

SYNTHESIS, CHARACTERIZATION AND QUENCHING BEHAVIOR OF A CATIONIC POLY(*p*-PHENYLENEVINYLENE) RELATED COPOLYMER*

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Abstract A cationic poly(*p*-phenylene vinylene) related copolymer without bulky phenylene substituents attached to the conjugated backbone was prepared through Wittig reaction. The molecular structure and optical properties were highly investigated through ¹H-NMR, UV and PL spectroscopy. The quenching behavior was also investigated, and the results demonstrate that incomplete quenching exists, which is consistent with the cationic poly(*p*-phenylene vinylene) related copolymer containing bulky phenylene substituents, probably correlated with the conformation of conjugated backbone and intermolecular aggregation.

Keywords: Water-soluble; Poly(*p*-phenylenevinylene); Quenching behavior.

INTRODUCTION

Recently, water-soluble fluorescent π -conjugated polymers have attracted much interest because of their potential application in the development of highly efficient chemo or biosensors^[1]. Much attention has focused on an anionic poly(*p*-phenylenevinylene) that features sulfonate side groups (PPV-SO₃⁻) because of its remarkable optical and electronic properties^[2–4], but apparently copolymers are more appropriate than the homopolymers such as PPV-SO₃⁻ to meet the requirement for the development of sensors and have been widely investigated^[5–7] because of their tunable sensitivity and selectivity through introducing suitable units into conjugated backbone.

Our group has synthesized^[8] a series of cationic poly(*p*-phenylene vinylene) related copolymers containing bulky phenylene substituents attached to the conjugated backbone (such as PhPPV-NEt₃⁺ as shown in Scheme 1) by Wittig reaction. Our research showed that PhPPV-NEt₃⁺ containing bulky phenylene substituents exhibited a downward Stern-Volmer curve (quenched by Fe(CN)₆⁴⁻ in aqueous solution)^[8] (as shown in the inset of Fig. 3), which was contrary to the typical upward curve of PPV-SO₃⁻ (quenched by MV²⁺ in aqueous solution)^[2]. Generally, such downward curves were explained by the existence of two populations of fluorophores, one of which was inaccessible to the quencher^[8,9]. With the introduction of a quencher, only those accessible fluorophores were quenched while the fluorescence from the inaccessible ones remained. Thus, there existed inaccessible fluorophores in PhPPV-NEt₃⁺, which might be buried in the polymer chains and inaccessible by quenchers for the steric hindrance of bulky phenylene substituents. To improve new sensors

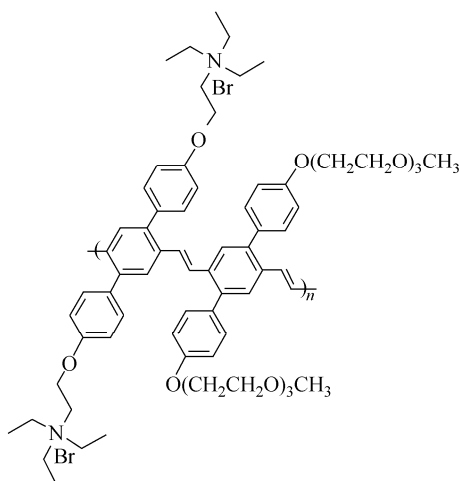
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with high sensitivity, it appears necessary to investigate the influence of the bulky side groups on the quenching behavior.



Scheme 1 Structure of PhPPV-NEt₃⁺

With the background above, we targeted the synthesis of a cationic PPV related copolymer without the bulky phenylene substituents. The optical properties of this cationic PPV were characterized, and its quenching behavior was also investigated to compare with PhPPV-NEt₃⁺.

EXPERIMENTAL

Materials

All reagents and solvents were purchased from either Shanghai Chemical Reagent Co. Ltd. or Aldrich Chemical Co. THF and ethanol were purified by distillation in the presence of sodium. Other organic solvents were used without any further purification. Thionyl chloride was distilled prior to use.

The synthetic routes for monomer **2** and the target polymers were outlined in Scheme 2. Monomer **1** (2,5-dioctyloxyterephthalaldehyde) was more easily prepared according to the literature^[10]. Monomer **2** (2,5-bis(4'-2-(*N,N*-diethylamino)ethoxy)-1,4-xylene)bis(triphenylphosphonium chloride) dihydrochloride and the polymers were synthesized as the following text.

Measurements

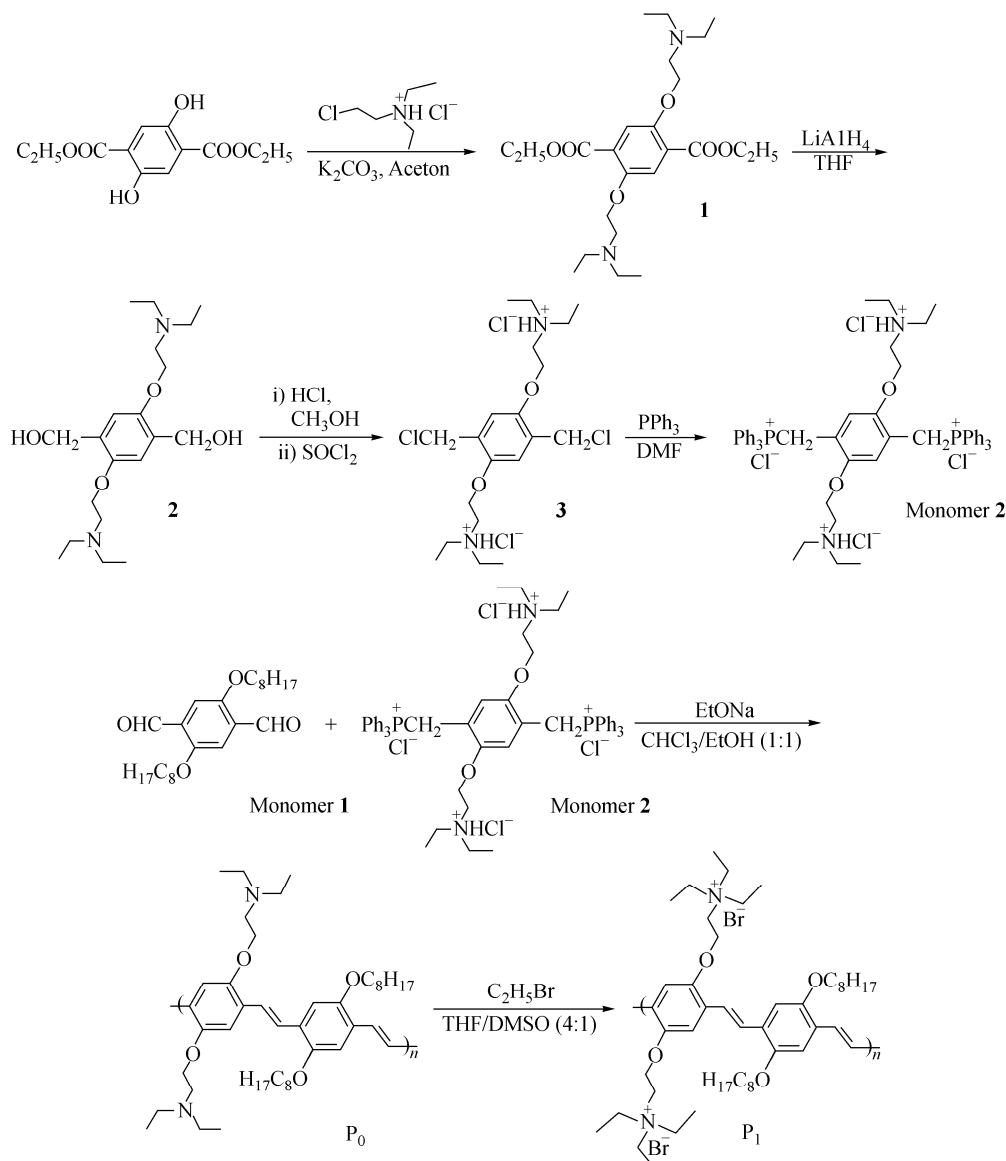
¹H-NMR (400 MHz) spectroscopy was performed on a Varian Mercury Plus 400 with tetramethylsilane as the internal standard. UV-Vis spectra were collected on a Shimadzu UV-3150 spectrophotometer. Fluorescence measurement was carried out on a Shimadzu RF-5300PC spectrophotometer. Number-average molecule weights (*M_n*) and weight-average molecule weights (*M_w*) were determined by Shimadzu GPC LC10A in THF using calibration based on polystyrene standards. Mass spectra (MS) were obtained using an HP 5973MS mass spectrometer at an ionizing voltage of 70 eV. Elemental microanalyses were carried out on a Vario EL III CHNOS element analyzer.

Monomer Synthesis

2,5-Bis(4'-2-(*N,N*-diethylamino)ethoxy)-1,4-phenylenemethylene diacetate (**1**)

10.0 g (39 mmol) of diethyl 2,5-dihydroxyterephthalate, 32.0 g (232 mmol) of potassium carbonate were added into 200 mL of acetone. After the reaction mixture was refluxed for 0.5 h under nitrogen atmosphere, 16.4 g (95 mmol) of 2-(diethylamino)ethyl chloride hydrochloride was added. After stirring for 72 h with refluxing, the acetone was evaporated at reduced pressure. The brownish residue was added into 300 mL of water, extracted with ethyl acetate. The extract was washed with water three times, with brine once, and then was dried over anhydrous magnesium sulfate. After the solvent was removed and 16.0 g brownish liquid was yielded (yield

90%). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.37 (s, 2H), 4.36 (q, 4H), 4.09 (t, 4H, $J = 5.2$ Hz), 2.90 (t, 4H, $J = 5.2$ Hz), 2.64 (q, 8H), 1.38 (t, 6H, $J = 5.2$ Hz), 1.06 (t, 12H, $J = 5.2$ Hz).



Scheme 2 Synthetic routes for the neutral and quaternized polymers

2,5-Bis(4'-2-(*N,N*-diethylamino)ethoxy)-1,4-bis(hydroxymethyl)benzene dihydrochloride (2**)**

15.0 g (33 mmol) of **1** in 200 mL THF was dropwise added into 5.0 g (132 mmol) of lithium hydride in 50 mL THF at 0°C under violent stirring. After stirring for 2 h with refluxing and cooled to room temperature, saturated aqueous sodium sulfate was dropwise added until there weren't air bubbles. THF of the filtrate was removed under vacuum evaporation and then the residue was recrystallized with ethanol to afford 11.1 g (30 mmol) white crystals with a yield of 91%. $^1\text{H-NMR}$ (D_2O , δ): 6.99 (s, 2H), 4.56 (s, 4H), 4.30 (t, 4H, $J = 4.8$ Hz), 3.54 (t, 4H, $J = 4.8\text{Hz}$), 3.26 (m, 8H), 1.25 (t, 12H, $J = 7.2$ Hz).

2,5-Bis(4'-2-(*N,N*-diethylamino)ethoxy)-1,4-bis(chloromethyl)benzene (3**)**

A 3.68 g (10 mmol) sample of **2** was dissolved in 100 mL methanol and then 50 mL saturated hydrochloride methanol solution was poured into the solution at room temperature. After stirred for 30 min, the solution was

concentrated and dropwise added into 400 mL acetone under violent stirring. The obtained crude white precipitate was filtered and washed with acetone for three times. The crude product was directly added into 10 mL SOCl_2 under nitrogen protection at 0°C and stirred for 10 min. The ice bath was removed and the reaction mixture was continued stirring at room temperature for 3 h. The SOCl_2 was removed under vacuum evaporation and then the residue was added into 100 mL acetone, stirred for 2 h, filtered and then washed with acetone three times. The crude product was recrystallized with ethanol to afford 3.82 g of white crystals with a yield of 80%. MS: m/z ($-\text{2HCl}$) 404.2. $^1\text{H-NMR}$ (CD_3OD , δ): 7.22 (s, 2H), 4.75 (s, 4H), 4.43 (t, 4H, $J = 4.0$ Hz), 3.69 (t, 4H, $J = 4.0$ Hz), 3.42 (m, 8H), 1.41 (t, 12H, $J = 7.0$ Hz).

(2,5-Bis(4'-2-(N,N-diethylamino)ethoxy)-1,4-xylene)bis(triphenylphosphonium chloride) dihydrochloride (Monomer 2)

A solution of 2.39 g (5 mmol) of **3** and 2.89 g (11 mmol) of triphenylphosphine in 10 mL of DMF and 5 mL H_2O was heated to 75°C for 24 h with stirring. The precipitate was filtered and recrystallized in ethanol to afford 4.50 g of white crystals (yield 90%). $^1\text{H-NMR}$ (DMSO , δ): 11.14 (br, 2H), 7.88 (t, 6H, $J = 7.2$ Hz), 7.63 (m, 24H), 6.60 (s, 2H), 5.33 (d, 4H, $J = 14.4$ Hz), 2.90 (d, 8H, $J = 3.6$ Hz), 2.73 (t, 4H, $J = 4.4$ Hz), 2.48 (t, 4H, $J = 3.2$ Hz), 1.14 (t, 12H, $J = 7.2$ Hz). Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{Cl}_4\text{N}_2\text{O}_2$: C 50.22, H 7.59, N 5.86, Cl 29.65. Found: C 50.01, H 7.55, N 5.78, Cl 29.59.

Preparation of the Polymers

The neutral polymer (P_0) was synthesized by Wittig reaction between monomer **1** and monomer **2** as the general procedure we reported^[8] (yield 76%). Conversion of P_0 to the corresponding cationic polymer (P_1) was achieved by stirring with bromoethane in DMSO/THF (1:4) at 50°C for 5 days (yield 64%). $^1\text{H-NMR}$ of P_0 (CDCl_3 , δ): 7.59–7.38 (br, Ar—H), 7.38–7.26 (br, Ar—H and *trans*-vinyl protons), 7.26–7.12 (br, Ar—H), 6.80–6.64 (br, *cis*-vinyl protons), 4.18–3.80 (br, $-\text{OCH}_2-$ in *trans*-vinyl groups), 3.50–3.66 (br, $-\text{OCH}_2-$ in *cis*-vinyl protons), 3.03–2.91 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{N}-$), 2.75–2.62 (m, 8H, $-\text{NCH}_2\text{CH}_3$), 2.55–2.42 (br, 8H, $-\text{OCH}_2\text{CH}_2\text{CH}_2-$), 1.87–1.21 (br, 24H, $-(\text{CH}_2)_6\text{CH}_3$), 1.17–0.88 (m, 12H, $-\text{NCH}_2\text{CH}_3$), 0.88–0.79 (br, 6H, $-(\text{CH}_2)_6\text{CH}_3$). $^1\text{H-NMR}$ of P_1 (DMSO , δ): 6.90–6.20 (br, 8H, Ar—H and vinyl protons), 3.80–2.50 (br, $-\text{OCH}_2-$ and $-\text{NCH}_2-$), 1.10–0.60 (br, $-(\text{CH}_2)_6\text{CH}_3$ and $-\text{NCH}_2\text{CH}_3$).

RESULTS AND DISCUSSION

Polymer Characterization

The number-average molecular weight and polydispersity of P_0 by GPC were 5300 and 2, respectively. The corresponding number of phenyl rings in the backbone is about 12. $^1\text{H-NMR}$ spectra of the obtained P_0 and P_1 are shown in Fig. 1. It can be seen that the aromatic protons of the quaternized polymer resonance appeared a little downfield chemical shifts, compared with those of the corresponding neutral one.

There are two groups of resonances for the protons of P_0 , in which the downfield and upfield ones caused by the *trans*- and *cis*-configurations, respectively^[11, 12]. $^1\text{H-NMR}$ spectra of P_0 show two groups of resonance signals near $\delta = 4.0$ and 3.5, according to the reference^[11], which could be attributed to the separation of the signals of $-\text{OCH}_2-$ unit in both the $-\text{OCH}_2\text{CH}_2\text{N}-$ unit and the $-\text{OCH}_2\text{C}_7\text{H}_{15}$ unit in alkoxy side chains, and the latter signals are related to *cis*-olefins. So the ratio of *cis*- to *trans*-vinyl groups is determined by comparing the relative integrations of the *cis*- $-\text{OCH}_2-$ resonance between $\delta = 3.50$ and 3.66 with the $-\text{OCH}_2-$ resonance between $\delta = 3.80$ and 4.18. As a result, the content of *cis*-configurations for P_0 was calculated to be 73%, which is relatively lower than the one of PhPPV- NEt_3^+ (80%)^[8] and indicates that bulky phenylene substituents could increase the content of the *cis*-olefins by Wittig reaction. Such high values of *cis*-configuration are consistent with the polymerization method, as reported^[13] that the contents of *cis*-olefin linkages in the polymers synthesized *via* Wittig reaction are higher than that *via* Wittig-Horner reactions.

UV-Vis and fluorescence spectra are shown in Fig. 2. The absorption spectrum of P_0 in CHCl_3 solution reveals a maximum at 428 nm, and the corresponding photoluminescence (PL) spectrum shows a peak at 523 nm. The absorption spectrum of P_1 in CHOH solution exhibits a peak at 484 nm. Upon excitation at 484 nm,

the PL spectrum of P_1 shows a vibronic fine-structure with a strongest peak at 539 nm, and a shoulder peak around at 583 nm. There is a very large redshift of the quaternized polymer P_1 's absorption and PL spectra relative to those of the neutral one (P_0), presumably introduced by interchain aggregation of P_1 ^[14–16]. On the contrary, quaternization was found to create more obviously blue-shifted absorption and fluorescence spectra of PhPPV-NEt₃⁺^[8]. Such a difference may result from the bulky phenyl groups attached to the polymer backbone in PhPPV-NEt₃⁺ which reduce the interchain aggregation^[8, 17]. Furthermore, the lower content of *cis*-configurations in P_1 may also influence the aggregation, because the lower *cis*-vinyl linkages make the conformation of P_1 ' chains not so disordered^[8] which could be beneficial to the formation of interchain aggregation.

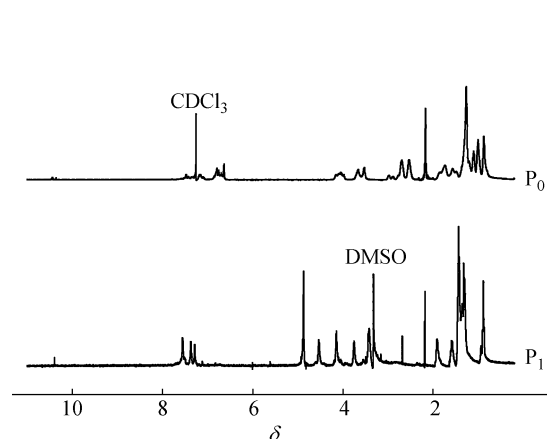


Fig. 1 ¹H-NMR spectra of P_0 in $CDCl_3$ and P_1 in DMSO

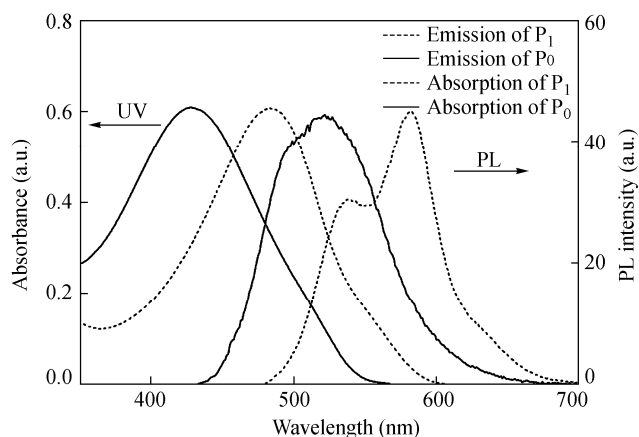


Fig. 2 UV-Vis absorption spectra of P_0 in $CHCl_3$ and P_1 in CH_3OH , and the fluorescence spectra of P_0 in $CHCl_3$ with excitation at 428 nm and P_1 in CH_3OH with excitation at 484 nm

Fluorescent Quenching

The quenching behavior was studied by comparing the fluorescence intensities of polymer in aqueous solutions in the presence of quenchers with different concentrations. UV-Vis absorption and PL emission spectra of P_1 (1.25 $\mu\text{mol/L}$) in the presence of $Fe(CN)_6^{4-}$ with different concentrations are shown in Fig. 3. The

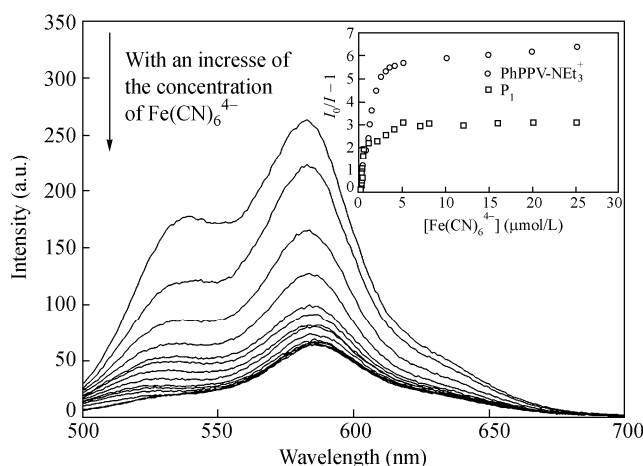


Fig. 3 PL emission spectra of P_1 (1.25 $\mu\text{mol/L}$) in the presence of $K_4Fe(CN)_6$ with different concentrations
Inset: Stern-Volmer plot of P_1 (1.25 $\mu\text{mol/L}$) and PhPPV-NEt₃⁺ quenched by $K_4Fe(CN)_6$ in aqueous solutions

corresponding Stern-Volmer plot for P_1 and PhPPV- NEt_3^+ quenched by $\text{Fe}(\text{CN})_6^{4-}$ in aqueous solutions is shown in the inset. It can be seen that an intriguing downward Stern-Volmer curve is also observed in this system, which is similar to the one of PhPPV- NEt_3^+ we reported earlier^[8]. As mentioned above, such a downward Stern-Volmer curve could be efficiently explained by the existence of inaccessible fluorophores^[8, 9], which results in part of unquenched fluorescence (as the platform in those downward curves indicate), and according to the modified Stern-Volmer equation f_a (the fraction of fluorescence from an accessible fluorophore) = 86% was obtained, which is lower than that of PhPPV- NEt_3^+ (91%)^[8, 18], and $K_{sv} = 2.5 \times 10^6 \text{ (mol/L)}^{-1}$ was also obtained. That is to say, 14% of the inaccessible fluorophores still remains, which is higher than that of PhPPV- NEt_3^+ (9%). Thus, the steric hindrance of bulky phenylene substituents in the side chains of PhPPV- NEt_3^+ seems not to be the main factor responsible for the inaccessible fluorophores, which could be attributed to the conformation of conjugated backbone and the interchain aggregation discussed above, as reported^[19] that the smaller surface-to-volume ratio in the larger aggregates enables weaker (ground state) chromophore/quencher interactions.

CONCLUSIONS

In this work, we have synthesized a cationic poly(*p*-phenylene vinylene) related copolymer through Wittig reaction, which does not contain bulky side groups. Based on those investigations above, it is reasonable to propose that the steric hindrance of bulky side groups is not the main factor responsible for incomplete quenching from the inaccessible fluorophores, which is correlated with the conformation of conjugated backbone and interchain aggregation. Further research is being done to investigate the key factors that provide inaccessible fluorophores in these polymers and to ultimately improve the quenching behavior.

REFERENCES

- 1 Achyuthan, K.E., Bergstedt, T.S., Chen, L., Jones, R.M., Kumaraswamy, S., Kushon, S.A., Ley, K.D., Lu, L., McBranch, D., Mukundan, H., Rininsland, F., Shi, X., Xia, W. and Whitten, D.G., *J. Mater. Chem.*, 2005, 15: 2648
- 2 Chen, L., McBranch, D.W., Wang, H.L., Helgeson, R., Wudl, F. and Whitten, D.G., *Proc. Natl. Acad. Sci. USA*, 1999, 96: 12287
- 3 Jones, R.M., Bergstedt, T.S., McBranch, D.W. and Whitten, D.G., *J. Am. Chem. Soc.*, 2001, 123: 6726
- 4 Fan, C., Plaxco, K.W. and Heeger, A.J., *J. Am. Chem. Soc.*, 2002, 124: 5642
- 5 Liu, B., Yu, W.L., Pei, J., Liu, S.Y., Lai, Y.H. and Huang, W., *Macromolecules*, 2001, 34: 7932
- 6 Chen, B.Z., Wu, Y.Z., Wang, M.Z., Wang, S., Sheng, S.H., Zhu, W.H., Sun, R.G. and Tian, H., *Eur. Polym. J.*, 2004, 40: 1183
- 7 Yasuda, T. and Yamamoto, T., *Macromolecules*, 2003, 36: 7513
- 8 Fan, Q.L., Lu, S., Lai, Y.H. and Huang, W., *Macromolecules*, 2003, 36: 6976
- 9 Lakowicz, J.R., "Principles of Fluorescence Spectroscopy", 2nd ed., Plenum Press, New York, 1999, p.238
- 10 Star, A. and Stoddart, J.F., *Macromolecules*, 2002, 35: 7516
- 11 Liao, L., Pang, Y., Ding, L. and Karasz, F.E., *Macromolecules*, 2001, 34: 7300
- 12 Pang, Y., Li, J., Hu, B. and Karasz, F.E., *Macromolecules*, 1999, 32: 3946
- 13 Liao, L., Pang, Y., Ding, L. and Karasz, F.E., *Macromolecules*, 2001, 34: 6756
- 14 Cornil, J., Dos Santos, D.A., Crispin, X., Silbey, R. and Bredas, J.L., *J. Am. Chem. Soc.*, 1998, 120: 1289
- 15 Nguyen, T.Q., Martini, I., Liu, J. and Schwartz, B.J., *J. Phys. Chem. B*, 2000, 104: 237
- 16 Jakubiak, R., Collison, C.J., Wan, W.C., Rothberg, L.J. and Hsieh, B., *J. Phys. Chem. A*, 1999, 103: 239
- 17 Kim, J., McQuade, D.T., McHugh, S.K. and Swager, T.M., *Angew. Chem. Int. Ed.*, 2000, 39: 3868
- 18 Lehrer, S.S., *Biochemistry*, 1971, 10: 3254
- 19 Gaylord, B.S., Wang, S., Heeger, A.J. and Bazan, G.C., *J. Am. Chem. Soc.*, 2001, 123: 6417