Available online at www.sciencedirect.com

SCIENCE DIRECT®

polymer

Polymer 46 (2005) 9803–9809

www.elsevier.com/locate/polymer

Synthesis and photophysical properties of a charm-bracelet type C_{60}-grafted PPV derivative

Yu Chen[a,b,*], Tatsuro Midorikawa[b], Jinrui Bai[a], Yin Liu[a], Yasuyuki Araki[b], Osamu Ito[b,*]

[a] *Lab for Advanced Materials, Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China*

[b] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, CREST, JST, Katahira 2-1-1, Sendai 980-8577, Japan*

Received 15 May 2005; received in revised form 24 July 2005; accepted 28 July 2005
Available online 15 August 2005

Abstract

Synthesis and photophysical properties of a new soluble C_{60}-grafted PPV polymer have been described. Fluorescence quenching of the PPV moiety in C_{60}-grafted PPV polymer was observed, suggesting the energy- and/or electron transfer within the polymer. The fluorescence decay profiles at around 500 nm of this polymer both in chloroform and benzonitrile display a single exponential decay giving the fluorescence lifetimes of 1.10–1.27 ns, which are slightly shorter than that of PPV (about 1.50 ns). The nanosecond transient absorption band of C_{60}-grafted PPV polymer was observed at 740 nm corresponded to the excited triplet state of C_{60}, which decreased in benzonitrile, indicating the existence of the extra decay path of the singlet excited state of the C_{60} other than intersystem crossing. Upon heating this polymer exhibits typical semilunar liquid crystalline texture, being closely associated with its polymeric structure with long solubilizing alkoxy side chains.

Keywords: PPV; C_{60}-grafted PPV; Synthesis

1. Introduction

Since the discovery of the first conducting polymer 'polyacetylene' in 1977 [1], conjugated conducting polymeric materials have continuously surprised in the scientific community with their outstanding optoelectronic properties over the past 25 years, and have been found in many applications e.g. photovoltaic cells, polymer light-emitting diodes (PLEDs), biosensors, lasers, transparent antistatic coatings, conducting photoresists and others [2]. Conjugated polymers are particularly versatile because their physical properties (color, emission efficiency) can be fine-tuned by manipulation of their chemical structures [3]. As one of the most investigated conjugated polymers, poly(1,4-phenylene vinylene) [PPV], a bright yellow fluorescent polymer, and its soluble derivatives, e.g. poly[(2,5-dialkoxy-1,4-phenylene)vinylene]s have received much attention [4]. The first electroluminescence from PPV, which exhibits two maximum emission peaks at 520 and 551 nm in the yellow–green region of the visible spectrum, was observed by Burroughes et al. when they incorporated PPV into a simple light-emitting diode structure in 1990 [5]. The introduction of the long solubilizing alkoxy side chain such as 2-methylpentyloxy, 3,7-dimethyloctyloxy, dodecyloxy and 2-ethylhexyloxy onto the backbone of PPV polymer results in the great enhancement of the solubility in various organic solvents, the red-shift of the emission maximum, and the improvement of the polymers's fluorescence and electroluminescence quantum yields as well [4]. With the increase of the size of the alkoxy group, electroluminescence efficiency passes through a maximum and decrease again with even larger side chains [4a]. The similar phenomena were also observed in the poly[(2,5-dialkoxy-1,4-phenylene)vinylene]s-based photovoltaic cells. The photocurrent is remarkably reduced for films

---

* Corresponding authors. Address: Lab for Advanced Materials, Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China. Tel.: +86 21 642 37260; fax: +86 21 642 52485.

E-mail addresses: chentangyu@yahoo.com (Y. Chen), ito@tagen.tohoku.ac.jp (O. Ito).

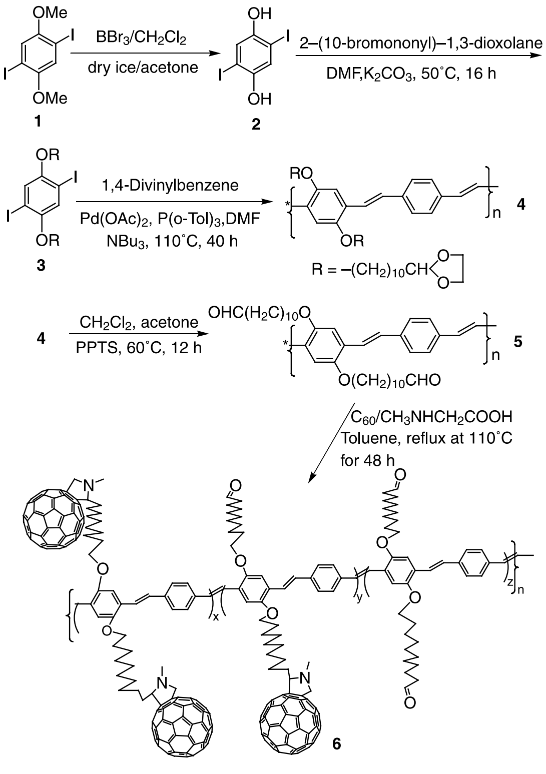
0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.07.087

with longer alkyl or alkyloxy chain lengths [6]. For the PPV-based solar cells, the most studied dialkoxy-substituted PPV polymers such as poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene) [MDMO–PPV], and poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) [MEH–PPV] have been generally used in the construction of so-called plastic solar cells [7], which offer great technological potential as a renewable, alternative source for electrical energy. More than 2.5% solar power (or energy) conversion efficiency of a photovoltaic cell with configuration 'ITO/PEDOT:PSS/MDMO-PPV:PCBM/LiF/Al' (PEDOT:poly(ethylenedioxythiophene); PSS:poly(styrene sulfonic acid); PCBM:[6,6]-phenyl-C_{61}-butyric acid methylester) has been achieved under AM1.5 illumination from a solar simulator [8]. In such a device, the active layer is a composite film of a conjugated donor polymer and a fullerene derivative as an electron acceptor. After photoexcitation of composite film an efficient charge separation occurs in a similar way to that in polar solvent, in which intermolecular electron transfer takes place via the excited triplet state of C_{60} [9]. A large number of research results have demonstrated that a phase-segregated bicontinuous network is required for efficient transport of the positive charge carriers through the donor phase and of electrons via the acceptor phase to the electrodes [10]. In order to achieve the desired nanoscopic biocontinuous networks, Ramos et al. report the synthesis of the first processable π-conjugated hybrid polymer of poly(*p*-phenylene vinylene) [PPV] and poly(*p*-phenylene ethynylene) [PPE] with pendant methanofullerenes through a palladium-catalyzed cross-coupling reaction of diiodobenzene, carrying a pendant methanofullerene, and oligo(*p*-phenylene vinylene), end-capped with two reactive ethynylenes, under inert conditions in 1,2-dichlorobenzene/triethylamine (7:3/v/v) [10]. This polymer exhibits a photo-induced electron-transfer reaction and has been used as the active layer of a photovoltaic cell. The results indicate that a bicontinuous network of donor and acceptors, confined to a molecular scale, is an attractive approach to new materials for photovoltaic applications. In this contribution, we report the synthesis and photophysical properties of a new charm-bracelet type [60]fullerene containing PPV derivative for potential light-harvesting application, as shown in Scheme 1. Monomer **3**, polymers **4** and **5** are synthesized according to the literature procedures [11].

2. Experimental

2.1. General

All chemicals were purchased from Aldrich and used without further purification. Organic solvents were purified, dried and distilled under dry nitrogen. The operations for synthesis prior to the termination reaction were carried out under purified argon. UV/vis absorption spectra of polymers **5** and **6** were measured on a JASCO V-530 UV/vis spectrophotometer in dilute anhydrous chloroform. The sample for the fluorescence measurement was dissolved in the dry chloroform, filtered, transferred to a long quartz cell, and then capped and bubbled with high pure argon (without O_2 and moisture) for at least 15 min before measurement. Similarly, the fresh argon-saturated solution of the sample was used to record the nanosecond transient absorption spectra at different time. The ^1H NMR spectra were performed with a LAMBDA 400 MHz spectrometer in $CDCl_3$ solvent. Gel permeation chromatography (GPC) trace of the resultant polymer was recorded on a LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd). THF was used as the eluent, and linear polystyrene was used as the standard. The texture of polymer was observed with a polarizing microscope (Axiolab Zeiss). Fluorescence spectra and lifetimes were measured by a single-photon counting method using an argon ion laser, a pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3960, FWHM 150 fs) with a pulse selector (Spectra-Physics, 3980), a second harmonic generator (Spectra-Physics, GWU-23PS), and a streakscope (Hamamatsu Photonics, C4334-01). Each sample was excited in deaerated anhydrous toluene with 410 nm laser light. Nanosecond-transient absorption measurements were carried out using a laser photolysis apparatus with a second harmonic generation (SHG, 532 nm) of Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 6 ns FWHM) as an exciting source. For transient absorption spectra in the



Scheme 1.

near-IR region (600–1400 nm), monitoring light from a pulsed Xe-lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834).

*2.2. Synthesis of 2,5-diiodohydroquinone **2***

To a solution of 2,5-dimethoxy-1,4-diodobenzene (6.5 g, 16.67 mmol) in dry dichloromethane (50 ml, distilled over CaH_2 at 40 °C, cooled in dry ice/acetone), was added dropwise BBr_3(25 g, Aldrich product) in dry dichloromethane (20 ml) over 2 h. After that, the reaction mixture was continued to stir for 6 h at the same temperature (−70 °C), followed by the reaction at room temperature overnight, and then poured into ice water. A white precipitate was collected by filtration and recrystallized from THF/hexane. Yield: 97.8%. ^1H NMR ($CDCl_3$): δ/ppm = 7.1 (s, 2H, aromatic protons); 9.72 (s, 2H,-OH); EA: Calcd (%) for $C_6H_4I_2O_2$: C19.91, H1.11, I 70.13; found C20.07, H1.13, I69.70; FD-MS (*m/z*): Calcd: 361.83; found: 361.6 [M^+].

*2.3. Synthesis of C_{60}-PPV polymer **6***

C_{60} (434 mg, 0.6 mmol, 99.95%, Aldrich product code: 572500), sarcosine (164 mg, 0.61 mmol) and polymer **5** (70 mg, $M_n = 1\times10^4$, Pd = 2.1) were refluxed in toluene (400 ml) under argon atmosphere for 48 h. After several minutes, the color of the reaction mixture turned to the deep-green quickly. After reaction for 3 h, the color of the reaction solution changed from deep green to the brown–red. After 48 h, the solvent was removed under higher vacuum. The reaction residue was dissolved in THF, stirred for 24 h at room temperature, filtered to give transparent brown–yellow solution. After removal of THF, to the reaction mixture was added the acidified $MeOH/H_2O$ (v/v 90/10) solution (60 ml, PH = 4–6), stirred for additional 30 min at room temperature. The resultant polymer was extracted from MeOH solution by CH_2Cl_2, dried to give 43.7 mg of brown solid. $M_n = 2.47\times10^4$, $M_w = 1.19\times10^5$, Pd = 4.82; UV/vis (in THF): λ/nm = 253, 260, 326, 425; ^1H NMR (in $CDCl_3$): δ/ppm = 1.2–1.8 (m, $-CH_2-$), 2.1 (s, N–CH_3), 3.4 (s, pyrrolidine-H), 3.7–3.8 (m, $-OCH_2-$), 6.8–6.9 (m, –CH=CH–), 7.4–8.5 (m, aromatic protons on the phenyl ring), 10.3 (s, –CHO).

3. Results and discussion

It is well-known that the C_{60} molecule may be introduced into the main chain of an organic polymer to form a ‘pearl necklace’ polymer, in which the C_{60} unit is part of the polymer chain, or into the side chain of a polymer as a pendant group to form a ‘charm-bracelet’ polymer. In addition, it may be mixed with other polymers to form C_{60}-doped polymers, and it also forms organometallic macromolecules and lattice type polymers [12]. There are several excellent reviews on the polymerization of [60]fullerene, with or without emphasis on materials application in the past 8 years [12,13]. Fullerene-containing conjugated polymers can basically be prepared in three ways: (a) reaction of C_{60} or a C_{60} derivative with a preformed conjugated polymer; (b) electrochemical polymerization of oligothiophene–fullerene dyads, and (c) copolymerization of C_{60}, or C_{60}-containing monomer with a monomer [12–14]. In our experiment, the aldehyde substituted PPV polymer **5** as a synthetic precursor was used to react with C_{60} in the presence of an excess of *N*-methylglycine in refluxing anhydrous toluene to afford C_{60}-grafted PPV polymer **6**. The actual amount of C_{60} incorporated in the polymer is usually much less than that in feed [15]. All known methods are only suitable for quantification of specific types of C_{60} polymers, such as thermogravimetry (TG), UV/vis spectroscopy and gel permeation chromatography (GPC), or give an estimated value of the C_{60} content from the mass ratio of a reacted monomer and C_{60} [15]. Among these methods, thermogravimetric analysis (TGA) should comparably be a reliable method for the determination of the C_{60} content in the fullerenated polymer [16]. The onset of weight loss of pure C_{60} in flowing N_2 at a heating rate of 10 °C min^{-1} is about 600 °C. By assuming that before 600 °C the other residues remaining in the C_{60}-containing polymer have the same wt% as that of the parent polymer as synthetic precursor except undecomposed C_{60} residues, the wt% of C_{60} in the copolymer may be roughly calculated. In this paper, we only roughly calculated the average numbers of C_{60} grafted onto the polymer backbone by comparison of the M_n values of polymers **5** and **6**, which was estimated to be 19. If C_{60} molecules could be completely grafted onto the polymer backbone of **5**, the average C_{60} numbers per polymer chain would reach up to 40. However, this result can not be obtained due to the strong steric hindrance from C_{60} molecules random dispersed onto the polymer backbone. In the case of **6**, such a higher C_{60} content in the polymer would give rise to the more rigid structure with respect to **5**, and the relatively lower solubility of the resultant polymer in the polar solvents, e.g. THF, benzonitrile and others (The pure C_{60} is almost insoluble in the polar solvents in the room temperature). In contrast to **6**, polymer **5** exhibits very high solubility in many common organic solvents.

The ^1H NMR results measured in deuterated chloroform confirm the covalent grafting of C_{60} onto the polymer backbone. The chemical shifts at 6.8–6.9 ppm is ascribed to the vinyl protons; the proton signal of pyrrolidine attached onto the C_{60} cage appears at 3.4 ppm; the proton signals from the unreacted aldehyde group is located at δ/ppm = 10.3 with a down-field shift of 0.5 ppm when compared to the chemical shift (9.8 ppm) of aldehyde groups of polymer **5**. This down-field shift is probably due to the strong electron-withdrawing effect from the C_{60} moieties. The assignment for other proton signals has been given in Section 2.

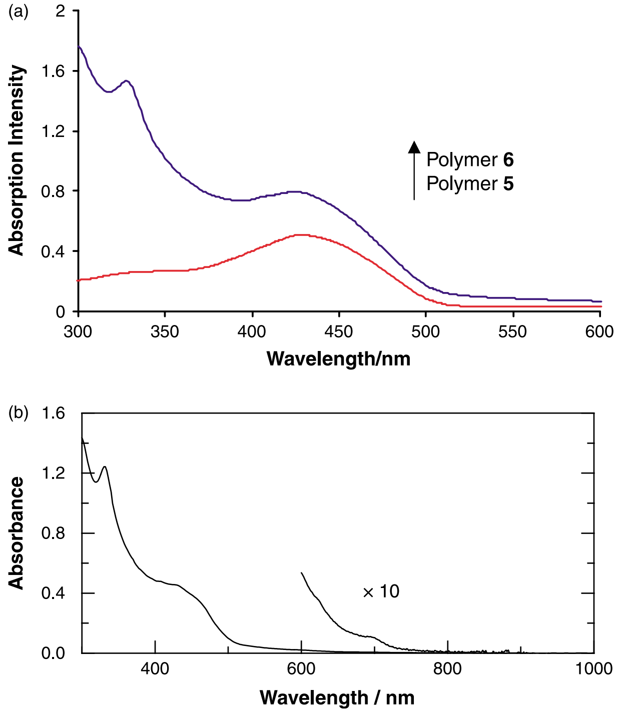


Fig. 1. (a) UV/vis absorption spectra of **5** and **6** in dilute anhydrous chloroform and (b) Magnified spectrum of **6** in the longer wavelength region.

Fig. 1 shows the UV/vis absorption spectra of polymers **5** and **6** in anhydrous chloroform, from which it can be clearly seen that covalently attachment of C_{60} as the end group onto the PPV polymer side chains results in a little bit blue-shift of the absorption peak at 428 nm with respect to **5**, and appearance of new absorption peaks at 326 and 700 nm, which correspond to the [6,6] closed monosubstituted fullerene derivatives. Another weak absorption band at 430 nm typically assigned to the monoaddition of [60]fullerene was hidden in the UV/vis absorption spectrum of PPV.

Excitation of **6** in dry deoxygenated chloroform at 400 nm reveals that, as shown in Fig. 2, the photoluminescence spectrum of **6** shows a maximum emission peak centered at about 504 nm, which is quite similar to that displayed by **5** under the same experimental conditions, implying that the fluorescence of **6** results from the contribution of the PPV moiety. Furthermore, considerably quenching of the fluorescence intensity of **6** was found in comparison with the emission of **5**, suggesting the energy- and/or electron transfer between the excited singlet states of the PPV moiety and the C_{60} moiety in polymer **6**. This finding is also indicative of the covalent linkage of the C_{60} moieties to the polymer backbone in **6**.

The fluorescence decay profile at around 500 nm of **6** in the anhydrous chloroform (Fig. 2(b)), displays a single exponential decay giving the fluorescence lifetime of 1.10 ns, slightly shorter than that of PPV (about 1.5 ns) because of the covalent attachment of C_{60} as electron acceptor onto the polymer side chains. If a more polar benzonitrile was used as the solvent of **6**, a much shorter fluorescence lifetime would be expected for the charge-separation process; however, the measured fluorescence lifetime is found to be 1.27 ns. This suggests that the charge-separation is not always prominent process even in the strong polar solvent. From these lifetimes, the rate (k_q) and quantum yield (Φ_q) of the quenching of PPV by C_{60} were calculated using Eqs. (1) and (2):

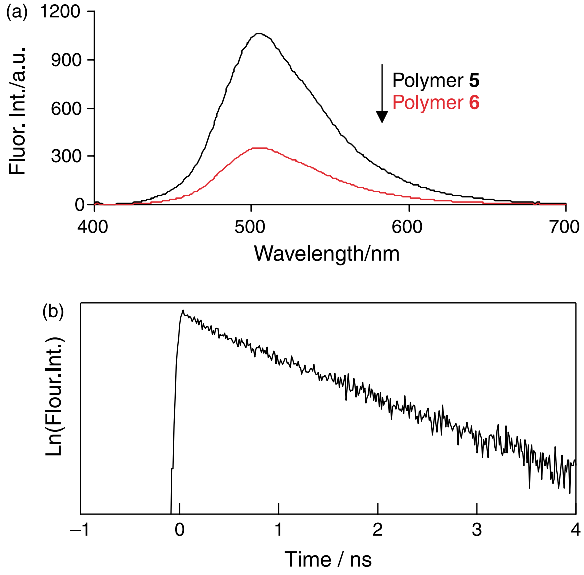


Fig. 2. (a) Photoluminescence spectra of **5** and **6** (0.3 mg/ml for each sample) in anhydrous chloroform ($\lambda_{ex}=400$ nm); and (b) Fluorescence decay profile of **6** at around 500 nm.

$$k_q = (1/\tau_f)_{sample} - (1/\tau_0)_{ref} \quad (1)$$

$$\Phi_q = \frac{[(1/\tau_f)_{sample} - (1/\tau_0)_{ref}]}{(1/\tau)_{sample}} \quad (2)$$

The k_q and Φ_q were evaluated to be in the order of $(1.3–2.4)\times10^8\ s^{-1}$ and 0.17–0.26, respectively. The longer side chains linked between the C_{60} moieties and the PPV backbone render the efficient energy- and/or electron transfer difficult to occur.

The excitation-wavelength dependence of the steady-state fluorescence spectrum of **6** at 504 nm was observed in

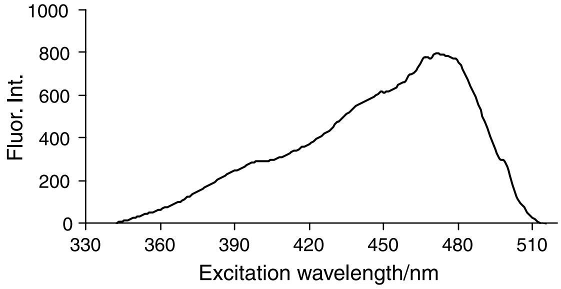


Fig. 3. Excitation spectrum of **6** in anhydrous chloroform (monitor wavelength: 504 nm).

$CHCl_3$ solution (Fig. 3). The maximum peak appeared at 475 nm in the excitation spectrum, which is located at the red edge of the absorption band of **6** in the longer wavelength region. From these observations the lowest excited state of the PPV moiety was evaluated to be 2.50 eV. Although the fluorescence intensity of the C_{60} moiety of **6** at 700 nm was very weak compared to that of PPV at 500 nm, the measurement for the fluorescence lifetime of **6** is still possible. It should be noted, however, that the fluorescence time profile at 700 nm may be strongly influenced by the tail of the strong fluorescence from the PPV moiety. As a result, the lifetime measured at 700 nm (1.18 ns) is comparatively close to that obtained at 500 nm (1.27 ns) in the same solvent.

Excited singlet and triplet properties of the PPV and C_{60} and its organic and polymeric derivatives have been widely investigated by using pico- and nanosecond laser flash photolysis techniques [17,18]. One of the important photophysical properties of pristine C_{60} is almost quantitative triplet generation, giving rise to effective photochemical bimolecular reactions [9,17,18]. Upon the excitation of 532 nm laser light, which excites the C_{60} moieties predominately, the nanosecond transient absorption spectra of polymer **6** in Ar-saturated chloroform were observed, as shown in Fig. 4. On addition of O_2, the rapid decay of the transient absorption band at 740 nm implies that this band can be assigned to the triplet state of C_{60} ($^3C_{60}^*$). Although the transient absorption band attributed to $C_{60}^{\cdot-}$ can not be clearly observed in chloroform solution, the weak absorption in the longer wavelength region comprised between 1000 and 1300 nm may be attributed to the formation of the radical ion pair, $PPV^{\cdot+}$–$C_{60}^{\cdot-}$, with long lifetime.

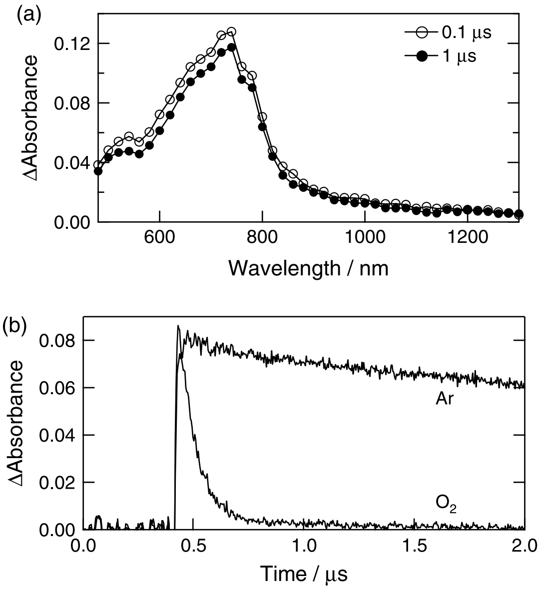


Fig. 4. (a) Nanosecond transient absorption spectrum of **6** (5 mM, in repeat unit) in Ar-saturated anhydrous chloroform; and (b) Decay time profiles at 740 nm in Ar-saturated and O_2-saturated anhydrous chloroform, respectively.

With increasing of the polarity of the solvent, for example, using benzonitrile instead of chloroform, the absorbance of the excited triplet of C_{60} decreases, as shown in Fig. 5. Although this decrease might be in part due to the relatively low solubility of **6** in benzonitrile, the prominent decrease in the absorbance at 740 nm is likely indicative of the increase in the generation of $C_{60}^{\cdot-}$, since strong polar solvent is favorable for the dissociation of the radical ion pair in the excited and ground states.

These photophysical observations can be summarized in the energy-diagram as shown in Fig. 6, in which the excited states were evaluated from the 0–0 transitions. The oxidation (E_{ox}) and reduction potentials (E_{Red}) of PPV and C_{60} are 0.80, −0.60 V vs. SCE, respectively. From these data the energy level of charge-separated state can be evaluated to be 1.4 eV. By the photo-excitation of the PPV moiety, the charge-separation is thermodynamically possible in addition to the energy transfer to C_{60} moiety. The charge-separation via the excited singlet state of the C_{60} moiety is also thermodynamically possible, although this process is competitive with the intersystem crossing, yielding the triplet excited state of the C_{60} moiety as observed in the transient absorption spectra.

Fig. 7 depicts the polarized optical images of **6**. In comparison with optical image took at the room temperature, upon heating this polymer exhibits typical semilunar liquid crystalline texture, being closely associated with its polymeric structure with long solubilizing alkoxy side chains, which keep the conjugated polymer backbones apart from each other. Similarly, the aldehyde-substituted PPV polymer as the synthetic precursor also displays apparent birefringent phenomena after heating at 150 °C for several minutes.

In summary, we synthesized a new soluble C_{60}-grafted PPV polymer. ^{1}H NMR results from polymer **6** confirmed the covalent attachment of C_{60} onto the polymer backbone. The covalent attachment of C_{60} as the end group onto the polymer side chain results in appearance of new absorption peaks at 326 and 700 nm corresponded to the monoaddition of C_{60}. The fluorescence decay profiles at around 500 nm of polymer **6** both in chloroform and benzonitrile suggest that

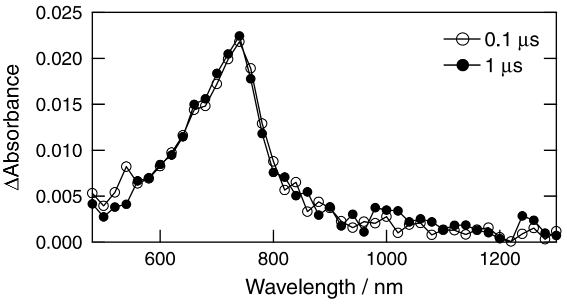


Fig. 5. Nanosecond transient absorption spectrum of **6** (1 mM, in repeat unit) in Ar-saturated anhydrous benzonitrile.

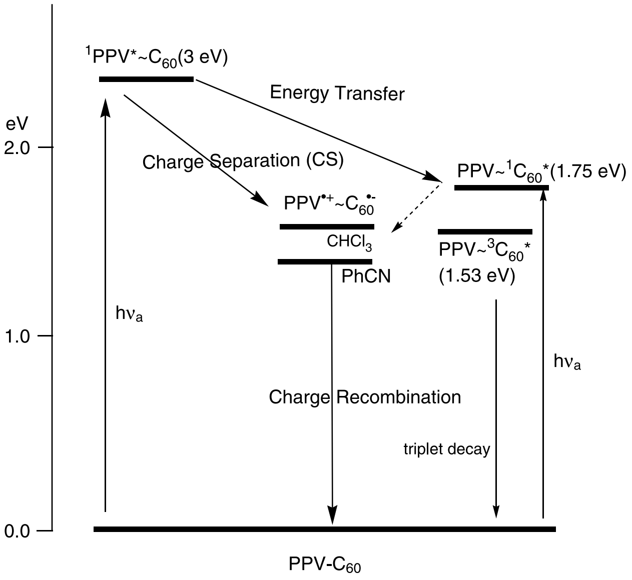


Fig. 6. Energy diagram.

the energy- and/or electron transfer between the excited singlet states of the PPV moiety and the C_{60} moiety take place in polymer **6**. The transient absorption spectra show that the excited triplet state of C_{60} is located at 740 nm with the broad absorption in near-IR region, giving indirect information for the generation of the radical ion-pair. Upon heating polymer **6** exhibits typical semilunar liquid crystalline texture, being closely associated with its polymeric structure with long solubilizing alkoxy side chains. The further studies on the optoelectronic and photonic properties of this polymer are being planned.

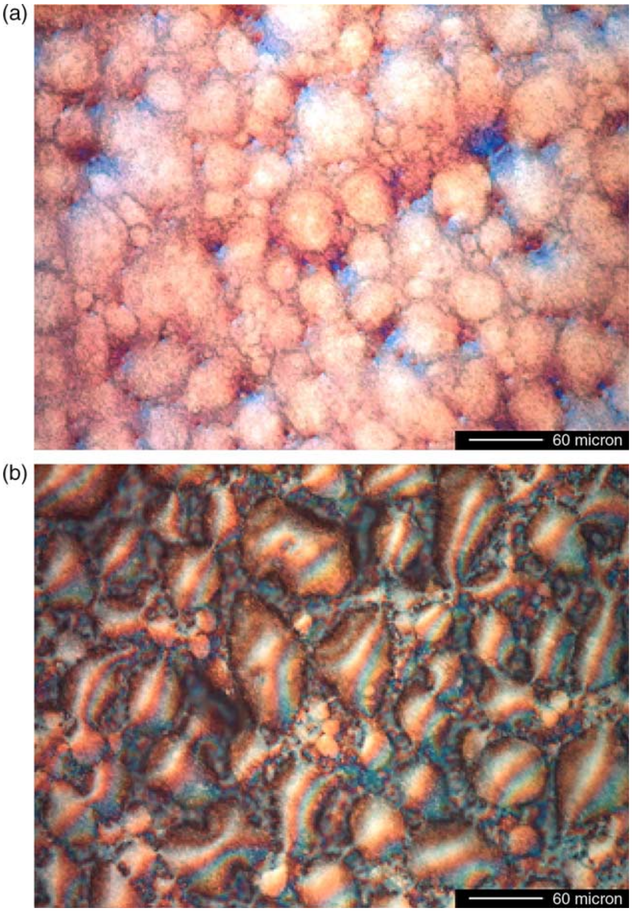


Fig. 7. Polarized optical images of **6** (a) at room temperature and (b) after heating at 150 °C for several minutes.

Acknowledgements

This work was kindly supported by China/Ireland Science and Technology Collaboration Research Foundation, National Natural Science Foundation of China, East China University of Science and Technology, SRF for ROCS, and STCSM (No. 05XD14004), respectively. Y. Chen also thanks the Japan Science and Technology Agency for a fellowship.

References

[1] Shirakawa H, Louis EJ, MacDiarmid AG, Chwan CK, Heeger AJ. Chem Commun 1977;578.
[2] (a) Leclerc M. J Polym Sci, Part A: Polym Chem 2001;39:2867.
  (b) Ego C, Grimsdale UF, Yu G, Srdanov G, Muellen K. Adv Mater 2002;14:809.
  (c) Cravino A, Sariciftci NS. J Mater Chem 2002;12:1931.
  (d) Chen Y, Araki Y, Doyle J, Strevens A, Ito O, Blau WJ. Chem Mater 2005;17:1661.
[3] Kraft A, Grimsdale AC, Holmes AB. Angew Chem Int Ed 1998;37:402.
[4] (a) Doi S, Kuwabara M, Noguchi T, Ohnishi T. Synth Met 1993;57:4174.
  (b) Gustafsson G, Cao Y, Treacy GM, Klavetter F, Colaneri N, Heeger AJ. Nature 1992;357:477.
  (c) Braun D, Staring EGJ, Demandt RCJE, Rikken GLJ, Kessener YARR, Venhuizen AHJ. Synth Met 1994;66:75.
  (d) Barashkov NN, Guerrero DJ, Olivos HJ, Ferraris JP. Synth Met 1995;75:153.
  (e) Egbe DAM, Tillmann H, Birckner E, Klemm E. Macromol Chem Phys 2001;202:2712.
[5] Burroughes JH, Bradley DDC, Brown AR, Marks RN, MacKay K, Friend RH, et al. Nature 1990;347:539.
[6] Takayama K, Kaneko M, Pandey SS, Takashima W, Kaneto K. Synth Met 2001;121:1565.
[7] (a) Padinger F, Fromherz T, Denk P, Brabec CJ, Zettner J, Hierl T, et al. Synth Met 2001;121:1606.
  (b) Hoppe H, Sariciftci NS. J Mater Res 2004;19:1924.
  (c) Winder C, Sariciftci NS. J Mater Chem 2004;14:1077.
  (d) Hal PAV, Wienk MM, Kroon JM, Verhees WJH, Slooff LH, Gennip WJHV, et al. Adv Mater 2003;15:118.
[8] Reidel I, Parisi J, Dyakonov V, Lusten L, Vanderzande D, Hummelen JC. Adv Funct Mater 2004;14:38.
[9] Onodera H, Araki Y, Fujitsuka M, Onodera S, Ito O, Bai F. J Phys Chem A 2001;105:7341.
[10] Ramos AM, Rispens MT, Duren JKJV, Hummelen JC, Janssen RAJ. J Am Chem Soc 2001;123:6714.
[11] Chan EWL, Lee DC, Ng MK, Wu G, Lee KYC, Yu L. J Am Chem Soc 2002;124:12238.
[12] Chen Y, Huang ZE, Cai RF, Yu BC. Eur Polym J 1998;34:137.

[13] (a) Geckeler KE, Samal S. Polym Int 1999;48:743.
  (b) Brusatin G, Signorini R. J Mater Chem 2002;12:1964.
  (c) Dai L. Polym Adv Techn 1999;10:357.
  (d) Dai L, Mau AWH. Adv Mater 2001;13:899.
  (e) Wang C, Guo ZX, Fu S, Wu W, Zhu D. Prog Polym Sci 2004;29:1079.
[14] (a) Cravino A, Zerza G, Naggini M, Bucella S, Svensson M, Andersson MR. Chem Commun 2000;2487.
  (b) Benincori T, Brenna E, Sannicolo F, Trimarco L, Zotti G, Sozzani P. Angew Chem Int Ed 1996;35:648.
[15] Wang ZY, Kuang L, Meng XS, Gao JP. Macromolecules 1998;31:5556.
[16] Chen Y, Huang ZE, Cai RF. J Polym Sci, Part B: Polym Phys 1996;34:631.
[17] Fujitsuka M, Ito O. Photoexcitation dynamics of fullerenes. In: Nalwa HS, editor. Encyclopedia of nanoscience and nanotechnology, vol. 8. California, USA: American Scientific Publishers; 2004. p. 593.
[18] Fujitsuka M, Ito O. Photochemistry of fullerenes. In: Nalwa HS, editor. Handbook of photo-chemistry and photobiology, vol. 2. California, USA: American Scientific Publishers; 2003. p. 111.