Materials Science-Poland, Vol. 22, No. 4, 2004

Semiconducting dye-functionalised poled polymers for photovoltaic applications

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In order to build efficient single-layer polymer photovoltaic devices, the realization of an equivalent distributed p-n junction is proposed. Orientation in the initially centrosymmetric material is obtained by ordering polar molecules contained in a polymer matrix with a DC field. The molecular rectification effect induced in an oriented polymer film improves the efficiency of polymeric semiconducting devices like solar cells. The first experiments were conducted with a poly(methylmethacrylate) (PMMA) matrix containing azo-dye compounds (such as the Disperse Red 1, DR1) as the polar molecules, grafted onto the chains of the polymer backbones. Although this material allows for high orientation efficiencies, it is not adapted for photovoltaic applications, since DR1-MMA has very poor semiconducting properties due to the dielectric nature of PMMA. Organic semiconductors are uncommon and it is difficult to find an appropriate polymer system. We present preliminary results obtained for two intrinsically semiconducting and dye-functionalised polymer systems which may be found applicable in the fabrication of organic photovoltaic solar cells using the concept of polar molecular ordering. We use polymer systems with a covalent bond between the dye molecule and conjugated backbone to obtain a high dye content and to avoid phase separation problems. To achieve the largest stable molecular polar orientation possible and to optimise the electric field stored in an oriented structure, we studied the orientation parameters of samples, i.e., the orientation field, temperature, poling duration, and cooling conditions.

Key words: *organic semiconductors; polymer semiconducting film; molecular diode; organic photovoltaic cell*

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1. Introduction

Semiconducting polymers are receiving growing attention in view of the fabrication of flexible and low-cost organic photovoltaic cells, with standard coating and printing processes taking advantage of their easy processability [1, 2]. In order to create efficient solar cells, building a rectifying junction is mandatory. The structure leads to the existence of an internal field allowing a charge separation after exciton generation [3]. Such a junction can be of the Schottky-type, between an organic semiconductor and a metal, or it can be a p-n junction, between p- and n-type organic semiconductors. p-n type junctions, in which the metal to polymer contacts are ohmic, turn out to be the most efficient in the realization of optoelectronic devices. They also permit to avoid degradation problems, characteristic of the Schottky junctions and resulting from electrochemical potential differences at the rectifying contacts that induce the diffusion of the electrode material into a polymer film. This is corrected in p-n junctions by the ohmic nature of their metal-polymer contacts. The realization of a standard p-n junction requires the use of two polymer layers bearing wet-processing compatibility. Moreover, n-type organic semiconductors are less common than p-type ones, due to their lower stability under oxygen in consequence of their reductive behaviour. A further limitation of this approach concerns a weak extension of the depletion zone (between 10 nm and 50 nm), where the majority of the exciton dissociation occurs. This limits the maximum thickness of the devices, making it very difficult to efficiently harvest the visible light.

To increase the efficiency of a photovoltaic polymeric device, we propose an alternative to the classical p-n junction: induction of an internal field over the whole thickness of a photovoltaic layer through orientation of polar molecules, obtained by the application of a static electric field. Oriented molecules (push-pull type) induce a rectifying effect, behaving as a distributed homojunction in an initially centrosymmetric material [4]. The junction is distributed throughout the entire thickness of the device. All photogenerated excitons are likely to find a junction and split before recombination, thus avoiding recombination channels (radiative and non-radiative).

It has also been demonstrated that molecular-induced orientation in a polymer device increases the charge mobility in the material [5] and that the barrier height between the electrode material and the polymer decreases with growing polar order [6]. The improvement of the efficiency of photovoltaic cells based on a polymeric single layer bearing oriented polar chromophores has also been clearly evidenced [5]. In fact, it is known that the photogenerated excited states in organic molecules, termed excitons, which are exploited in organic photovoltaic devices, split themselves into electrons and holes in presence of strong electric fields, such as those provided by physical interfaces between different materials. In view of this, it is interesting to investigate if the proposed poling method, which is capable of providing molecularly distributed homojunctions, may be of help in enhancing the photovoltaic performance of organic solar cells when applied to the appropriate polymer systems. Organic solar cells are seriously affected by the recombination of relatively long-living excitons.

A polymer fulfilling the basic requirements for application in oriented photovoltaic solar cells should possess the following characteristics:

- It should be intrinsically semiconducting and produced with high purity and low defect concentration, in order to prevent trapping, and possess ordered regions in the 100 nm scale to guarantee efficient transport channels of charges.
- It should be grafted with dye molecules possessing high dipolar moments; moreover, these molecules should have good photochemical stability.
- It should possess a high T_g (typically higher than 80 °C). Another solution would be a crosslinkable system, in order to ensure a higher stability of the induced molecular polar order. Indeed, crosslinkable polymers permit the polar molecular orientation to be frozen by the induction of covalent bonds between the chromophore and conjugated backbone after the orientation process.
- It should be easily soluble in common organic solvents, to permit an easy fabrication of thin films of good optical quality and low roughness, avoiding short circuits during electrode deposition. If the surface of a polymer layer is not smooth, the surface of an evaporated electrode will consequently be rough. A rough polymer surface means that there are zones where the thickness of the film is lower than in neighbouring ones. These low-thickness zones may be destroyed during electrode evaporation, which results in short circuits.

Further, as the molecular polar orientation is directly related to the number of oriented molecules, it will also be necessary to optimise the grafting ratio of the polymer matrix in order to obtain the optimal molecular concentration, at which the dipolar interactions (intermolecular interactions) do not hinder the orientation of molecules; typically, a 30% molar concentration in chromophores is chosen. Additionally, its synthesis must exhibit high yields, in order to test the reproducibility of the results in the long term. Furthermore, grafted dye polar molecules should possess very little or no photoinduced molecular movements. This avoids any disorientation following illumination with solar light. The polymer systems described above are uncommon and till now few materials have been investigated in view of their potential applications in ordered photovoltaic devices [5].

In this work, we report the results for two polymer systems grafted with the Disperse Red 1 (DR1) molecules that are intrinsically semiconducting. The optimisation procedure of the induced molecular orientation is presented in view of the potential application of the studied polymers in the fabrication of photovoltaic organic solar cells.

2. Experimental

In previous studies, the DR1-MMA copolymer system has been used [4]. The PMMA polymer matrix is optically inactive and transparent in the visible and near-infrared ranges. DR1-MMA was tested, as the orientation process is very effective in this material. PMMA is not appropriate for photovoltaic applications due to its poor semiconducting properties (very weak currents, in the range of several nA/cm^2). In order to optimise the polymer system and to obtain a maximal photovoltaic device efficiency, we performed preliminary studies on two intrinsically semiconducting polymers grafted with dye polar molecules, namely poly(1-methoxy-4-(*O*-disperse red 1))-2,5-phenylenevinylene) and (poly((3-hexyl)-co-(3-(2-(4-(4’-Nitrophenyl-azo)phenoxy)-ethyl))thiophene. Polar molecular order is induced in the studied materials through the electric field poling method (Corona poling).

We have identified two polymer materials that may be employed in the preparation of plastic photovoltaic devices. The first is the commercially available poly-(1-methoxy-4-(*O*-disperse red 1))-2,5-phenylenevinylene) (DR1-PPV), purchased from Aldrich and tested without any additional purification procedure. Disperse Red 1 (4-(N-(2-hydroxyethyl)-N-ethyl)-amino-4'-nitroazobenzene, or DR1 (with the dipole moment of 7 D), grafted to a polyphenylenevinylene (PPV) matrix, was used as the active polar molecule. DR1-PPV, shown in Fig. 1, is grafted at a 100% molar ratio. Its glass transition temperature T_g, measured by Differential Scanning Calorimetry (Mettler DSC 20 TC 11), was found to be 65 °C. A solution of DR1-PPV in 1,1,2-trichloroethane (15 g/1 l) was first filtered through 0.45 μm and then 0.2 μm PTFE Teflon Millipore filters in order to remove any insoluble parts of the polymer. The solution was then spin-coated onto ITO-coated glass substrates. The thickness of the obtained samples was determined with a Dektak profilometer to be about 48 nm (± 2%). The resulting films were baked in an oven at 60 °C for 30 minutes to remove any residual solvent.

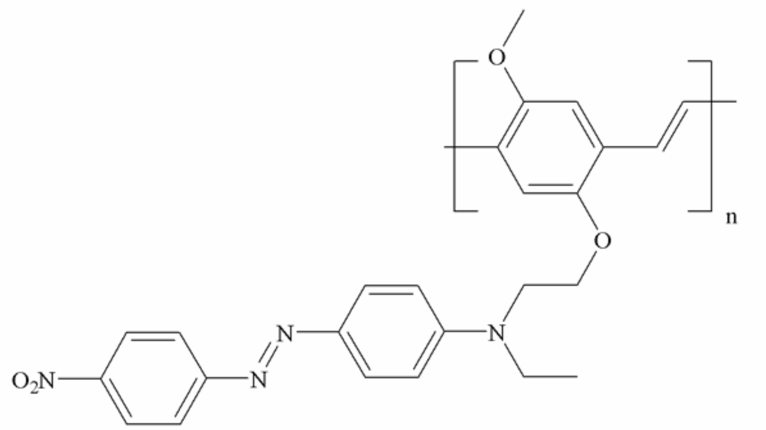

Fig. 1. Chemical structure of poly(1-methoxy-4-(*O*-disperse red 1))-2,5-phenylenevinylene) (DR1-PPV). The polymer matrix is grafted at 100% with the chromophore molecule

The thin films of DR1-PPV were oriented without an upper semitransparent metal electrode. The polymer thin films were oriented under 10 kV (positive charge) for 10 minutes at 60 °C, after which the samples were cooled down to room temperature with the tension still applied in order to freeze the molecular order.

The second polymer system was an azo dye-substituted, solution-processable polythiophene, namely poly((3-hexyl)-co-(3-(2-(4-(4′-Nitrophenyl-azo)phenoxy)ethyl))-thiophene, or PEAHT. The synthesis of the polymer and its characteristics are described elsewhere [7, 8]. The structure of the polythiophene-based copolymer, functionalised with NLO-active chromophoric units, is presented in Fig. 2. The molecular weight of the polymer (M_w) was 44 000, as determined by GPC measurement vs. polystyrene standards. The amount of dye incorporated in the copolymer was equal to the 33% molar ratio. This polymer is easily soluble in common organic solvent due to the presence of flexible alkylic side chains.

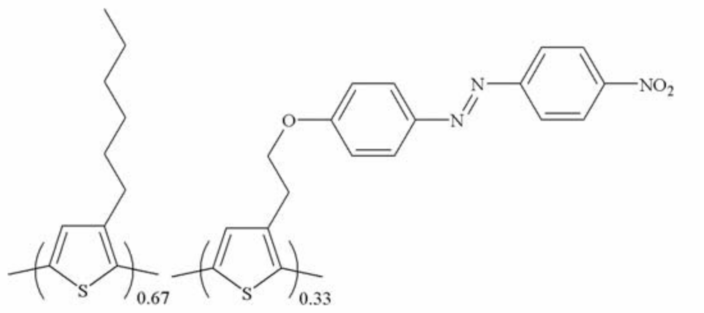

Fig. 2. Chemical structure of the polythiophene copolymer with alkyl side chains, partially functionalised with chromophore groups (PEAHT). The chromophore molar concentration is 33%

T_g of this polymer was estimated to be around 100 °C upon poling evidences, while DSC measurements delivered a value of about 80 °C. This difference may be ascribed to the partial crosslinking occurring during polymer storage (several months), as the tests on this polymer were not performed directly after its synthesis. For the preparation of the device, 33 mg of the PEAHT were dissolved in 1 ml of chloroform ($CHCl_3$). The solution was then filtered through a 0.45 μm filter and spin-coated onto clean ITO substrates. The film thickness, measured with the Dektak profilometer, was 130 nm. The sample was oriented under 6 kV for 15 minutes at 100 °C by Corona poling, in order to test the orientation.

The spin-coating of thin polymer films onto substrates is usually followed by Al electrode deposition by thermal evaporation in vacuo 10^{-6} Torr (20 nm upper semi-transparent aluminium electrode). The resulting device consists of a polymer layer sandwiched between two electrodes (ITO as a bottom one). The active surface of the device was 28 mm^2. The structure of a typical cell fabricated by this procedure is shown in Fig. 3. In complete devices, the polar order is induced through applying the electric field directly to electrodes. Nevertheless, this requires a very precise control of the metal electrode deposition. In our studies, the Corona poling method was used, as it is much easier to realize than orientation through the electrodes of a cell and permits the procedure of orientation itself to be optimised, and to obtain the most stable polar order and largest internal electric field possible.

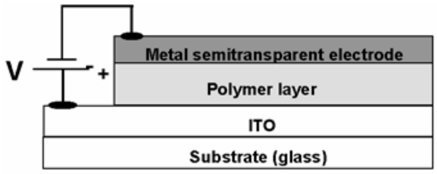

Fig. 3. Side-view of a Schottky type photovoltaic cell sandwich-type structure. The glass substrate is 10 mm thick, the ITO transparent electrode – 150 nm, the organic thin film – around 100 nm, and the semitransparent metal electrode (Al) – 20 nm

Experimentally, the molecular order was controlled using second harmonic generation, as the SH intensity is directly related to the induced dipolar molecules orientation [4]. The samples were always mounted in such a way that the ITO coated glass or glass surface faced directly toward the incident beam. The fundamental IR laser source at 1.064 μm was an actively Q–switched Nd:YAG laser with 25 ps pulses at a 10 Hz repetition rate. The fundamental p-polarized infrared light beam impinged upon the sample at a non-normal incidence angle, passing through the glass substrate and/or the ITO coating and then a polymer layer. The second harmonic signal generated by the sample was detected using a photomultiplier tube (PMT) and integrated by a boxcar. The whole experiment was computer controlled.

3. Results and discussion

The UV-Vis absorption spectra of the studied polymers were taken using a Lambda 19 Perkin-Elmer spectrometer. As can be noticed in Fig. 4 presenting

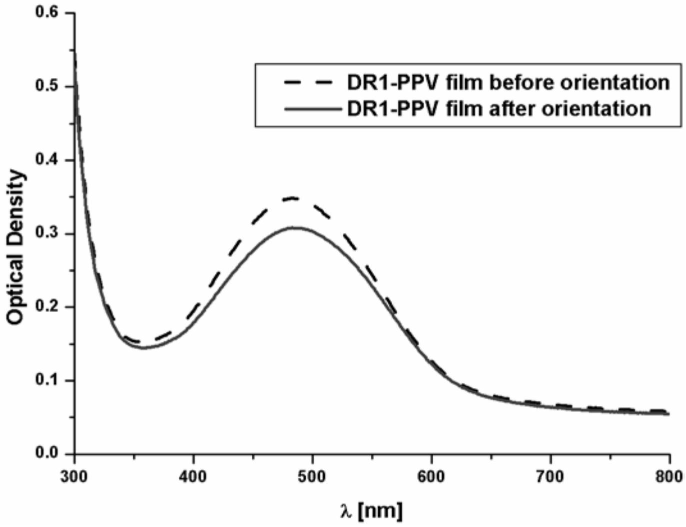

Fig. 4. UV-Vis absorption spectra of the DR1-PPV copolymer before (48 nm thick, dashed line, *OD* at 532 nm equal to 0.28) and after orientation by Corona poling (solid line, *OD* at 532 nm equal to 0.26). The absorption maximum is found at 483 nm (*OD* before and after orientation is 0.35 and 0.30, respectively)

the absorption spectra of DR1-PPV (before and after the polarization process), the optical density decreases after the orientation process. This means that, after the polarization process, a certain number of polar molecules are oriented perpendicular to the polymer surface, making the absorption lower. The maximal orientation degree obtained was 14% (±12%) (calculated as $\Delta OD_{\mathrm{max}}/OD_{\mathrm{max}}$, where ΔOD_{max} is the change in optical density after the polarization process at the absorption maximum and OD_{max} is the optical density at the absorption maximum before orientation). The error of the optical density measurement is equal to 0.02, which is the value obtained from measuring the reference calibrated filters. The orientation degree obtained also seems to be rather low when compared to the value of 30% normally reached by grafted polymers. Due to a grafting ratio of 100%, however, there are problems of steric congestion and the movements of molecules may be hindered by the movements of others.

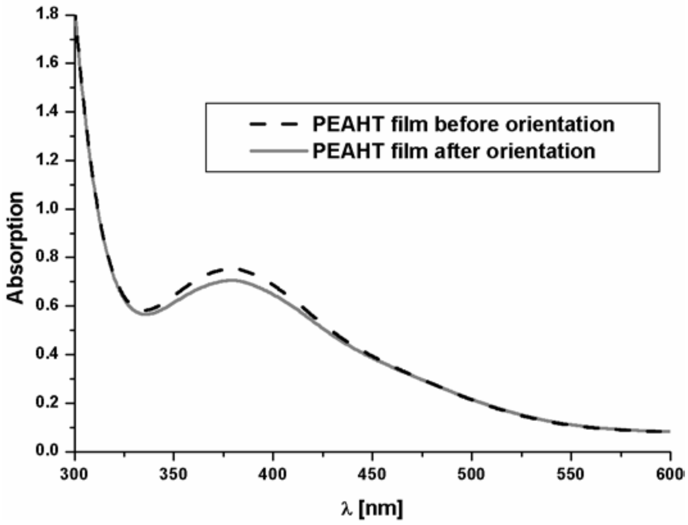

Fig. 5. UV-Vis absorption spectra of the PEAHT polymer film (130 nm thick) (dashed line, *OD* at absorption maximum at 380 nm equal to 0.75) and after orientation by Corona poling (solid line, *OD* at 380 nm equal to 0.70). The optical density at 532 nm almost does not change during the polarization process (*OD* before and after orientation is 0.138 and 0.135, respectively)

The absorption spectra of spin-coated thin films of PEAHT are given in Fig. 5 (before and after orientation, and on glass substrates). The degree of orientation obtained was 7% (±5%). The absorption maximum of the PEAHT polymer was found at 380 nm (*OD* was 0.92), which is typical of the π-π^* transition of the azobenzene moiety in the *trans* isomeric form; the broad band found around 450 nm corresponds to the overlapping of the π-π^* transition of the conjugated polythiophene backbone and the weaker n-π^* transition of the azobenzene group [8]. The error of the optical density measurement was 0.02.

Polythiophenes are very attractive materials in the class of intrinsically semiconducting polymers, because of their good thermal and chemical stability and ease of functionalisation with various chromophores, thus permitting their physical and electronic properties to be engineered [9]. The low ordering degree obtained for this polymer, however, may be attributed to a probable crosslinking of the polymer, which renders it more rigid with respect to non-crosslinked ones, and hence less prone to the poling process.

Second harmonic generation studies were performed for all oriented samples. These measurements are necessary as they permit the exact value of the SH generated signal to be calculated, which is in turn needed to determine the value of the internal field stored in an oriented structure. Moreover, this technique allows for the optimisation of the orientation process itself (the electric voltage applied, the temperature, the poling duration, the cooling conditions, etc.).

SHG in DR1-PPV on ITO and in PEAHT on glass substrates was measured in order to estimate their potential application in photovoltaic organic solar cells. The thermal and photostimulated relaxation of polar orientation was registered. By photostimulated relaxation we understand that an intense monochromatic light induces much faster relaxation than a moderate heating [10]. In both cases, the decay of the SH signal was tested until it disappeared completely due to continuous illumination with an infrared beam and thermal diffusion.

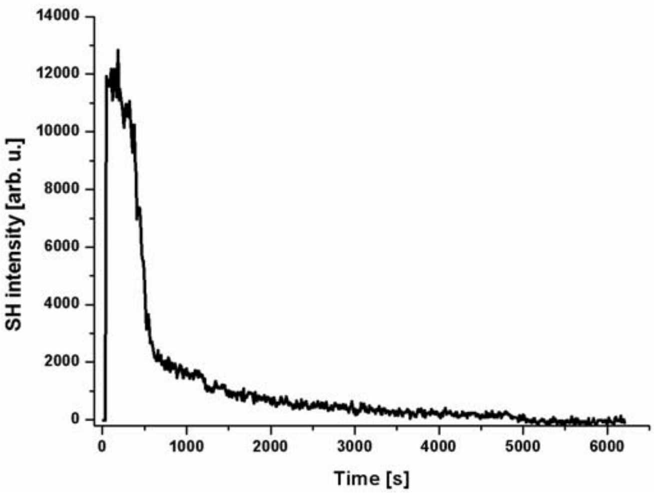

Fig. 6. A study of the temporal decrease of the SH signal generated by DR1-PPV on a glass substrate, oriented by Corona poling. The sample is heated up to 60 °C, starting at ambient temperature with a heating rate of 10 °C/minute. The SH signal decays as the molecular polar order disappears due to thermal diffusion. At the beginning of the measurement, a “zero” level signal is registered, for which there is no sample placed on the heating plate

In Figure 6, we present the decay of the SH signal generated by DR1-PPV. The sample, oriented by Corona poling (10 kV applied for 15 minutes at 60 °C), was cooled to room temperature and then heated up to 60 °C (a heating rate of 10 °C/min) and kept at this temperature. The decay of the SH signal with temperature indicates that the observed decrease in optical density in the absorption spectrum after orientation is due to the molecular ordering induced in the sample.

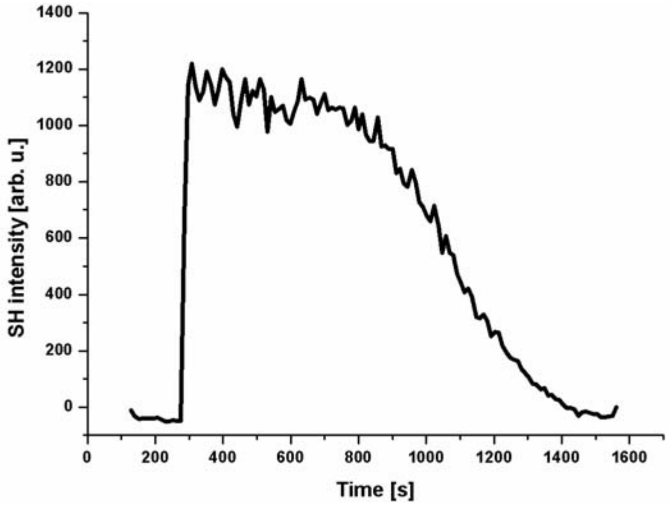

Fig. 7. The decay of the SH signal generated by PEAHT on a glass substrate, oriented by Corona poling. The sample is heated up to 100 °C, starting at ambient temperature with a heating rate of 2.6 °C/minute. The SH signal decreases as the molecular polar order disappears due to thermal diffusion. The “zero” level signal corresponds to no sample on the heating plate

In Figure 7, the decrease of the SH signal generated by PEAHT, heated up to T_g with a heating rate of 2.6 °C/minute and starting from ambient temperature, is shown, after Corona poling (a voltage of + 6 kV applied for 15 minutes at 100°C).

Thermally induced disorientation is at the origin of the decrease in the SH signal for both polymer systems, which permits the conclusion that both materials at least do not deteriorate chemically in a strong electric field. Although the errors of the calculated orientation degrees induced after Corona poling are quite high (several percent), the studies of the decay of the SH signal with temperature prove that the observed decrease in optical density after orientation is due to molecular ordering. Studies of this material are now under way in order to optimise the orientation parameters (the applied temperature and electric field, orientation duration, and cooling conditions), to optimise the internal field stored in the structure, and to realize organic photovoltaic devices.

4. Conclusions

In this paper, we have presented preliminary results of studies on the effects of Corona poling on dipolar dyes covalently attached as side chain substituents to two different conjugated polymers. An evidence for successful poling have been found for both considered polymers, although more work is required for a quantitative evaluation of the poling effectiveness.

Although preliminary, these results are very interesting in view of the potential applications of dye-substituted polymers in the realization of oriented single layer organic photovoltaic solar cells, since they indicate that it could be possible to realize devices that have a large electric field stored in the cell. This would in turn be an advantage in creating local strong electric fields, paving the way for fast exciton splitting on an intramolecular basis.

As an outlook, the main goal now is to optimise the polymeric material itself (i.e. the grafting ratio and glass transition temperature, solubility and processability, etc.) and the device construction conditions (poling conditions, photovoltaic cell structure, electrode choice and evaporation, etc).

Another optimisation process will concern the orientation method itself. Indeed, in semiconducting polymers, charge injection may occur during electric field poling, which reduces the efficiency of the whole process. Moreover, thin polymer films tend to degrade in strong electric fields. Different orientation techniques are therefore being optimised: optically assisted and all-optical polarization methods. The orientation degree attained by all-optical poling should be close to that obtained by Corona poling, since the efficiency of orientation by all-optical poling is the same as that of electric field poling [10].

We believe that the intrinsically semiconducting DR1-PPV and PEAHT polymer systems presented here are good candidates for potential photovoltaic applications.

References

[1] BURROUGHES J.H., BRADLEY D.D.C., BROWN A.R., MARKS R.N., MACKAY K., FRIEND R.H., BURN P.L., HOLMES A.B., Nature, 347 (1990), 539.

[2] GUSTAFSSON G., CAO Y., TREACY G.M., KLAVETTER F., COLANERI N., HEEGER A.J., Nature, 357 (1992), 477.

[3] BRABEC C.J., SARICIFTCI N.S., HUMMELEN J.C., Adv. Funct. Mater., 11 (2001), 1526; HOPPE H., SARICIFTCI N.S., J. Mater. Res., 19 (2004), 1924.

[4] SENTEIN C., FIORINI C., LORIN A., NUNZI J.-M., Adv. Mat., 9 (1997), 809.

[5] SENTEIN C., FIORINI C., LORIN A., NUNZI J.-M., RAIMOND P., SICOT L., Synth. Metals, 102 (1999), 989.

[6] SENTEIN C., FIORINI C., LORIN A., SICOT L., NUNZI J.-M., Optical Materials 9 (1998), 316.

[7] DELLA-CASA C., FRALEONI A., COSTA-BIZZARRI P., LANZI M., Synth. Metals, 124 (2001), 467.

[8] DELLA-CASA C., FRALEONI A., COSTA-BIZZARRI P., LANZI M., PAGANIN L., Macromol. Symp., 180 (2002), 217.

[9] PADINGER F., RITTBERGER R., SARICIFTCI N.S., Adv. Funct. Mat., 13 (2003), 1.

[10] FIORINI C., CHARRA F., NUNZI J.–M., RAIMOND P., J. Opt. Soc. Am. B, 14 (1997), 1984.

Received 20 October 2004
Revised 3 November 2004