).

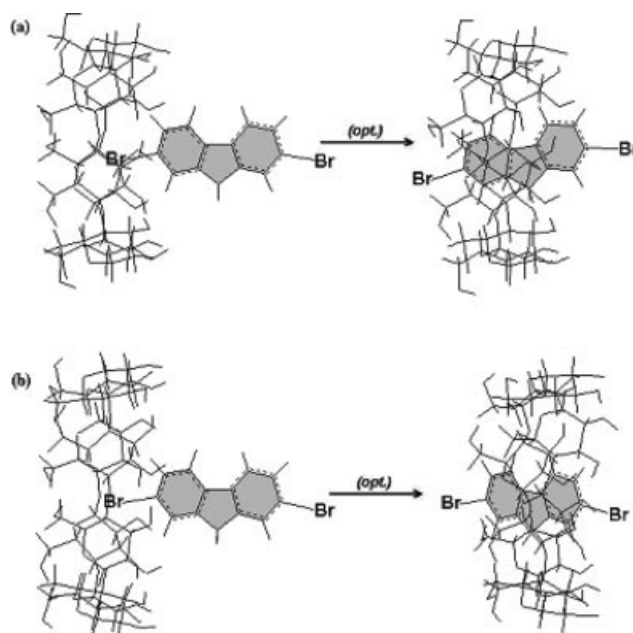
### Synthesis of poly[2,7-(9,9-dioctylfluorene)-alt-fluorene] (PF)

The synthesis of PF was performed under experimental conditions similar to those used for the preparation of PFc, except that **2** was used instead of **2c** and the reaction was performed in toluene. The yield was 79.6%. The copolymer was obtained as an orange solid.

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 7.54–7.59 (m, 12H), 3.70 (s, 2H), 2.02 (not resolved t, 4H), 0.90–1.16 (m, 24H), 0.63–0.66 (t, 6H).

### Measurements

$^1\text{H-NMR}$  spectra were obtained on a Bruker Advance 400 spectrometer (Karlsruhe, Germany). Thermogravimetric analysis was performed with a TA Instruments Q50 (New Castle, DE) at a flow rate of 100 mL/min (samples were heated at  $10^\circ\text{C}/\text{min}$  from room temperature to  $480^\circ\text{C}$  in a dynamic nitrogen atmosphere). Differential scanning calorimetry (DSC) was measured on a TA Instruments Q100 calorimeter calibrated with indium under a nitrogen flow of 50 mL/min and at a heating rate of  $10^\circ\text{C}/\text{min}$ ; data were collected during the first and second heating runs. Elemental microanalysis was carried out on a PerkinElmer 2400 series II CHNS analyzer (Shelton, USA). Size exclusion chromatography was performed in DMF with UV (wavelength = 345 nm) and refractive-index detection. A preparative column (WATO45810) was used, and the flow rate was 0.3 mL/min. Solutions containing analytic quantities (3 mg/mL) of the polymers were used to limit the diffusion phenomena and adsorption of CD. The reported molecular weights were expressed in poly(ethylene oxide) equivalents. The infrared (IR) spectra were obtained on a Specord Carl Zeiss Jena Fourier transform infrared spectrometer (KBr pellets) [Ettlingen, Germany]. The UV–vis electronic absorption spectra of the polymers were obtained on a Specord M42 spectrophotometer. Fluorescence properties were measured on a PerkinElmer LS 55 spectrofluorimeter. The surface profile was evaluated by



**Figure 1** Geometry optimization *in vacuo* through semi-empirical PM3 calculations of (a)  $\beta\text{-CD}$  and (b)  $\gamma\text{-CD}$  inclusion complexes with **2**.

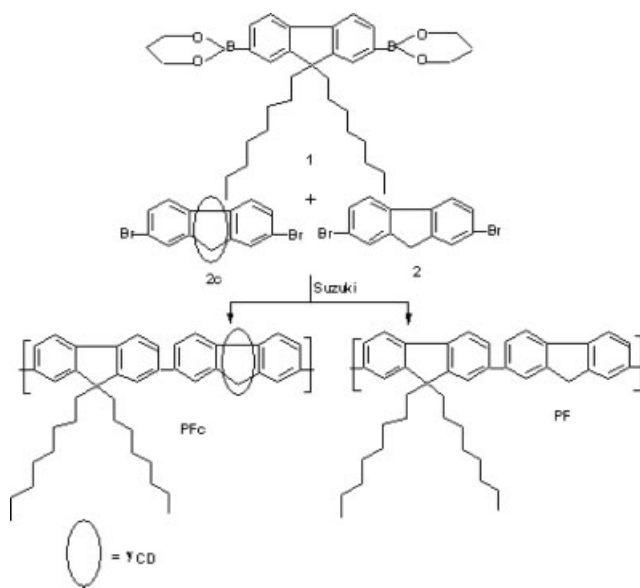
atomic force microscopy (AFM) on an SPM Solver PRO-M device (Zelenograd, Moscow, Russia), and the experiments were performed in the semicontact mode. The samples for AFM were prepared on a glass substrate by solution evaporation (PF from toluene and PFc from a 1/1 v/v toluene/DMF mixture).

The structure of the inclusion complexes was simulated by geometry optimization performed with the HyperChem version 5.11 software package.<sup>23</sup> The initial geometries of  $\beta\text{-cyclodextrin}$  ( $\beta\text{-CD}$ ),  $\gamma\text{-CD}$ , **2**, and **1** were constructed with HyperChem and optimized with the semiempirical PM3 calculation method.<sup>24,25</sup> The geometry of both CDs was compared with crystallographic data.<sup>26</sup> The molecules were considered to be *in vacuo* in a gas phase.

The geometries of the **2** complexes with both  $\beta\text{-CD}$  and  $\gamma\text{-CD}$  were also constructed and submitted to PM3 calculation without any symmetric restriction together with previously PM3-optimized **2**. The initial models were constructed with one of the bromophenyls of **2** placed in the front of the CD cavity under the consideration that the **2** molecule enters by the wider sides of the CD. From these starting models, the semiempirical PM3 calculation was applied without any symmetric restriction, and the final complex structures were determined (Fig. 1).

## RESULTS AND DISCUSSION

The Suzuki polycondensation, a step-growth polymerization of aromatic monomers to polyarylenes,



**Scheme 1** Synthesis of PFc and PF copolymers.

allows the preparation of alternating polymers by the suitable choice of monomers.<sup>27,28</sup> This article describes the use of this method in the preparation of a multiply blocked rotaxane in the main chain (Scheme 1). As appropriate comonomers able to build through polycondensation the mentioned rotaxane structure, **2c** and **1** were chosen. To compare the properties of the copolymers with and without a rotaxane architecture, a noncomplexed fluorene copolymer (PF) was also synthesized through the polycondensation of **2** with **1** (Scheme 1).

The preparation of copolymer polyrotaxane PFc involves a 1/1 **2c** inclusion complex precursor. **2c** was made through the mixing of  $\gamma$ -CD with **2** in water. The resultant precipitate was isolated, purified, and checked by <sup>1</sup>H-NMR and elemental analysis, which indicated a 1/1 molar composition. The inclusion of the aromatic compound was not further investigated but was demonstrated through the formation of the copolymer polyrotaxane.

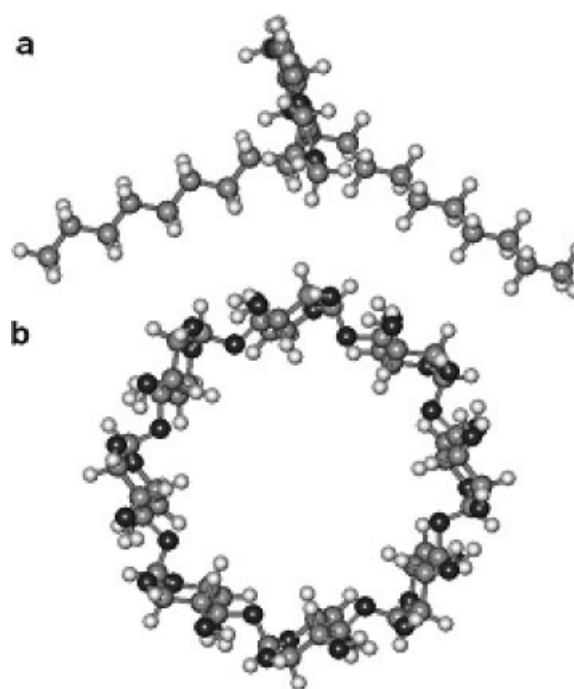
The complexation of **2** in water was also checked for  $\beta$ -CD, but a lower content of  $\beta$ -CD was evidenced in comparison with  $\gamma$ -CD. Hadziioannou et al.<sup>11</sup> also reported a difficult complexation between **2** with an excess of  $\beta$ -CD in DMF.<sup>11</sup>

The computational calculations showed that both  $\beta$ -CD and  $\gamma$ -CD had cavities large enough to accommodate **2** inside, in good agreement with the literature.<sup>29,30</sup> However, when the inclusion process was simulated, starting from a molecule of CD and a molecule of **2**,  $\beta$ -CD was proved not to be able to accommodate the whole host molecule of **2** inside its cavity [Fig. 1(a)]. For  $\gamma$ -CD, an assembly containing **2** inside the cavity with bromine substituents oriented toward the base of the truncated molecule

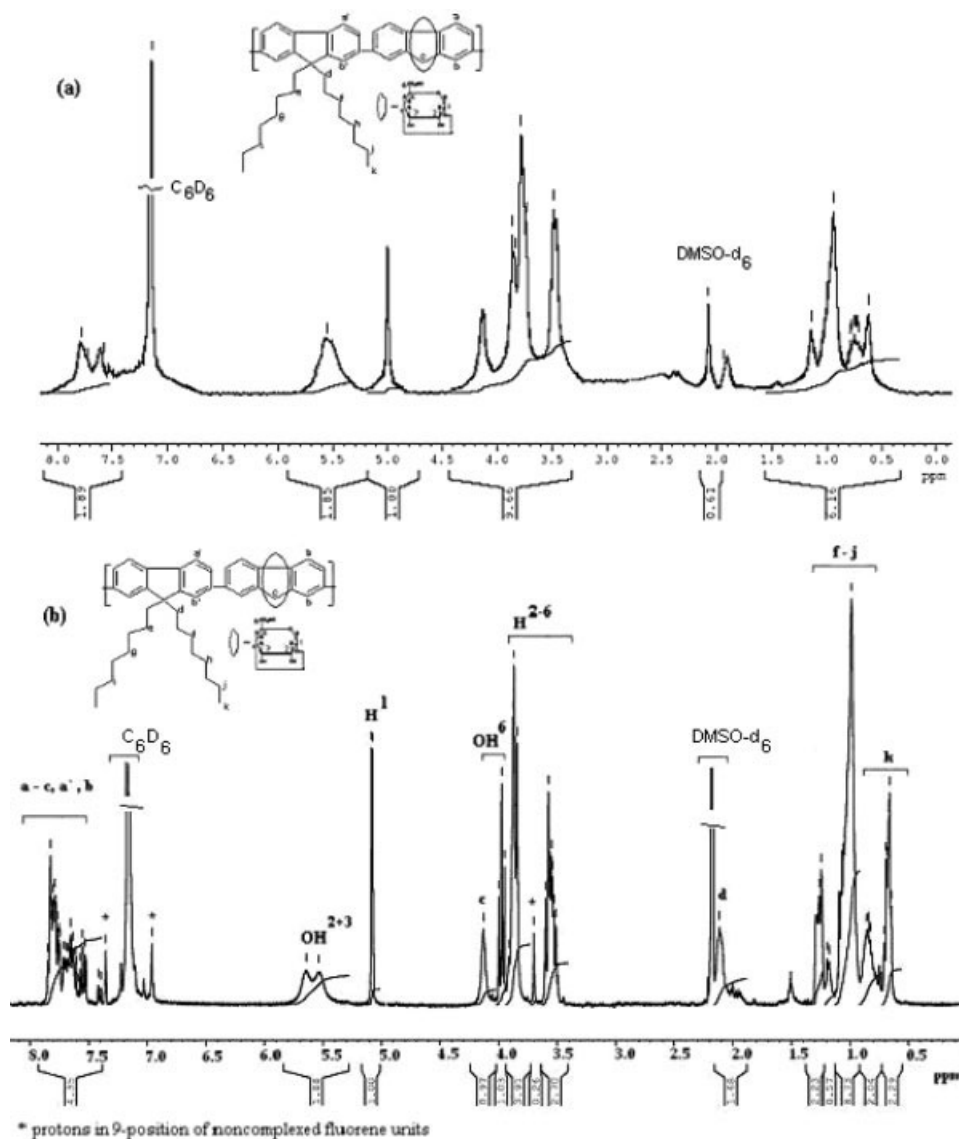
was obtained [Fig. 1(b)]. Based on simulation results compared with experimental finding, the low yield of complexation of **2** by  $\beta$ -CD seems to be a solvent effect (more than 10 times lower solubility of  $\beta$ -CD in water versus  $\gamma$ -CD). Moreover, the substitution of bromine with rather bulky trimethylene borate groups should take place close to the cavity surface, and  $\gamma$ -CD has a diameter only large enough to allow the access of the reagent to the reaction site. Thus,  $\beta$ -CD was not further considered as a macrocycle guest for **2** in the synthesis of the inclusion complex in water.

The computation method was also used to determine if a 9,9-dioctylfluorene unit could be used as blocker of the pseudorotaxane (Fig. 2). As one can see from the comparison of simulated geometrical structures of **1** and  $\gamma$ -CD, the spatial distribution of octyl bulky substituents is larger than the diameter of the inner cavity of  $\gamma$ -CD, and this indicates their blocking effect.

As the partners in the polycondensation reaction are soluble in solvents with different polarities (**2c** is soluble in polar solvents and **1** is soluble in nonpolar solvents) and as one of them is a pseudorotaxane susceptible of dethreading by dilution, the choice of the reaction solvent was crucial for the success of the rotaxane copolymer formation. Through the performance of the reaction in THF, the complete dethreading of the pseudorotaxane (**2c**) and the formation of a mixture of  $\gamma$ -CD and the pure fluorene copolymer were evidenced. In DMF/toluene mixtures with 1/1 and 3/1 volume ratios, the



**Figure 2** Simulated structures of (a) **1** and (b)  $\gamma$ -CD.



**Figure 3**  $^1\text{H-NMR}$  spectra of PFC at  $68^\circ\text{C}$  in (a) 1/1  $\text{C}_6\text{D}_6/\text{DMSO-}d_6$  and (b) 3/1  $\text{C}_6\text{D}_6/\text{DMSO-}d_6$ .

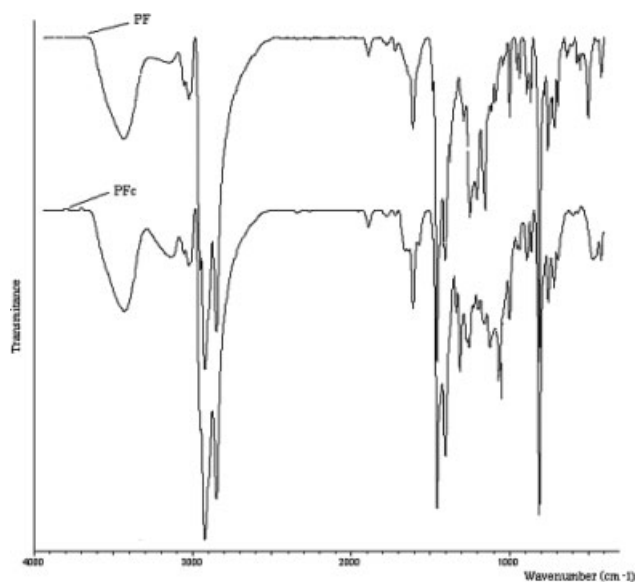
dethreading of the pseudorotaxane was also important, and rotaxane copolymers with quite low contents of  $\gamma\text{-CD}$  were obtained ( $\gamma\text{-CD}/\text{structural unit}$  ratios of ca. 1/5 and 1/10, respectively). The best results were achieved in a 1/3 DMF/toluene mixture. However, the partial dethreading of **2c** was not completely avoided, and a copolymer polyrotaxane characterized by a  $\gamma\text{-CD}/\text{structural unit}$  molar ratio of about 1/1.4 was obtained.

The copolymer with a rotaxane architecture (PFC) showed a marked contrast with the polymer without a rotaxane architecture (PF). The precipitation with methanol of PF from the toluene solution was easy, and the polymer could be almost totally recovered. The DMF solutions of PFC after the addition of water became opalescent, and the copolymer precipitated in time. Also, whereas the PF copolymer was obta-

ined as an orange solid, the PFC copolymer was obtained as a yellow product.

The structure of the copolymer polyrotaxane was proved by  $^1\text{H-NMR}$  and IR spectroscopy.

Because of the large difference in the solubilities of the polyfluorene chains and  $\gamma\text{-CD}$ , it was quite difficult to determine the solubility of the PFC polyrotaxane. Polar ( $\text{DMSO-}d_6$ ) and nonpolar ( $\text{C}_6\text{D}_6$ ) solvent mixtures were used, but complete solubilization of the sample was not achieved at room temperature. Figure 3 presents  $^1\text{H-NMR}$  spectra of the PFC polyrotaxane in  $\text{C}_6\text{D}_6/\text{DMSO-}d_6$  solvent mixtures of different volume ratios. The NMR spectrum in a 1/1 (v/v)  $\text{C}_6\text{D}_6/\text{DMSO-}d_6$  mixture [Fig. 3(a)] shows characteristic peaks for both the PF chain and  $\gamma\text{-CD}$ , but the signals are not very well resolved. A  $\gamma\text{-CD}/\text{structural unit}$  molar ratio of 1/1.4 was calculated



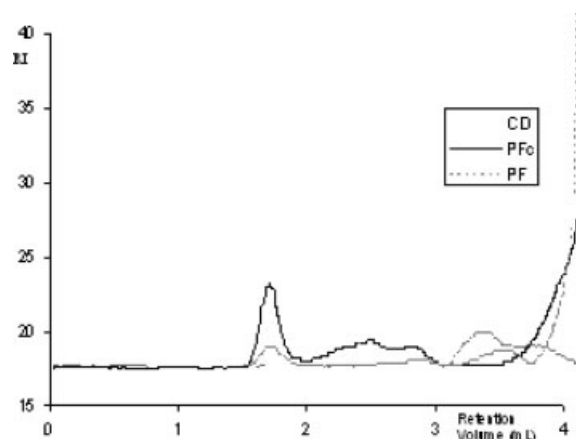
**Figure 4** Fourier transform infrared spectra (KBr pellets) of PF and PFc samples.

from this spectrum. A better resolved spectrum was obtained for the solution of the copolymer polyrotaxane obtained in a solvent mixture enriched in a nonpolar solvent [a 3/1 v/v  $C_6D_6/DMSO-d_6$  mixture; Fig. 3(b)]. Under these experimental conditions, the ratio of  $\gamma$ -CD on the structural units was lower (ca. 1/3) than the molar ratio of 1/1.4. In the PFc sample, the peaks corresponding to fluorene copolymer chains were enlarged and high-field-shifted by 0.01–0.08 ppm in comparison with the noncomplexed sample, whereas the anomeric proton of  $\gamma$ -CD was down-field-shifted by more than 0.1 ppm. The shift of the characteristic peaks of both the fluorene copolymer chain and CD confirmed the formation of a rotaxane structure, as reported for other polyrotaxanes.<sup>12,13</sup>

The IR spectrum (Fig. 4) of PFc shows specific absorption bands at 3370 (OH stretching H bonded), 2930 (OH stretching), 1627 (OH bending), 1368 (OH deformation), 1243 (OH bending), 1156 (COC stretching and OH bending), and 1079 and 1032  $cm^{-1}$  (COC stretching) characteristic for  $\gamma$ -CD. The weak absorbance in the IR spectra of the bands at 1469 and 810  $cm^{-1}$ , attributed to the vibrations of the fluorene group, led to the conclusion that an unsubstituted fluorene unit is included in the inner cavity of  $\gamma$ -CD.

After Soxhlet extraction with methanol and a second reprecipitation in water of the rotaxane copolymer solution in DMF, the intensity of the characteristic CD bands remained unchanged.

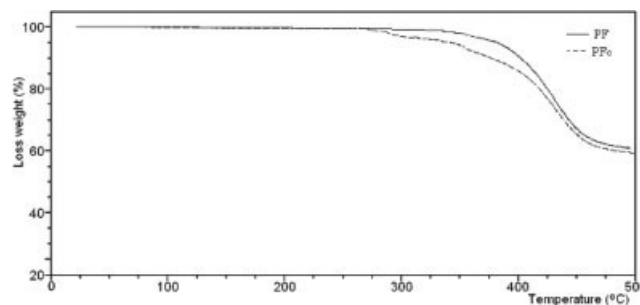
The molecular weights of PFc and PF samples were evidenced by size exclusion chromatography. Figure 5 presents the characteristic curves of complexed and noncomplexed copolymer samples and



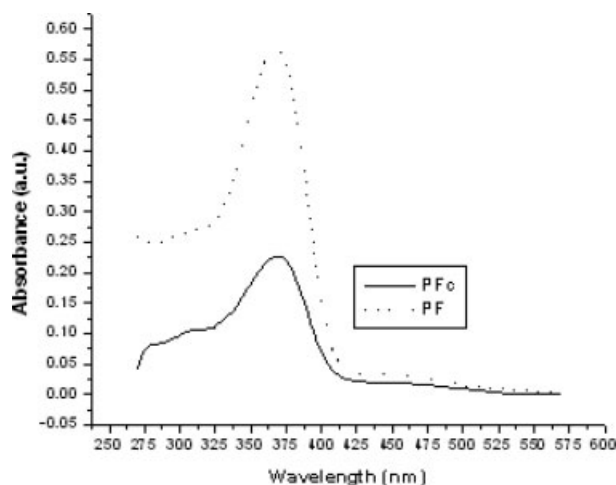
**Figure 5** Size exclusion chromatography curves of PF, PFc, and  $\gamma$ -CD.

$\gamma$ -CD. PFc was analyzed as a solution in a 1/1 (v/v) toluene/DMF mixture with DMF as an eluent, whereas PF was injected as a solution in toluene, and the curve was determined with DMF as an eluent. The PF sample showed a unimodal distribution of the molecular weight, with a number-average molecular weight of 38,000 g/mol and a weight-average molecular weight/number-average molecular weight ratio of 2.21. The curve corresponding to the copolymer polyrotaxane was bimodal, suggesting the separation on the chromatographic column of species with lower and higher contents of CD macrocycles threaded on the copolymer chain with number-average molecular weights of 68,000 and 21,000 g/mol, respectively. The polydispersity index calculated for the whole curve was about 2.5. No free  $\gamma$ -CD was evidenced in the sample.

The thermal stability of the copolymers was investigated with thermogravimetric analysis (Fig. 6). The presence of  $\gamma$ -CD on the copolymer chain induced slightly lower thermal stability of the copolymer polyrotaxane. The PF copolymer started to decompose at about 340°C, whereas its polyrotaxane homologue showed the beginning of decomposition at about 305°C, which was not much higher than the decomposition temperature of  $\gamma$ -CD (290°C). No weight loss



**Figure 6** Thermogravimetric analysis scans of PF and PFc (10°C/min).



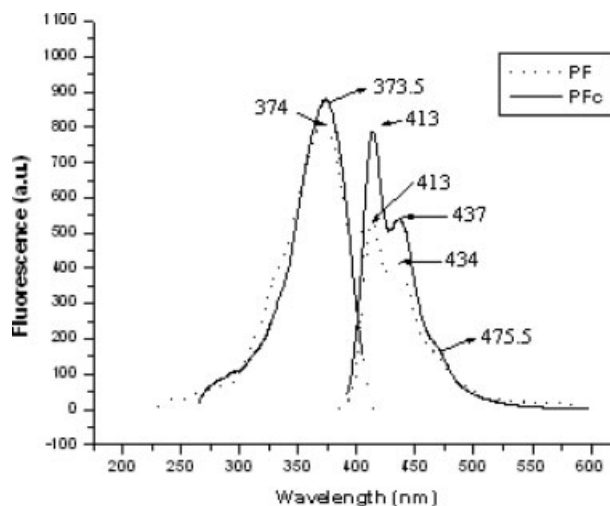
**Figure 7** UV-vis spectra of copolymers PF and PFc in DMF solutions.

was recorded at lower temperatures. This result could prove that the PF copolymer increased the stability of the macrocycle in the rotaxane architecture.

The DSC thermogram of the copolymers in the heating run (not shown) does not indicate any evidence of an endothermic peak due to the melting or glass transitions in the 50–250°C interval. PF presents an exothermic peak at about 227°C during the first heating, which can be attributed to the crosslinking of the end chain. Indeed, at the end of the polymerization of these products, no excess of **1** was added to have esters as end groups; only a bromobenzene end-capping reagent was added. In the second heating, the exothermic peak disappeared because of the fully cured sample during the first run.

The DSC thermogram of the rotaxane copolymer (PFc) in the first heating run does not indicate an exothermic peak in the 50–250°C interval. This could be attributed to the presence of a rotaxane architecture, which reduced the interpolymer interactions and stabilized the polymeric end chain. The second run (when heating was stopped at 200°C) was identical to the first one. The DSC thermogram, previously reported for the corresponding poly(9,9-di-*n*-octyl-2,7-fluorene) homopolymer, shows a crystallization peak at about 80°C and a melting endothermic peak at 157°C at the heating rate of 20°C/min.<sup>31</sup> The DSC study of both copolymers indicated that the transition temperature could be increased compared to that of the corresponding PF homopolymer as a result of the incorporation of the rigid unsubstituted fluorene with or without rotaxane architecture moieties in the 50–250°C interval.

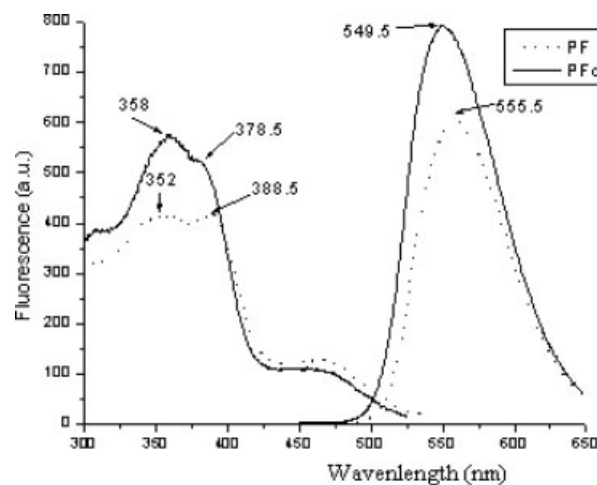
It was expected that the presence of  $\gamma$ -CD on the copolymer chain would induce the modification of its optical properties. The UV-vis spectra of PF and PFc in DMF solutions are similar (Fig. 7). The



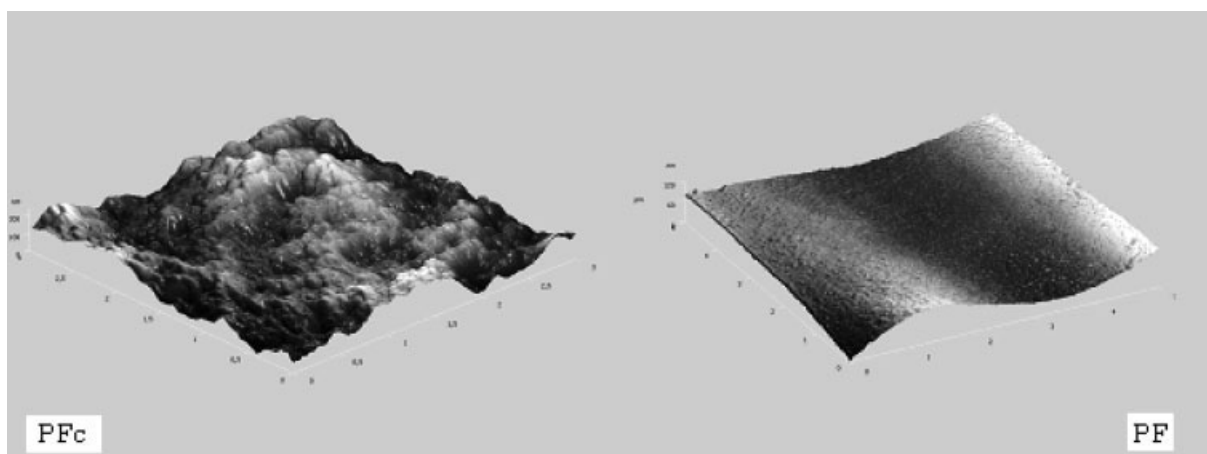
**Figure 8** Excitation (emission wavelength = 413 nm) and emission (excitation wavelength = 380 nm) fluorescence spectra of PF and PFc (DMF solutions).

absorption peaks at 368 nm can be attributed to the fluorene unit in both copolymer structures. However, even when the concentration of the fluorene copolymer chain was identical (1.31 mg/mL), whether it was complexed or not, the absorption intensity of the PFc sample decreased because of its complexation into the CD cavity. This absorption was stable over time. A decrease in the intensity was observed more often upon complexation in a macrocycle.<sup>32</sup>

The fluorescence excitation (emission wavelength = 413 nm) and emission (excitation wavelength = 380 nm) spectra of the polymers in DMF solutions are presented in Figure 8. The excitation spectrum of PF exhibited one absorption maximum at 374 nm, whereas that of PFc showed one at 373.5 nm, which corresponded to the  $\pi$ - $\pi^*$  transition of the backbone



**Figure 9** Excitation (emission wavelength = 550 nm) and emission (excitation wavelength = 380 nm) fluorescence spectra of PF and PFc (thin films).



**Figure 10** Tapping-mode height images in air over a  $5 \times 5 \mu\text{m}^2$  area for PFc and PF.

of the polymer. The excitation band of PFc was slightly sharper than that of PF, and this could be attributed to reduced interchromophore interactions and increased conformational homogeneity.

From fluorescence emission spectra in DMF solutions, one could observe that the ratio of the intensities of the peaks in a DMF solution of PFc (absorption intensity  $I_{413}$  for the 0–0 band and absorption intensity  $I_{437}$  for the 0–1 band; Fig. 8) was higher than that in PF, reflecting that the encapsulation reduced the quenching effect of the environment.<sup>33</sup>

The fluorescence excitation (emission wavelength = 550 nm) and emission (excitation wavelength = 380 nm) spectra of the copolymer films are presented in Figure 9. Excitation fluorescence spectra of copolymer thin films showed that the ratio of the intensities of the peaks was higher in PFc than in PF. This observation revealed that the vicinity of a chromophore from PFc was changed. Fluorenyl unsubstituted structural units were partially surrounded by  $\gamma$ -CD, which reduced interchromophore interactions. In emission spectra, the global intensity of PFc was higher than that of PF, and this demonstrated the same conclusion.

Figure 10 shows the AFM surface profiles of PF and PFc samples. There were significant differences between the roughnesses of the copolymer films. The film of PF was almost flat, whereas PFc presented globular formations over the same scanning scale area. Under the assumption that the AFM method is sensitive enough to highlight the supramolecular structures, it is obvious that the PFc AFM scan shows tight packing of the polymer chains.

## CONCLUSIONS

In conclusion, a multiply blocked polyrotaxane with a conjugated polymer core based on a fluorene co-

polymer and  $\gamma$ -CD threaded onto a macromolecular chain was prepared through Suzuki coupling of the appropriate monomers. The bulky 9,9-dioctylfluorene alternating groups prevented the macrocycles from slipping off the polymer chains. However, starting with a 1/1 2/CD inclusion complex, we found that the content of CD molecules in the polyrotaxane was not lower than expected (1/1 CD/structural unit ratio) because of the partial decomposition of **2c** during the reaction. The rotaxane copolymer was more hydrophilic than the noncomplexed homologue and presented a maximum emission wavelength at 413 nm in the blue region. The presence of  $\gamma$ -CD in the polyrotaxane induced the reduction of the thermal stability and the increase in the solubility in polar solvents.

The next step in our studies is to develop further aspects of this material and to study its properties for practical applications.

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