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Synthesis and optical properties of poly(phenylenevinylene) modified with 3,4-bis(phenylene)-3-cyclobutene-1,2-dione moiety

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Summary

A new class of soluble poly(*p*-phenylenevinylene)-modified conjugated polymers with a simple aromatic unit of 3,4-bis(phenylene)-3-cyclobutene-1,2-dione in the main chain was synthesized by the dehalogenation polycondensation and the Heck reaction. The monomer and the polymers were characterized by FT-IR, ^{1}H-NMR, UV-visible, Elemental Anaylsis, TGA and DSC. The resultant polymers were obtained as yellow powder, formed the brittle film from the DMAc solution. These polymers were soluble in polar aprotic solvents, such as NMP, DMAc, DMF and DMSO. The present polymers show absorption bands in the range of 286~325nm, corresponding to the π-π^* electronic transition of the conjugated polymer backbones. The photoluminescence spectrum of the polymer **1** shows a peak at 471nm while the polymer **2** has the peak at 522nm with DMAc solution, in the blue emission region.

Introduction

The development of aromatic and/or heteroaromatic π-conjugated polymers showing electroluminescence has become an extensive area of academic and industrial research because of the potential application such as light-emitting diodes (LEDs) of this technology[1-5]. Application of conjugated polymers as active layers in LEDs offers the several advantages such as low cost and easy fabrication due to the spin coating processibility. Since the first report of polymer light-emitting diodes based on poly(*p*-phenylenevinylene) (PPV) by Burroughes *et al.*[2], a variety of conjugated polymers, such as poly(phenylphenylenevinylene)[6], poly(*p*-phenylene)[7-9], polythiophene[10-11], poly-quinoline[12], polypyridine[13-14] and poly(pyridylylene)[14-16], have been investigated to fabricate high performance display devices. Recently, other groups[17] have reported new soluble conjugated polymers that could be achieved by introducing well-defined lumophores into the polymer main chain to obtain the blue emission. But, these polymers inevitably contain saturated and non-conjugated spacer groups between the lumophores that act as a barrier to the injection and mobility of the charge carriers. Therefore, it seems desirable to develop a new series of soluble π-conjugated polymers that control the conjugation length to realize the short wavelength emission.

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Recently, we reported a new class of soluble poly(*p*-phenylenevinylene)-modified conjugated polymer having a simple aromatic unit, 3,4-bis(phenylene)-3-cyclobutene-1,2-dione, in the polymer main chain[18]. The optical properties of which, however, have not been reported yet.

In this paper, we report synthesis and optical properties of new soluble PPV derivatives containing an electron withdrawing 3-cyclobutene-1,2-dione moiety in their main chains.

Experimental

Materials

All chemicals were purchased from Aldrich, Junsei and Merck chemical company. $NiCl_2 \cdot 6H_2O$ was dried at 60°C under vacuum. Triphenylphosphine (PPh_3) was purified by recrystallization from hexane. Powdered zinc was purified by stirring with acetic acid, filtering, washing thoroughly with ethyl ether, and drying at 60°C under vacuum. All the solvents such as DMAc and DMF were dried with appropriate drying agents such as magnesium sulfate, then distilled under reduced pressure, and stored over 4Å molecular sieve. The *p*-divinylbenzene was separated from a mixture of *p*- and *m*-divinylbenzene according to the literature procedure[19]. The triethylamine was distilled over CaH_2 and stored with a 3Å molecular sieve.

Measurements

^{1}H-NMR spectra were taken on a Bruker AMX 500 using standard parameters and DMSO-d_6 or $CDCl_3$ as a NMR solvent. FT-IR spectra were taken on a Bio-Rad Digi Lab Division FTS-165 using KBr pellet. Elemental analysis was taken on a EA 1108 Fisons. Thermogravimetric analysis (TGA) was measured on a Du Pont model 915 coupled to a Du Pont Thermal Analysis Station 9900 at a heating rate of 10°C/min^{-1} under nitrogen. Differential Scanning Calorimetric (DSC) analysis was performed on a Du Pont 910. Mass spectra were recorded on a Jeol JMS-DX 303 GC/MS system using an electron impact method. UV-visible absorption (Abs) and Photoluminescence (PL) spectra were investigated in DMAc solution and thin films cast from DMAc solution onto glass, using a Shimadzu UV-2101PC UV-visible scanning spectrophotometer and ISS PC1 spectrofluorometer.

Synthesis of monomer[18] (3,4-bis(4-bromophenylene)-3-cyclobutene-1,2-dione)

The mixture of squaric acid (3.04g, 26.6mmol), thionyl chloride (6.42g, 54.0mmol) and catalytic amount of DMF was stirred at 65°C for 2h. Then the Friedel-Crafts reaction was carried out with bromobenzene (20mL) and aluminum chloride (8.50g, 63.8mmol). The mixture was poured into water (20mL) and extracted from ethyl ether. The ether layer was dried over magnesium sulfate and then evaporated to obtain the crude residue. The crude residue was crystallized from ethanol and collected by filtration and dried. Yield: 4.84g (46%); m.p. (DSC) 172°C; ^{1}H-NMR ($CDCl_3$) δ 7.9 (4H, 2-H and 6-H), δ 7.6 (4H, 3-H and 5-H); IR (KBr) 1780cm^{-1} and 1718cm^{-1} (C=O), 1585cm^{-1} and 1489cm^{-1} (aromatic C=C); Mass (M^+): 392g/mol; ANAL. Calcd. for $C_{16}H_8O_2Br_2$: C, 48.9; H, 2.04; O, 8.16; Br, 40.77, Found: C, 48.58; H, 2.04

Synthesis of polymer: Poly(3,4-bis(phenylene)-3-cyclobutene-1,2-dione)[18] [**1**]

To a stirred, deep blue solution of $NiCl_2 \cdot 6H_2O$ (1.18g, 5mmol) and triphenylphosphine (5.2g, 20mmol) in DMF (25ml) under nitrogen at 50°C, zinc powder (0.32g, 5mmol) is added. After 1h, the color of the mixture has changed to reddish brown. After the red-brown catalyst had formed, dibromide monomer (1.96g, 5mmol) was added to the reaction mixture. The reaction was conducted at 80°C for 24h. The resulting mixture was poured onto a large amount of concentrated hydrochloric acid-methanol (1:9). The polymer was collected, washed with methanol and dried in vacuum at 80°C for 24h. The yield was 0.68g. (60%); ^{1}H-NMR (DMSO-d_6) δ 7.5-7.6ppm (8H, aromatic C-H); IR (KBr) 1759cm^{-1} and 1724cm^{-1} (C=O) 1604cm^{-1} and 1489cm^{-1} (aromatic C=C)

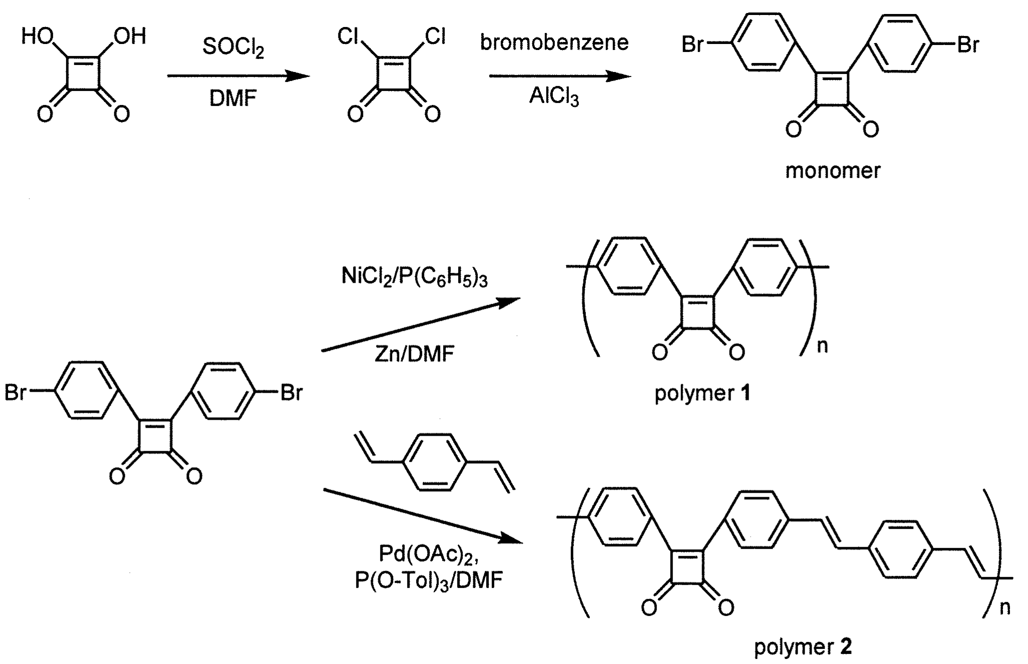
Poly(3,4-bis(phenylene)-3-cyclobutene-1,2-dione-1,4-phenylenevinylene) [**2**]

Triethylamine (0.35mL, 2.5mmol) was added to a solution of *p*-divinylbenzene (130mg, 1mmol), dibromide monomer (392mg, 1mmol), $Pd(OAc)_2$ (9.0mg, 0.04mmol) and tri-*o*-tolyphosphine (60.9mg, 0.2mmol) in 5mL of DMF. The reaction mixture was heated at 100°C for 5h under a nitrogen atmosphere and then poured onto 20mL of methanol. The precipitated polymer was collected by filtration and further purified by redissolving in a minimum amount of hot DMAc and precipitating from acetone. The yield was 0.30g (83%); ^{1}H-NMR (DMSO-d_6) δ 7.5-8.0ppm (8H, aromatic C-H) δ 5.5-6.5ppm (2H, CH_2); IR (KBr) 1777cm^{-1} and 1720cm^{-1} (C=O) 1595cm^{-1} and 1510cm^{-1} (aromatic C=C)

Results and Discussion

The synthetic routes to the monomer and the modified PPV polymers are described in Scheme 1. The polymer **1** was prepared by the dehalogenation polycondensation of a dibromoaromatic compound with a squaric unit as a monomer, in the presence of a zerovalent nickel complex[20] and the polymer **2** was easily carried out in DMF in the presence of a catalytic amount (2%-mol.) of $Pd(OAC)_2$ with the tertiary amine and triarylphosphine under a nitrogen atmosphere[21]. The polymers were obtained as yellow powder and formed the brittle film from the DMAc solution and polymers were soluble in polar aprotic solvents, such as NMP, DMAc, DMF and DMSO. The polymers were measured at inherent viscosity in DMAc at 30°C. At the concentration of 0.5g/dL, inherent viscosity was in the vicinity of 0.16dL/g in the polymer **1** and 0.40dL/g in the polymer **2**. The glass transition temperature of the polymers can't be detected by DSC. The thermal stability of the polymers was examined by TGA. The weight loss of a the polymers began to start at 200°C in accordance with the onset ring-opening temperature of the cyclobutenedione, as assessed by TGA. It is known that the cyclobutenedione ring can open to form a highly reactive bisketene upon thermolysis and further yields the acetylene by ejecting two molecules of carbon monoxide at elevated temperature[22].

The polymer **1** exhibited an IR absorption band at 1759cm^{-1} and 1754cm^{-1}(two-carbonyl absorption band) and an absorption band of C-Br band (428cm^{-1} for the monomer) disappeared. In the polymer **2**, a weak sharp absorption peak at 950cm^{-1}, corresponding to the out-of plane bending mode of the *trans*-vinylene groups, appeared, and this implied that the newly formed double bonds were mainly in the *trans* configuration. The ^{1}H-NMR spectrum of the polymer **1** showed peaks in the range of δ 7.5~8.2ppm due to the aromatic protons of the benzene ring. The aromatic proton *ortho* to a cyclobutenedione moiety in the monomer had a chemical shift of δ 7.9ppm, which was as high as that of the proton *ortho* to the carbonyl group in 4,4'-difluorobenzophenone. This implied that the whole of the cyclobutenedione moiety itself provided better electron-withdrawing character than a single-carbonyl group. In the polymer **2**, new vinylic proton peaks appeared at δ 5.5ppm (doublet) and δ 6.5ppm (doublet). These results indicated that polymerization was successfully carried out.



Scheme 1. Synthesis of Monomer and Polymers

Figure 1 and 2 show the UV-visible absorption spectra and the photoluminescence spectra of the polymers in DMAc solution and thin film coated on a quartz plate. As shown in the absorption spectra (Figure 1), the polymer **1** had an absorption band at 286nm in DMAc solution and at 300nm in the case of the film. These absorption bands attributed to the π-π^* electronic transitions of the conjugated polymer backbones. Then, the polymer **2** had the maximum absorption wavelength at 325nm for both DMAc solution and film (Figure 2). It has been well established that the wavelength of maximum absorbance in the *p*-phenylenevinylene series increased (red shift) as the number of conjugated phenylenevinylene sequence increased[23]. Thus, the differences in the UV absorption for the polymer **1** verses the polymer **2** suggested that the conjugation length of the consecutively substituted phenylenevinylene be different in two polymers. Since the polymer **2** exhibits a longer wavelength of absorption maximum than the polymer **1**, it is suggested that the polymer **2** have the structural sequence with the extended conjugation length. With an excitation wavelength of 310nm, the emission spectra of the polymer **1** gave a peak at 471nm in DMAc solution, and at 492, 530nm in the film, indicating a blue emission. On the other hand, because an aliphatic vinyl group was incorporated into polymer main chain, the polymer **2** exhibited maximum emission bands at 522nm (an excitation wavelength of 322nm) in DMAc solution and 589nm (an excitation wavelength of 340nm) in the film, respectively. The PL spectra of the polymer **2** show longer wavelength emission than the polymer **1**. This result indicates that the extended π-conjugation system was effectively formed in the polymer **2**. In the polymer **2**, the PL spectra for the film are strongly red-shifted versus the solution samples. The strong PL band at 589nm, which disappeared on dilution by the solvent, might be generated by the excitons, which migrated to the aromatic pairs to form the excimers or the aggregate states developed by interchain interactions[24].

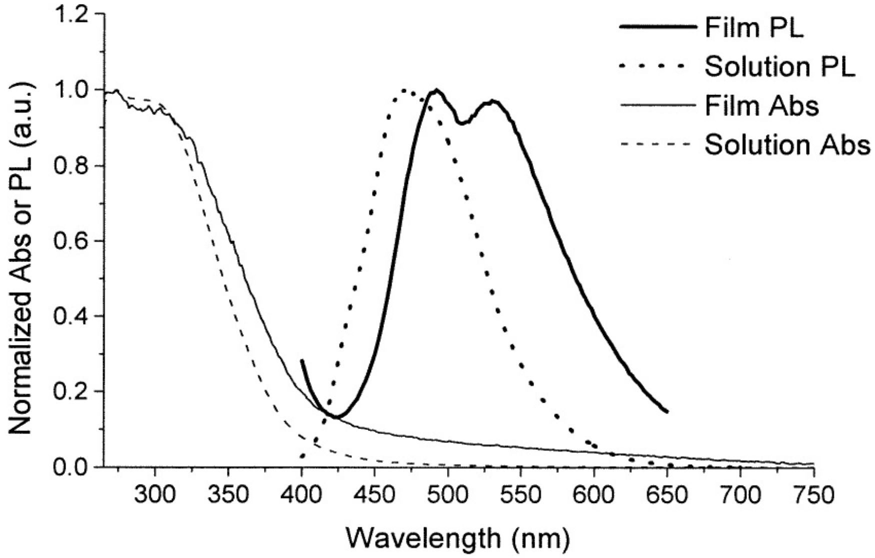


Figure 1. UV-visible absorption and photoluminescence spectra of polymer **1** ; The concentration of the polymer **1** / DMAc solution was 2.4×10^{-5} M (repeating unit based).

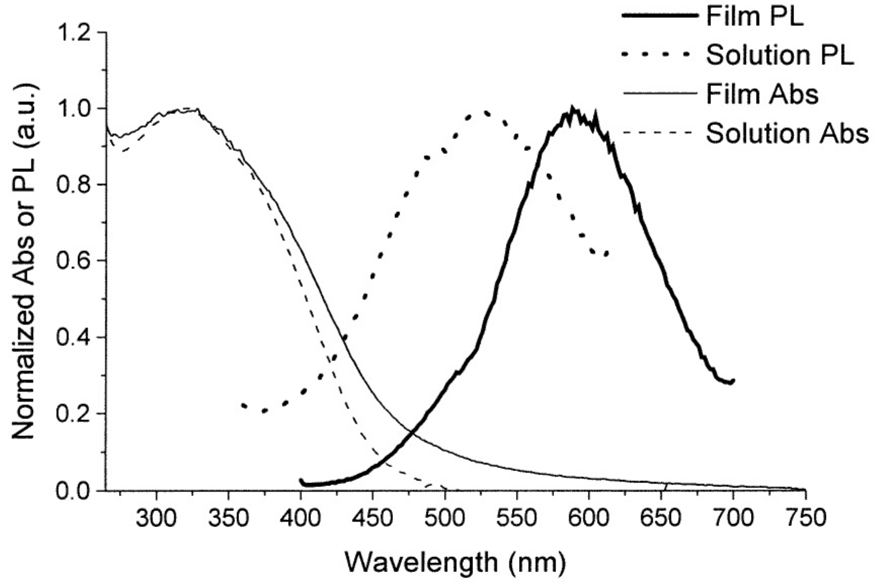


Figure 2. UV-visible absorption and photoluminescence spectra of polymer **2** ; The concentration of the polymer **2** / DMAc solution was 8.0×10^{-5} M (repeating unit based).

In conjunction with the change in the optical spectra presented above, these results indicate the presence of additional low-energy emitting states in these systems. We may suggest that these low-energy states be charge transfer effect between a cyclobutenedione ring moiety and a phenylenevinylene moiety or the aggregate sites[25,26], where the ground state and excited state wavefunction can delocalize over the several chains. The film samples show a tendency towards the formation of the aggregate states, and it is possible that higher PL efficiencies may be achieved through the control of aggregate formation.

In conclusion, we report here the synthesis and the properties of a new, soluble modified PPV polymers, which have a simple aromatic unit, 3,4-bis(phenylene)-3-cyclobutene-1,2-dione, in the polymer main chain. These polymers were synthesized by the dehalogenation polycondensation and the Heck reaction. These well-known methods in principle can be applied to the preparation of a great number of polyconjugated systems having aromatic rings in the main backbone. The resulting polymers were soluble in polar aprotic solvents, such as NMP, DMAc, DMF and DMSO. The present polymer-DMAc solutions show photoluminescence at 471nm and 522nm in case of the polymer **1** and the polymer **2**, respectively. The electroluminescence of light-emitting diode structures fabricated with the present polymers is being investigated.

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References

1. Tang CW, VanSlyke SA (1987) Appl Phys Lett 51: 913
2. Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burns PL, Holmes AB (1990) Nature 347: 539
3. Gusafasson G, Cao Y, Treacy GM, Klavetter F, Colaneri N, Heeger AJ (1992) Nature 357: 477
4. Bradley DDC (1993) Synth Met 54: 401
5. Greenham NC, Moratti SC, Bradley DDC, Friend RH, Holmes AB (1993) Nature 365: 628
6. Vestweber H, Greiner A, Lemmer U, Mahrt RF, Richert R, Heitz W, Bassler H (1992) Adv Mater 4: 661
7. Grem G, Leditzky G, Ulrich B, Leising G (1992) Adv Mater 4: 36
8. Gruner J, Hamer PJ, Friend RH, Huber H-J, Scherf U, Holmes AB (1994) Adv Mater 6: 748
9. Yang Y, Pei Q, Heeger AJ (1996) J Appl Phys 79: 934
10. Ohmori Y, Uchida M, Muro K, Yoshino K (1991) Sol St Comm 80: 605
11. Ohmori Y, Morishima C, Uchida M, Yoshino K (1992) J Appl Phys 31: L568
12. Parker ID, Pei Q, Marrocco M (1994) Appl Phys Lett 65: 1272
13. Gebler DD, Wang YZ, Blatchford JW, Jessen SW, Lin L-B, Gustafson TL, Wang HL, Swager TM, MacDiarmid AG, Epstein AJ (1995) J Appl Phys 78: 4264
14. Wang YZ, Gebler DD, Lin LB, Blatchford JW, Jessen SW, Wang HL, Epstein AJ (1999) Appl Phys Lett 68: 894
15. Tian J, Wu C-C, Thompson ME, Sturm JC, Register RA (1995) Chem Mater 7: 2190

16. Onoda M (1995) J Appl Phys 78: 1327
17. Yang Z, Sokolik I, Karasz FE (1993) Macromolecules 26: 1188
18. Jeong JK, Choi SJ, Rhee, TH, Yang NC, Suh DK (1998) Polym Bull in press
19. Strey BT (1965) J Polym. Sci Part A3 265
20. a) Semmelhack MF, Helquist PM, Jones LD (1971) J Am Chem Soc 93: 5908 b) Semmelhack MF, Ryono LS (1975) J Am Chem Soc 97: 3874 c) Semmelhack MF, Helquist PM, Jones LD, Keller L, Mendelson L, Ryono LS, Smith JG, Staufter RD (1981) J Am Chem Soc 103: 6460
21. Heck RF (1982) Org React 27: 345
22. a) Bock H, Ried W, Stein U (1981) Chem Ber 114: 673 b) Eggerding D, West R (1976) J Am Chem Soc 98: 3641 c) Chickos JS (1973) J Org Chem 38: 3642 d) Rubin Y, Lin SS, Knobler CB, Anthony J, Boldi AM, Diederich F (1991) J Am Chem Soc 113: 6943
23. Elsenbaumer RL, Shacklette LW (1991) Handbook of Conducting Polymer p40 Skotheim TA. Ed Marcel Dekker New York
24. Baigent DR, Holmes AB, Motatti SC, Friend RH (1996) Synth Mat 80: 119
25. Blatchford JW, Jessen SW, Lin LB, Lih JH, Gustafson TL, Epstein AJ, Fu DK, Swager TM, MacDiarmid AG, Yamaguchi S, Hamaguchi H (1996) Phys Rev Lett 76: 1513
26. Epstein AJ, Blatchford JW, Wang YZ, Jessen SW, Gebler DD, Lin LB, Gustafson TL, Wang H-L, Park YW, Swager TM, MacDiarmid AG (1996) Synth Met 78: 253