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CHARACTERIZATION OF POLY[9,9-BIS(2-ETHYLHEXYL)-FLUORENE-CO-9-ETHYLCAPRONATE -FLUORENE-2,7 DIYL] CONDUCTING POLYMER

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A copolymer based on polyfluorene with pseudo-rotaxanes architecture in the side chain have been prepared through nickel(0)-catalyzed couplings between 2,7-dibromo-9-ethylcapronate-fluorene/ 24-crown-8 as adduct, and 9,9-bis(2-ethylhexyl)-fluorene. Chemical modification of this copolymer was performed by saponification in the presence of LiOH solution resulting ionic structures. This copolymer has good solubility, in organic solvents (chloroform, tetrahydrofurane) and can be easily processed into homogeneous transparent thin film by usually method. The primer structure were investigated by ^{1}H NMR and ^{13}C NMR and InfraRed spectroscopy, photo-conducting properties of *in solution* polymer by fluorescence technique and electrical conducting properties *in film* by UV-VIS transmission spectroscopy and by studying the temperature dependence of electrical resistance of the polymer in thin film. The polymer presents semiconducting properties with the activation energy of the electrical conduction of 1.41 eV that makes it suitable for electronic solid state devices.

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1. Introduction

Supramolecular chemistry has afforded material scientists to the new point of view for the design of smart materials mimicking nature [1, 2]. The focus is in using supermolecular chemistry to achieve control, at the single-molecule level, in the design of responsive organic materials. Recently, many research groups have focused on new molecular assemblies, wherein two or many molecules are bound together only by mechanical entanglement and not by covalent bonds.

Organic conducting materials, such as π-conjugated polymers, continue to be the subject of intense research due to their unique optical and electronic properties. The processing advantages, together with the versatility of molecular structures and tunable physical properties, make these organic electroactive materials attractive for a wide range of applications, from electronic devices to mechanical actuators. Remarkable progress can be observed in the development of fluorene based polymers, since they are among the most promising candidates for efficient electroluminescence diode (ELD) [3]. Several conjugated poypseudorotaxanes have been reported [4 - 9]. Through the formation of pseudorotaxanes (rotaxanes without end blocking groups) using 24-crown-8 crown and a monomer with very long side chain (2,7-dibromo-9-ethylcapronate-fluorene) we obtained a new polypseudo-rotaxane in which macrocycles are threaded onto side-chain. The novel structural features of polyrotaxanes are expected to confer many unusual properties, offering new concepts of macromolecular design that may be exploited, for example, in terms of traditional mechanical behaviour, as sensors and in electroactive applications.

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In this paper have been investigated the conducting properties of the poly[9,9-bis (2-ethylhexyl)-fluorene-co-9-ethylcapronate-fluorene-2,7diyl] with pseudo-rotaxane architecture in the side-chain (PFD).

2. Experimental

PFD synthesis, realised via Yamamoto poly-condensation procedure [10], was reported in detail elsewhere [11, 12].

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500 (500 and 125 MHz, respectively). The molecular structure was investigated by InfraRed (IR) with a Nicolet FT-IR 320. Elemental analyses were performed by using a Perkin-Elmer CHN 2400 elemental analyzer.

The fluorescence properties in solution were determined using a SLM 8000 spectrofluorometer; the solvent was chloroform Sigma spectrophotometric grade.

The thin film samples were deposited onto glass substrates using the spin-coating technique. The precursor solution was prepared by dissolving the polymers in chloroform. A controlled quantity of solution was spread on the substrate and spinning with 1000 rpm for 30s.

The film resistance was measured with a Keithley model 6517 digital electrometer in a coplanar configuration with silver electrodes (at an internal width of 2-3 mm and length 6-8 mm) evaporated onto substrate before the deposition of the polymeric films. The measurements were performed by applying static electrical fields of low intensity ($E < 10^2$ V/cm). It was experimentally established that, under these conditions non-ohmic effects were not noticed in investigated electrode/polymeric film/electrode systems.

The transmission spectra of thin film samples were recorded in the 350-700 nm range using an UV-VIS M-40 (Carl Zeiss) spectrophotometer, in order to compare the *in film* characteristic energies with *in solution* polymer behaviour.

3. Results

Following standard Yamamoto reaction conditions copolymer with molecular weight M_n = 27 016 g/mol, M_w = 61 650 g/mol and polydispersity index, PDI = 2.28 was obtained.

^{13}C-NMR (CDCl$_3$, δ ppm) spectrum (Fig. 1) indicates the characteristic peaks: the aromatic region of the ^{13}C-NMR (119.2; 120.1; 123.1; 126.8: 127.1; 127.4; 133.4; 141.1; 151.5;152), aliphatic 14.4; 22.9; 24.1; 31.8; 33.9; 44.6; 55.4), 60 for -O-CH$_2$ from crown ether and 173.8 for carboxylate group.

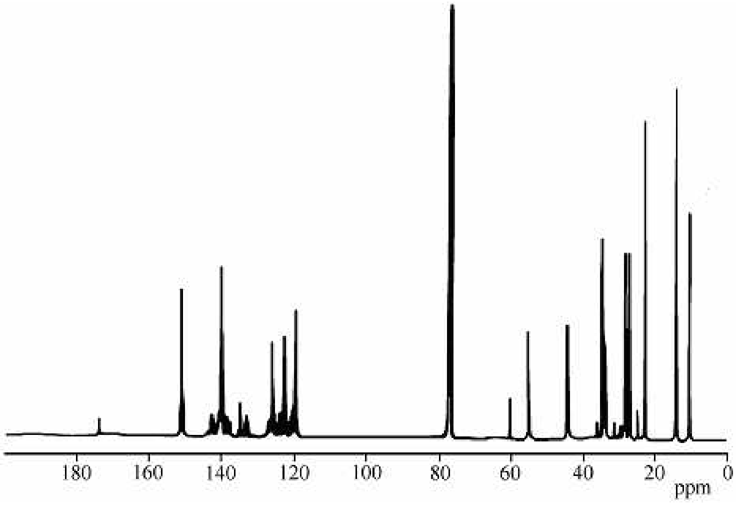

Fig. 1. ^{13}C-NMR (CDCl$_3$, δ ppm) of poly[9,9-bis (2-ethylhexyl)-fluorene-co-9-ethylcapronate-fluorene-2,7 diyl] with pseudo-rotaxane architecture.

The side-chain polypseudorotaxanes were purified by multiple reprecipitations in good solvents for the crown ether. The copolymer without pseudo-rotaxane architecture has not signal at 60 ppm for $-O-CH_2$.

In order to obtain the ionic copolymer, the saponification reaction PFD was performed, in heterogeneous system, in the presence of $LiOH:H_2O$ (Fig. 2). A red-yellow solid resulted in 81.7% yield. This saponified copolymer has a good solubility in chloroform and thetra hidrxi furane.

Elemental analysis: Calculated (%) for 0.78(C29H40)+0.22(C19H17O2Li)=365.098 g x mol^{-1} C: 86.74; H: 9.56; O: 2.51, Li: 0.415. Found: C: 84.06; H: 9.50; O: 2.425; Li: 0.393.

Li calculated for 1 mol of saponified copolymer (%) = 0.415. Found: 0.393. Yield of saponification reaction = 94.7%.

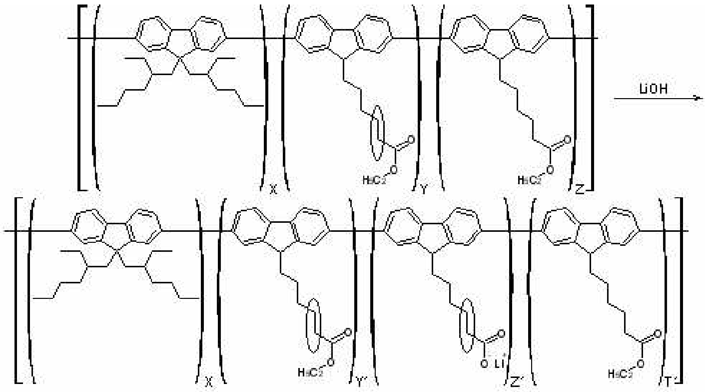

Fig. 2. Global saponification reaction of PFD.

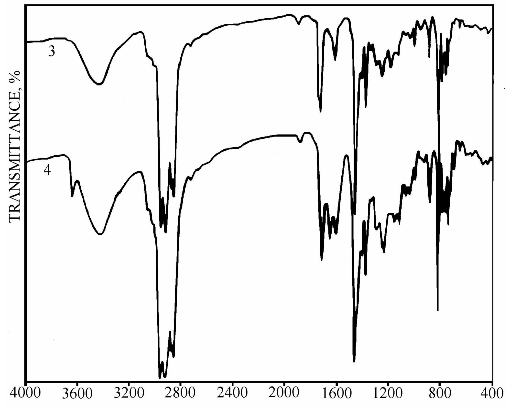

Fig. 3. IR spectra of dimmer precursor (curve 3), and PDF (curve 4).

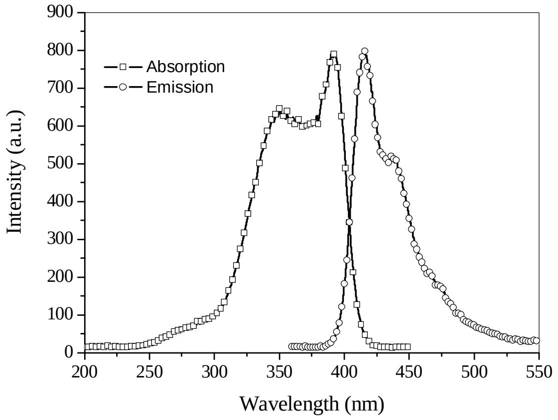

Fig. 4. PFD in solution UV-VIS absorption and fluorescence spectra.

The primary structure of PFD determined bu NMR spectrum was confirmed by IR spectrum (Fig. 3).

Fluorescence spectra are presented in Fig. 4; excitation scan (UV_VIS absorption spectrum) - profile of excitation wavelengths which produce emission at 416 nm fixed wavelength and emission scan (fluorescence spectrum) - profile of emitted wavelengths produced by 391 nm fixed excitation wavelength.

The activation energy of electrical conduction was determined by studying the temperature dependence of electrical resistance of the polymer in thin film.

It was experimentally established that samples with stable structure, can be obtained by subjecting them, after preparation, to a heat treatment consisting of several successive heating/cooling cycles within a certain temperature range, *ΔT*, characteristic for each polymer.

It can be observed that after the heat treatment, the temperature dependence of the electrical conductivity becomes reversible (Fig. 5). This fact shows that the sample structure becomes stable in the respective temperature range.

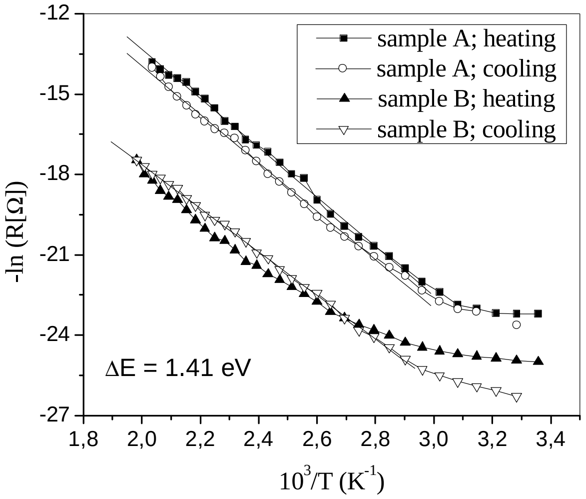

Fig. 5. PFD film electrical resistance vs. reciprocal temperature.

The dependence on the photon energy, obtained from thin film UV-VIS transmission spectrum, is shown in Fig. 6.

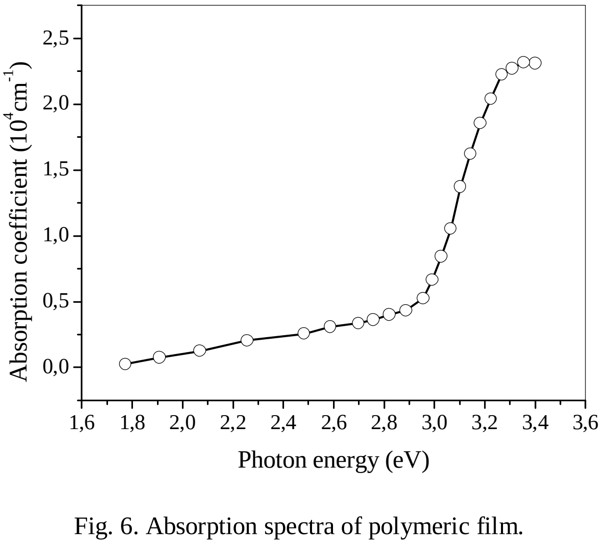

Fig. 6. Absorption spectra of polymeric film.

4. Discussion

The IR (KBr) spectrum of the dimmer precursor (Fig. 3 curve 3) shows the ester carbonyl absorption at 1721.996 cm^{-1} and the stretching vibration for C-O-C at 1249 cm^{-1}. The aliphatic rest can be identified in the range 2855-2923 cm^{-1} while the characteristic absorption of the aromatic group is present at 814, 1610 and 3027 cm^{-1}. The IR (KBr) spectrum of the saponified polymer (Fig. 3 curve 4) show the absorption bands at 1363.785; 1390.27; 1630.57 and 1657.781cm^{-1} characteristic to the carboxylate ions (COO^-). The stretching vibration for C-O-C at 1249 cm^{-1} is absent. The aliphatic remainder can be identified in the range 2855-2923 cm^{-1} while the characteristic absorption of the aromatic part is present at 814, 1605 and 3023 cm^{-1}, that are in good concordance with NMR spectrum.

The UV-VIS absorption spectrum from Fig. 5 reveals the two chromophores bands structure of the PFD. The transitions responsible for the two absorption bands are intense π-π^* transitions at 391 nm long wavelength, due to π electrons in the carbon-carbon and carbon-oxygen double bonds and a lower n-π^* transitions at 350 nm due to carbonyl's oxygen's lone pair electron n-π^*. The polymer exhibit fluorescence at λ_{max}=391 nm with maximum quantum efficiency. Note that the fluorescence spectrum is approximately a mirror image of the absorption spectrum shifted to longer wavelength. Qualitatively, fluorescence spectrum appears to contain at least two components: a relatively sharp component on 415 nm and a relatively broad feature on the 437 nm, both in the blue domain of the visible spectrum.

In thin film, as predicted by theory, the low dimensional structure of a polyene is unstable and the coupling of electrons and phonons with lattice distortions, leads to a localization of single and double bounds which lifts the degeneracy and results in a localization of π electrons with the opening of a bandgap, E_g, generally larger than 1.50 eV.

The HOMO-LUMO energy gap of a linear conjugated system, ΔE, and the E_g value of the resulting materials are usually determined from the low energy absorption edge of the electronic absorption spectra. Both values can also be determined from solution oxidation and reduction potentials.

From Fig. 5 it can be observed that $\ln R = f(10^3/T)$ dependences cannot be approximated by a single activation energy within investigated temperature range. The $\ln R = f(103/T)$ is characterized by two distinct parts: a part with a larger slope (within the higher temperature range) and a part with a smaller slope (within the lower temperature range). These results are similar to extrinsic and intrinsic temperature ranges observed in inorganic semiconductors.

In previous papers [12-14] related to the electronic transport properties of other polymers, it was shown that the temperature dependence of the electrical conductivity, σ, can be written as

$$\sigma = \sigma_0 \exp(-\Delta E/2kT), \tag{1}$$

where ΔE denotes the thermal activation energy of electrical conduction, σ_0 is a parameter depending on the polymer nature and k is Boltzmann's constant.

The semiconducting properties of the studied polymers are due to their molecular structure, which affords extended conjugation of the electrons in the polymer chain. The activation energy, computed with (1), was found to be 1.41 eV.

The absorption coefficient was calculated from transmission spectra. Its dependence on the photon energy is presented in Fig. 6.

Near the fundamental absorption edge the absorption coefficient, α, can be expressed as [15]:

$$\alpha h\nu = A\left(h\nu - E_g\right)^p, \tag{2}$$

where $h\nu$ denotes the photon energy, A is a characteristic parameter (independent of photon energy), E_g is the energy bandgap and p = ½ or 2 for allowed direct or indirect transitions, respectively. Eq. (2) shows that $(\alpha h\nu)^{1/p}$ linearly depends on the photon energy $h\nu$.

Therefore, by extrapolating the linear portions of $(\alpha h\nu)^{1/p} = f(h\nu)$ curves to $(\alpha h\nu)^{1/p} \rightarrow 0$, the values of E_g can be determined.

Correlated with the result from fluorescence spectra it can be considered that a band model with direct transitions describes well the absorption spectra. In this case $p = ½$ and a bandgap energy of 3.1 eV was calculated.

5. Conclusions

A copolymer based on polyfluorene with pseudo-rotaxanes architecture in the side-chain has been obtained.

The decoration of the polyfluorene backbone with pseudo-rotaxane architecture in the side-chain leads to an increased chemical stability, reduced interchain energy transfer and photooxidative stability.

This copolymer has good solubility in organic solvents and can be easily processed into homogeneous transparent films by usual method.

The PFD fluorescence in the blue domain of the visible spectrum makes it a promising candidate for electroluminescent diodes.

The polymer present semiconducting properties with an activation energy of conduction of 1.41 eV that makes it suitable for electronic solid state devices.

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