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Synthesis of fluorene copolymer with persilylated γ-cyclodextrin in the main chain

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Polyfluorene copolymers with and without persilylated γ-cyclodextrin (γ-CD) threaded onto the main chain were synthesized by using the well-known Suzuki copolymerization of 2,7-dibromofluorene/persilylated γ-CD inclusion complex or 2,7-dibromofluorene with 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) catalysed by tetrakis-(triphenylphosphin)-palladium (0) in heterogeneous conditions. By using a 50:50 molar ratio between comonomers, copolymers having alternating substituted and non substituted fluorene units were obtained. The copolymers were characterized by ^{1}H-NMR, IR, GPC, TGA, UV-Vis and AFM analyses. The fluorescence spectra of the copolymers exhibit typical well resolved blue emission bands arisen from the fluorene chromophore units.

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1. Introduction

Conjugated polymers have attracted widespread interest due to their applications in light-emitting diodes, field effect transistors, and photovoltaic devices [1-3]. They are often loosely described as molecular wires because of the high charge-mobility along individual polymer chains [4]. Intermolecular π–π interactions in organic materials have a fundamental role in a variety of processes spanning from charge transport to the photophysics of neutral excited species. For example, π–π stacking is essential for high mobility in polymer-based field-effect transistors [5], whereas formation of intermolecular excited states in luminescent materials may lead to both reduced photoluminescence efficiency, and a reduced energy gap [6,7]. Among the conjugated polymers, particularly a number of polyfluorene polymers and their derivatives have been attracting great interest as very promising candidates for blue light-emitting diode (LED) materials because polyfluorenes (PFs) exhibit a high luminescence efficiency, good charge transport, excellent thermal and oxidative stability, and good solubility in common organic solvents. Remarkable progress can be observed in the development of fluorene based copolymers, since they are among the most promising candidates for efficient electroluminescence diode [8]. Last years, poly(9,9-dialkylfluorene)s [9] have emerged as a very promising class of conjugated polymers, which can be utilized as blue emission layers in polymer light emitting diodes (PLEDs) [10-12] also for linearly polarized light emission [13] due to the liquid crystallinity of polyfluorene derivatives with long alkyl chains. A major problem with pure blue light emission from PFs under device operating conditions is the appearance of a long wavelength band in the emission spectra [14]. A first explanation of this behavior is the formation of fluorenones by oxidation of fluorene units not fully alkylated in the C9 position [15].

In this perspective, we tried to protect the C9 position by threading 2,7-dibromofluorene through a insulating macrocycle to form a pseudorotaxane structure. Alternating polycondensation of a bifunctional compound with a bulky group and a pseudorotaxane complex gave a novel type of polyrotaxane containing a blocking group in every structural unit of the main chain. In this system macrocycle rings are fixed between two blocking groups. A large variety of main and side chain linear polyrotaxanes were prepared [16-25].

Polyrotaxanes are typical supramolecular assemblies, composed of many cyclic molecules threaded onto a straight macromolecular chain. They are built by physical interactions between the macrocyclic host and the polymer guest. In recent years, a large number of concepts, that make use of the non-covalent interactions, have been disclosed. Systems based on these concepts hold promise as a unique class of novel materials. Polyrotaxanes serve as prototypes for versatile strategy in the design, synthesis and control of supramacromolecules with unusual properties. Polyrotaxane architectures are relevant building blocks of *molecular-level machines*. They are considered as promising candidates for the construction of supramolecular devices which represent, structural - functional organized systems.

The paper presents the synthesis and physicochemical characteristics of polyfluorene copolymers having persilylated γ-CD threaded onto polymer chain as compared to non complexed copolymer. The alternating polycondensation of a pseudo-rotaxane of 2,7-dibromofluorene/persilylated γ-CD (CPBF) with 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) was used to prepare the copolymer that was showing enhanced solubility in

unpolar solvents and a slightly higher thermal stability as compared to the copolymer without persilylated γ-CD.

2. Experimental

2.1. Materials and Methods

All manipulations were carried out under inert argon atmosphere. All solvents were carefully dried and freshly distilled before using. 2,7-dibromofluorene, 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) and tetrakis-(triphenylphosphin)-palladium (0) were purchased from Aldrich Chemical Co. and were used as received. Persilylated γ-cyclodextrin was obtained by the silylation of native γ-CD with 1-trimethylsilylimidazole [26].

2.1.1 Synthesis of 2,7-dibromofluorene/persilylated γ-CD (CPBF)

In a 50 mL round bottom flask equipped with magnetic stirrer, persilylated γ-CD (0.3786 g, 0.202 mmol) of was dissolved in heptane (2 mL) at room temperature. 2,7-dibromofluorene (0.0654 g, 0.202 mmol) dissolved in methylene chloride (3 mL) was then added and solution was stirred for 3 days at room temperature. No precipitate was formed. 0.4 g (yield, 83%) of a white solid product were obtained by solvent removing, washing with acetone (3 ml) and drying. A persilylated γ-CD/fluorine molar ratio of 0.625 was calculated from ^{1}H-NMR spectrum. γ-persilylated cyclodextrin do not show clear peaks in the region of anomeric protons. A rather large resonance signal with two maxima at 4.9 and 5.05 ppm was observed in the ^{1}H-NMR spectrum.

2.1.2 Synthesis of fluorene copolymer with persilylated γ-CD (PF1)

In a three necked round bottom flasks of 100 ml CPBF (0.458 g, 0.206 mmol), 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (0.1187 g, 0.206 mmol), tetrakis-(triphenylphosphin)-palladium (0) (7.6 mg, 1 mol %), toluene (6 mL) and 2 ml of a 2.0 M sodium carbonate solution were added in this order under argon stream. The mixture was refluxed at 90–95^{0}C, in dark, under argon protection for 3 days. Upon completion, 1 μl of bromobenzene was added as an end capper and the reaction was continued for 10 hours. The mixture was then transferred into a funnel and extracted with toluene (50 ml). The toluene solution was washed with water three times and dried over sodium sulphate. The solvent was removed and the resulted viscous product was poured into petroleum ether (50 ml) to remove the non complexed persilylated γ-CD. The obtained solid was filtered, washed with methanol and purified in a Soxhlet apparatus with methanol. Finally, the solid was dissolved in toluene and precipitated in methanol to give 0.182 g of a pale yellow powder. Yield = 60 %.

^{1}H NMR ($CDCl_3$) (Fig. 1a) δ: 7.36-7.92 (m, 12H); 3.60-4.09 and 5.05 (persilylated γ-CD); 0.54-2.24 (alkyl groups); 0.00 (persilylated γ-CD).

According to ^{1}H NMR spectrum, one persilylated γ-CD for 7 fluorene units was identified in the structure of the copolymer. The copolymer shows a solubility of 16 % by weight in hexane.

2.1.3 Synthesis of fluorene copolymer without persilylated γ-CD (PF2)

In a three necked round bottom flask of 100 ml, 2,7-dibromofluorene (0.133 g, 0.4 mmol), 9,9-dioctylfluorene-2,7-bis(trimethylene borate) (0.231 g, 0.4 mmol), tetrakis-(triphenylphosphin)-palladium (0) (16.1 mg, 1 mol %), toluene (6 mL) and 2 ml of a 2.0 M sodium carbonate solution were added. The mixture was refluxed at 90–95^{0}C, in dark, under argon protection for 3 days. Upon completion, 1 μl of bromobenzene was added as an end capper and the reaction was continued for 10 hours. The mixture was transferred into a funnel and extracted several times with toluene (30 ml). The toluene solution was washed with water three times. After concentration (by removing the organic solvent) the solution was precipitated in methanol. The filtered solid was washed with methanol and purified in a Soxhlet apparatus with methanol. Finally, the solid was dissolved in toluene and precipitated in methanol to give 0.1 g of a light green powder. Yield = 61.68 %.

^{1}H NMR (400 MHz, $CDCl_3$) (Figure 1b) δ: 7.61-8.01 (m, 12H); 1.75-2.17 (m, 4H); 1.08-1.28 (m, 24H); 0.74-0.87 (m, 6H)

The copolymer is very soluble in toluene and less soluble in polar organic solvents.

2.2. Analysis

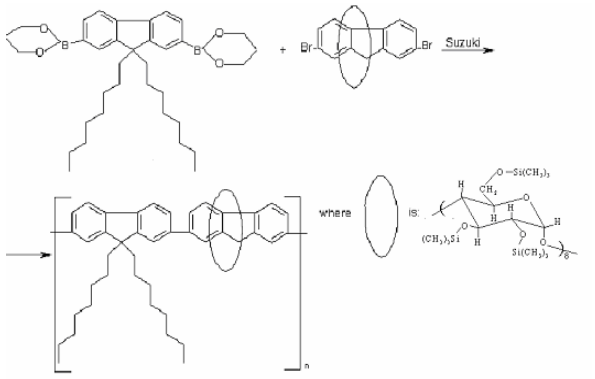
^{1}H NMR spectra were registered on a Bruker Avance 300 MHz in $CDCl_3$. The relative molecular weights were determined by size exclusion chromatography using a Polymer Laboratories (PL-EMD England) instrument with light scattering detector, polystyrene standards for the calibration and toluene as solvent. TGA results were obtained on a MOM Budapest Derivatograph. The UV-VIS electronic absorption spectra were obtained on a SPECORD M42 spectrophotometer. Luminescence spectra were made on a Perkin Elmer LS 55 spectrofluorimeter at the excitation wavelength of 380 nm. Atomic Force Microscopy (AFM) images were performed on a SPM solver PRO-M (NT-MDT), in the semi-contact mode on polymer films cast onto glass plates.

3. Results and discussion

The synthesis of fluorene copolymers was performed through conventional aromatic nucleophilic substitution *via* Suzuki coupling technique by using tetrakis-(triphenylphosphin)-palladium (0) as catalyst [27]. The advantage of the Suzuki protocol consists in the possibility of obtaining alternating copolymers by suitable choice of the monomers. Fluorene copolymer containing persilylated γ-CD as macrocyclic compound (PF1) was prepared according to Scheme 1. To compare the properties of

copolymers, PF2 was synthesized under the same experimental conditions by polycondensation of 2,7-dibromofluorene with 9,9-dioctylfluorene-2,7-bis(trimethylene borate) in toluene.

Theoretically, the alternating polycondensation of 2,7-dibromofluorene/persilylated γ-CD complex with 9,9-dioctylfluorene-2,7-bis(trimethylene borate) (a bulky group) can give polyrotaxanes containing a blocking group in each structural unit of the main chain.



Scheme 1: Synthesis of the polyfluorene copolymer with persilylated γ-CD in the main chain.

The chemical structure of both copolymers was proved by ^{1}H NMR (Fig. 1) and IR analysis (not shown). As one can see from Fig. 1, PF1 and PF2 copolymers present similar resonance peaks, but PF1 signals are larger and less resolved. In PF1 spectrum additional signals at 0 ppm and in 3-5 ppm region attributed to persilylated γ-CD are also observed.

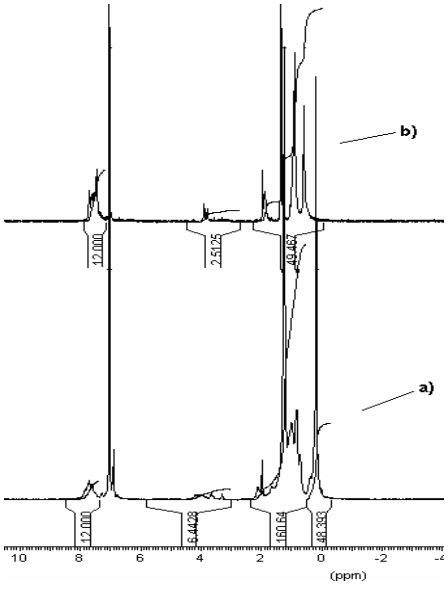


Fig. 1 .^{1}H NMR spectra of PF1 (a) and PF2 (b).

From the integral ratios of the characteristic peaks of fluorene units and persilylated γ-CD a molar ratio of about 1/7 was calculated. The lower value of this ratio as compared to CPBF adduct used in the polycondensation reaction should be attributed to the decomposition of 2,7-dibromofluorene/persilylated γ-CD complex during the polycondensation reaction and to the participation of non complexed 2,7-dibromofluorene in the formation of the rotaxane copolymer chain.

Infrared spectra (not shown) of the PF1 copolymer shows all the characteristic bands of PF2 copolymer and additional bands located in 750–1500 and 2800–3000 cm^{-1} regions.

The number-average molecular weight of the PF1 copolymer determined by gel permeation chromatography using toluene as solvent is M_n = 26800 g mol^{-1}, higher than the values for the PF2 copolymer (Mn about 12000). These values have to be taken as indicative only, since calibration with polystyrene may induce questionable results when the polarity and backbone stiffness of the studied polymer deviate strongly from those of polystyrene.

The electronic absorption spectra of PF1 and PF2 copolymers in chloroform solutions are shown in Fig. 2 (left). The absorption spectra of both copolymers evidence a maximum at 379.5 nm corresponding to the π-π* transitions of the polymer backbones [28]. The absorption spectra are less affected by the presence of macrocycle.

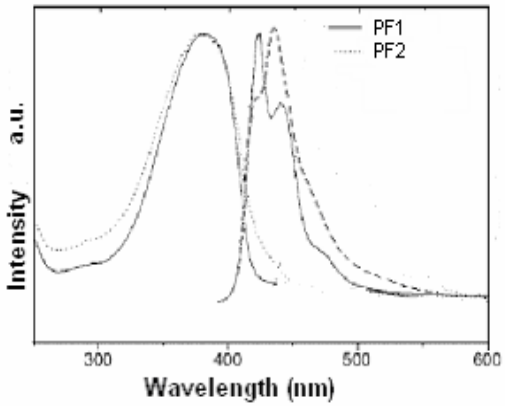


Fig.2. UV-vis and PL spectra of the polymers PF1 and PF2.

The photoluminescence spectra (Fig. 2, right) of the copolymers exhibit typical well resolved blue emission bands at 420.5, 435 nm for PF1 and 413, 437 nm for PF2 arisen from the fluorene chromophore units. The blue-shifted emission of PF1 in solution as compared to PF2 suggests that the rotational freedom of the chains in the complexed copolymer might be restricted.

The thermal stability of the copolymers was investigated by TGA. The weight loss curves for PF1 and PF2 copolymers are presented in Fig. 3. Their decomposition curves are similar but PF1 sample starts the decomposition at 380^{0}C, about 100^{0}C higher as compared to PF2. Both copolymers show up to 600^{0}C a two stage decomposition

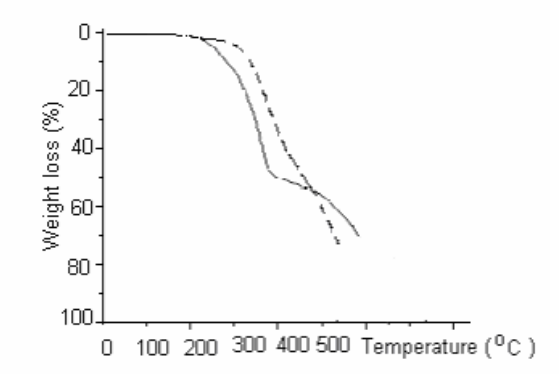


Fig. 3. TGA curve for PF1 (dotted line) and PF2 copolymer (full line).

Fig. 4 compares the surface images of PF1 and PF2 copolymers. It was not possible to obtain good film from 1/1 physical mixture of PF2 and persilylated γ-CD. As one can see from Fig. 4, there are obvious differences between the surface morphology of PF1 and PF2 copolymer films. In contrast to the copolymer with persilylated γ-CD (PF1), where very clear globular formations are present on the surface, the film of the copolymer without γ-CD (PF2) is almost flat over the same scanning scale area. The AFM method is considered to be sensitive enough to highlight such supramolecular structures.

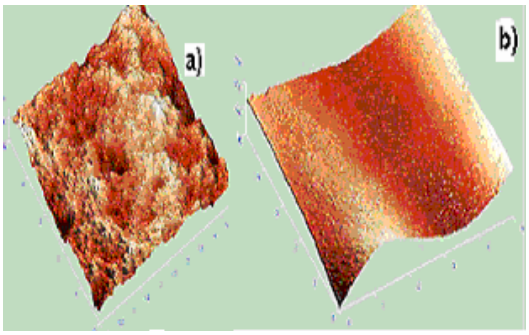


Fig. 4. Tapping–mode height images in air over 5x5 μm area in the case of PF1 (a) and PF2 (b).

4. Conclusions

In this study, a conjugated copolymer based on fluorene with one persilylated γ-CD per 7 repeating units was synthesized and characterized. The content of γ-CD threaded onto macromolecular chain was lower than expected. The presence of persilylated γ-CD in PF1 induces the increase of the thermal stability, of the solubility and a blue shift of its emission. In the light of these properties PF1 can be considered as a promising copolymer for the use as active layer in blue electroluminescence device, because of the easy synthesis and the control of the interchain interactions attainable with the incorporation of the macrocycle groups.

We are currently working to improve the synthesis and to develop new further aspects of this new material. Polyrotaxane are expected to protect C9 position of the polyfluorene chain.

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