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Synthesis and characterization of a novel water-soluble block copolymer with a rod–coil structure

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Abstract

In this letter, a novel water-soluble rod–coil block copolymer was designed and prepared via the facile polycondensation method using polyfluorene (PF) as rod segment and polyethylene glycol (PEG) as coil segment in the main chain. The molecular structure and morphology of the intermediate and block copolymer were characterized by ^{1}H NMR, FT-IR, UV-Vis absorption, photo-luminescence (PL) spectra, transmission electron microscope (TEM), fluorescence and polarizing microscopy, respectively; the molecular weight was examined by the gel permeation chromatography (GPC). The experimental results show that the block copolymer with rod–coil structures can dissolve in environment-friendly solvents, such as water and ethanol, possess self-assembling morphologies and take on a high photo-luminescence quantum efficiency *ca*. 52%.

Keywords: Polycondensation; Water-soluble; Fluorescence

1. Introduction

Water-soluble conjugated polymers are of particular interest for applications in the fields of chemical and biological detection, biosensor and so on [1,2]. However, there are several disadvantages to currently available water-soluble polymers, such as low intrinsic photo-luminescence (PL) quantum efficiency [3] and PL quenching through non-specific interactions [4]. In some cases, synthetic manipulations can be used to solve these issues [5], but such procedures are often complex and time-consuming.

As one of the most important role in the water-soluble fields, amphiphilic block copolymers have been extensively investigated both theoretically and practically in the past few decades. Traditional amphiphilic block copolymers containing chemically connected hydrophilic and hydrophobic coils provide a great variety of morphologies both in solid states and in selective solvents, especially between water and hydrophobe solvents [6,7]. The micelles of these block copolymers formed in selective solvents, which consist of an inner core composed of insoluble segments surrounded by an outer shell of soluble segments swollen by the solvent, are potentially useful in nanotechnologies and biomedical fields. Recently, novel amphiphilic rod–coil block copolymers containing at least one conjugated segment for optoelectronic applications has received attention as an alternative strategy for fabrication of molecular electronic devices because the combination of the physical properties contributed by the component segments in the block copolymers may exhibit unique characteristics suitable for developing novel supramolecular structures [8–10].

In our study, we have prepared a novel water-soluble rod–coil block copolymer, using polyfluorene (PF) as the rod segment and polyethylene glycol (PEG) as coil segment in the main chain. PF is one of the widely studied conjugated polymers, which is an excellent semiconducting materials for optoelectronic applications [11], and well known as a high-performance blue light-emitting polymer with excellent chemical and thermal stability [12]. Several examples of polyfluorene-based block

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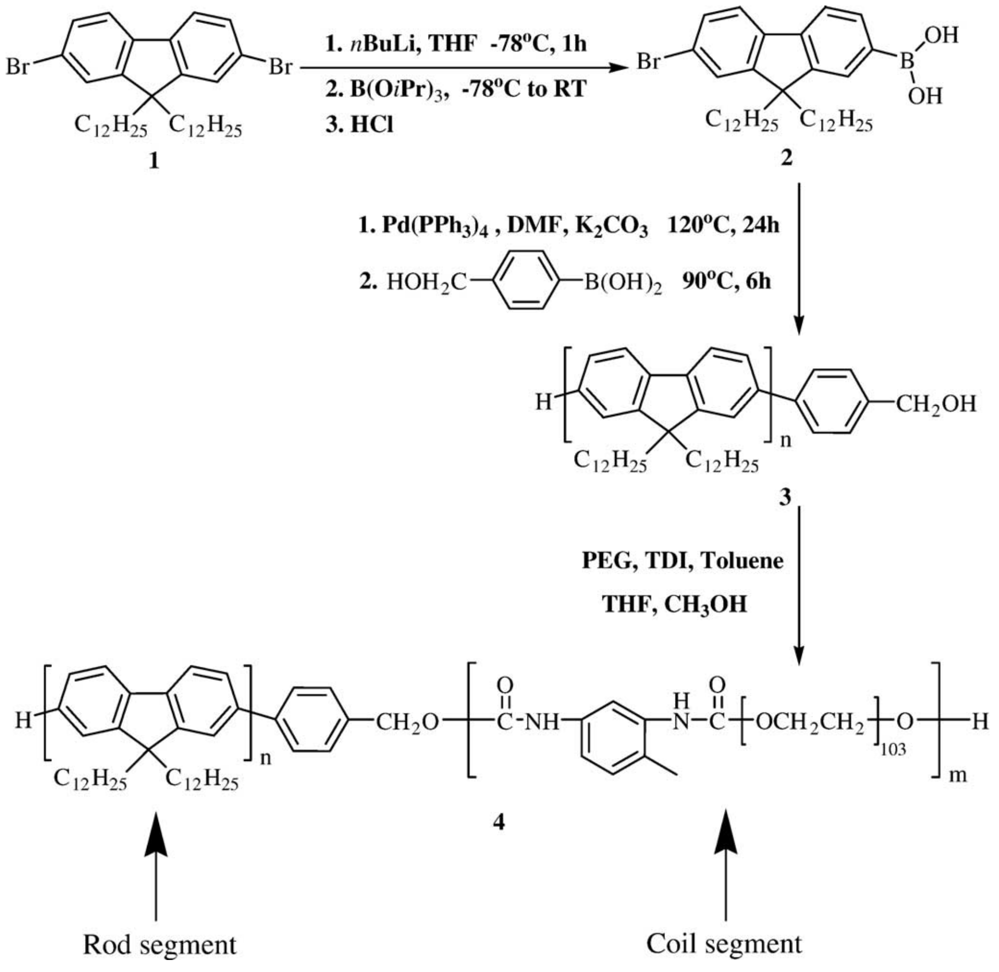
copolymers have been studied, appearing to be interesting supramolecular materials [13]. On the other hand, the nontoxic and hydrophile of PEG provides a great advantage in utilizing it as a component of PF materials for applications in chemical and biological detection, and its strong hydration power contributes to regulation of the hydrophilicity of the materials [14]. The copolymer can self-assemble into polymeric nanoparticles in aqueous systems with a diameter ranging from 50 to 150 nm. The copolymer nanoparticles are characterized by a core-shell architecture, in which a segregated core of associated hydrophobic segments (PF) is surrounded by a hydrophilic and sterically stabilized shell (PEG), and the shell could cause the nanoparticles to have a long half-life in the blood due to the reduced interaction with biological components [15].

In this letter, we chose isocyanate (−NCO) as a linkage between rod and coil chains, and we successfully prepared a novel of water-soluble block copolymer through employing polycondensation. Compared to traditional ATRP and ionic polymerization [8,16], the polycondensation used in our study is a new and simple method. Since the molecular bond reaction take place between isocyanate (−NCO) and hydroxyl of PF and PEG end group to produce polyurethane, it is more convenient and more easily control to the molecular structure and molecular weight of designed products. The new block copolymer with rod–coil structures can dissolve in environment-friendly solvents, such as water and ethanol etc, possesses richness of the self-assembling morphologies and display a high photoluminescence quantum efficiency *ca*. 52%, which can be use as a fluorescent marker for studying tissue distribution.

2. Experimental section

2.1. Measurements and instruments

^{1}H NMR spectra were collected on Varian Mercury Plus 400, using chloroform-d as a solvent and tetramethylsilane (TMS) as an internal standard. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu IR prestige-21 spectrometer. The GPC analysis of the precursor and product was conducted on Shimadzu 10A serious with THF as the eluent polystyrene standard. The transmission electron microscopy (TEM) image was taken on a Hitachi H-600 electron microscope operated at 75 kV. Polarizing and fluorescence images were taken on an Olympus-BX51 system microscope. Ultraviolet-visible (UV-Vis) absorption and PL spectra were measured using a Shimadzu UV-3150 UV-Vis-NIR spectrophotometer and RF-5300PC luminescence spectrometer with a xenon lamp as light source, respectively.



Scheme 1. Synthetic route of the block copolymer with a rod–coil structure.

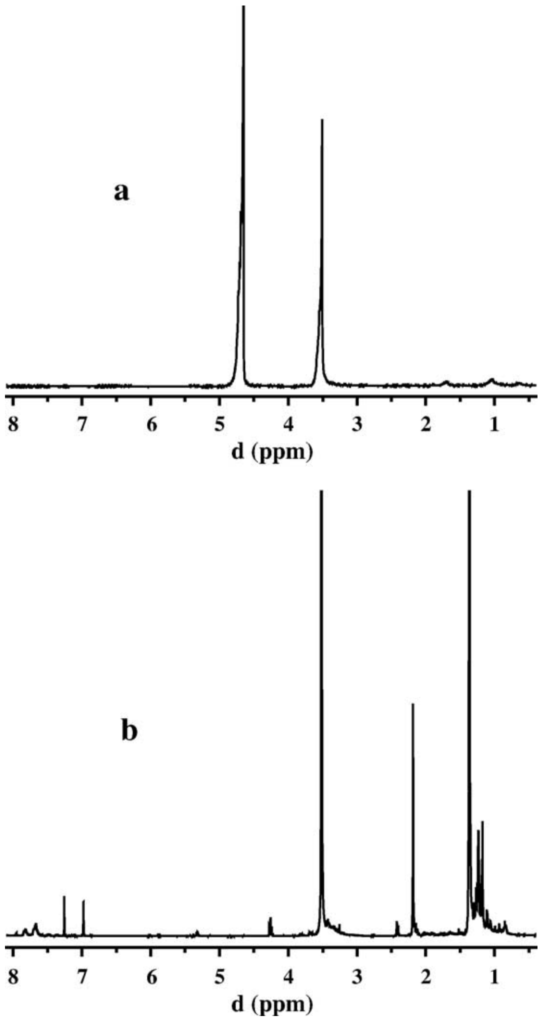


Fig. 1. ^{1}H NMR spectra of the block copolymer dispersed in (a) D_2O and dissolved in (b) $CDCl_3$.

2.2. Materials

2,7-dibromo-9,9-di-*n*-dodecylfluorene 97%, butyllithium (1.6 M solution in hexanes), triisopropyl borate 98+%, tetrakis(triphenylphosphine)palladium(0) 99% and 4-(hydroxymethyl) phenylboronic acid (containing varying amounts of anhydride) were purchased from Aldrich Chemicals Company. Potassium carbonate (K_2CO_3, AR) and polyethylene glycol 4600 (Mn = 4600, CP) were purchased from Shanghai Chemical Reagent Co. Ltd. 2,4-tolylene diisocyanate 95% (TDI) was kindly provided by Dupont Coating Company (China). All chemicals were used directly without further purification.

2.3. Preparation of the target copolymer with a rod–coil structure

All the synthetic routes are given in Scheme 1 [17–19]. The precursor **3** containing the end-group of hydroxyl should be prepared first of all. We prepared the compound **2** by monolithiation of the compound **1** (2,7-dibromo-9,9-di-*n*-dodecylfluorene) with 1.1 equiv of butyllithium followed by boronation with triisopropyl borate at −78 °C (Scheme 1) in high purity. Polymerization of the compound **2** using a modified Suzuki coupling protocol [20] followed by endcapping with 4-(hydroxymethyl)phenyl-boronic acid yielded the precursor **3** [4-hydroxymethylphenyl-poly(9,9-di-*n*-dodecylfluorene)] (Scheme 1). All the compounds and the precursor **3** were prepared according to literature methods [17 18] and confirmed by ^{1}H NMR and Elemental analyses. ^{1}H NMR (400 MHz, $CDCl_3$) of the precursor 3, δ: 0.86–1.43 (m, 644 H), 2.10–2.16 (m, 56 H), 4.99 (s, 2 H), 6.99–7.03 (m, 4 H), 7.25–7.91 (m, 85 H).

Then the target block copolymer **4** was prepared according to a classic reaction [19] (Scheme 1). One Schlenk tube containing the compound **3** (0.60 g) was degassed and filled with nitrogen. 2,4-tolylene diisocyanate (TDI, 0.03 ml, 0.20 mmol) was dissolved in 5 ml anhydrous toluene and added dropwise under vigorously stirring at room temperature for 30 min. The mixture is heated to 50°C, stirred for 4 h. Then the solvent and superfluous TDI were wiped off by reduced pressure distillation. Finally, PEG 4600 (0.92 g, 0.20 mmol) and anhydrous toluene (5 ml) were added vigorously stirring at room temperature, and the reaction lasts 24 h at 90 °C. The fresh copolymer is dissolved in THF, filtrated and then upon evaporating off the filtrate, the residue is again dissolved methanol, then filtered and dried. The target copolymer with a rod–coil structure **4** is obtained in powder-like form. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.84–1.44 (m, 644 H), 2.10–2.18 (m, 56 H), 2.40–2.42 (m, 3 H), 3.30–3.75 (m, 420 H), 4.26 (m, 4 H), 5.32 (d, 2 H), 6.99 (m, 6 H), 7.34–7.83 (m, 86 H), 7.94 (s, 2 H).

3. Results and discussion

During the preparation of block copolymer, FT-IR spectra are utilized to monitor the polymerization process [19]. The characteristic peak at 3600 cm^{-1}, 2280 cm^{-1} and 1700 cm^{-1} correspond to the group of −OH, −NCO and −C=O in the reactant and produce, respectively. When the −OH and −NCO groups were disappeared, it demonstrated that the polymerization was completed.

GPC analysis is used to determine the molecular weight of the precursor and the as-prepared block copolymer. The number average molecule weight of the precursor **3** is 7400 g/mol. Comparison of the

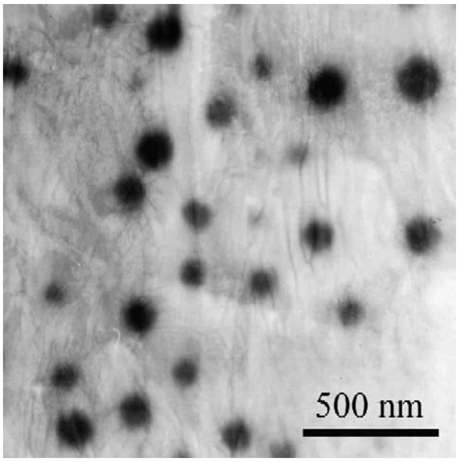


Fig. 2. TEM image of the nanoparticles of the block copolymer.

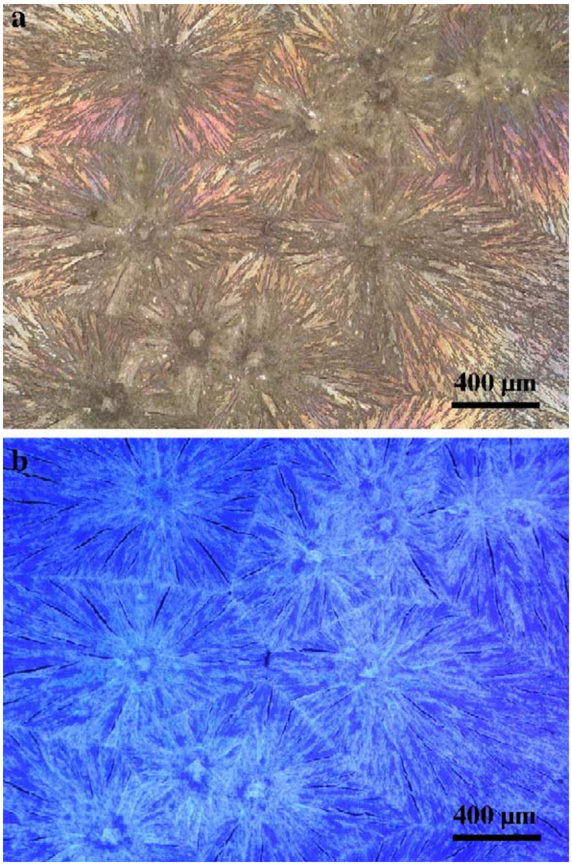


Fig. 3. The crystalline morphology of the block copolymer observed by (a) polarizing and (b) fluorescence microscopy.

relative ^{1}H NMR signal intensities of the fluorene repeating units (δ=7.25–7.91) and the 9-position of fluorene linking two methanols (δ=2.10–2.16), and the signal for the hydroxymethyl of methanol benzyl proton (δ=4.99) offers the opportunity to determine the molecular weight of the polyfluorene. The molecular weight of 7100 g/mol determined by ^{1}H NMR is in good agreement with the value determined by GPC analysis. The polymerization degree (**n** in the precursor 3) can be calculated above 14.6, which is close the result of the ^{1}H NMR about 14. The measurement of GPC show that the number average molecule weight of prepared block polymer is 12 600 g/mol. Compared to the relative ^{1}H NMR signal protons of the 9-position of fluorene linking two methanols (δ=2.10–2.18) and the protons on PEG chain (δ=3.30–3.75), the molecular weight of the prepared copolymer is calculated round 11 800 g/mol, which is also in accord with the value determined by GPC analysis. So it can be estimated that polymerization of the coil segment is about 1.1 [(12 600–7400) / 4600 = 1.1], indicating by this way the molecular weight and the molecular structure of the block copolymer were also successfully controlled.

^{1}H NMR can be employed to study the structure of polymeric nanoparticles due to the fact that the nanoparticle system is in the same conformational state whether the prepared block copolymer is dispersed in water or in D_2O. ^{1}H NMR spectra of polymeric nanoparticles dissolved in $CDCl_3$ (a) and dispersed in D_2O (b) are shown in Fig. 1. From Fig. 1(a) it is revealed that in $CDCl_3$, a nonselective solvent for the PEG block and PF block, peaks at 7.34–7.83, 2.10–2.18, 0.84–1.44 and 3.30–3.75 ppm [21] are observed, which are assigned to phenyl protons of the PF, two methylene protons linking to the 9-position of PF, rest alkyl protons of PF component and methylene protons of PEG component respectively. However, as shown in Fig. 1(b), only the signal of the PEG component is seen in the spectra of the prepared block copolymer, which indicates that the PEG segment is in an extended solvated state to form the hydrophilic outer shell of the particles and stabilize the colloidal particles. The protons in PF component have disappeared from the spectra, implying that PF segments are entrapped in the central solid-like hydrophobic core to minimize their interaction with water due to their hydrophobic character.

Amphiphilic conjugated block copolymers composed of mutually repulsive and chemically connected conjugated-coil segments with different hydrophilicities, may self-assemble into highly ordered periodical geometries in selective solvents [22]. Because the self-assembly process gives rise to the formation of various nanostructures with semiconducting characteristics, amphiphilic conjugated block copolymers may be promising to serve as unique optoelectronic materials. Fig. 2 is a TEM image of the nanoparticles of the block copolymer, in which the fluorescent nanoparticles can be seen with a spherical shape and they have a narrow size distribution on the nanoscale. As shown in Fig. 2, a series of pyrene-loaded nanoparticles were shaped and the mean diameter of the nanoparticles was around 100 nm. We suggest that the isolated aggregates are tending to coalesce together to form complex morphologies by further self-assembly [23], especially at the later stage of the film deposition due to higher solution concentrations. Similar phenomenon on such self-association behavior has also been observed in some amphiphilic block copolymer systems recently [24].

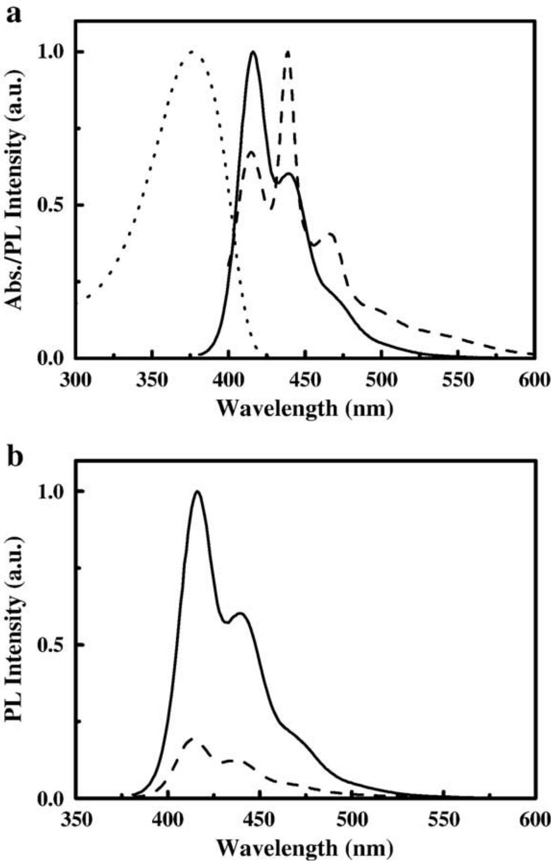


Fig. 4. (a) UV-Vis absorption (dash line) and PL spectra in THF (solid line) and film PL spectra (dash dot line) of the block copolymer; (b) PL spectra in THF (solid line) and in H_2O (dash line).

Recently, novel film deposition techniques such as layer-by-layer self-assembly [25] and inkjet printing [26] have been the subject of research as they find applications in fabrication of large-area electronic and photonic devices in a low-cost way. In these solvent-based approaches, the most attractive solvent is water. PF is known as a high-performance blue light-emitting polymer with excellent chemical and thermal stability [12]. Unfortunately, most PF derivatives are only soluble in organic solvents which limit the application of PF in water-based events. With a water-soluble chain PEG, the block copolymer can be dissolved in environment-friendly solvents such as water and ethanol, so we have succeeded preparing a novel water-soluble PF, which can form films by ink-jet printing.

The film morphology of the block copolymer is observed by polarizing and fluorescence microscopy on the glass surface. The self-assembly of the prepared block copolymer in THF solution leads to the formation of an isotropic crystalline precipitate. As shown in Fig. 3(a), this precipitate contains starlike crystals. Well known to all, the PEG has a strong property of crystallization [27], so it could make sure the presence of the PEG chain in the block copolymer. From the fluorescence microscope image (Fig. 3(b)), it can be observed that the copolymer could also exhibit the brightly blue light, so it could be concluded the existence of the conjugated PF backbone. Therefore, by polarizing and fluorescence microscopy, a favorable evidence is provide for the rod–coil block copolymer successfully prepared.

The block copolymer is well dissolved in THF because of existence of the conjugated PF backbone. UV-Vis and fluorescence spectra are shown in Fig. 4(a). The maximum absorption in THF solution is at the position of 376 nm (3.31 eV), due to the $\pi-\pi^*$ transition contributed from the conjugated PF backbone. Upon excitation of the polyfluorene main chain at 376 nm, the solution emission spectra display a vibronic fine-structure with a strongest peak at 416 nm (2.99 eV), a small band at 439 nm (2.83 eV), and a shoulder peak around at 465 nm (2.67 eV), which show that the UV-Vis absorption and PL fluorescence spectra nearly remains unchanged compared to that of polyfluorene reported previously [12,28]. The result implies that the introduction of the PEG chain onto the conjugated PF backbone does not cause perturbation of the main chain conjugation. In comparison to dilute solution, the absorption spectra of the thin film is slightly broadened but without spectral shift, whereas intensity of the emission spectra is changed. The change of the emission in solid state is probably due to the different congregation of excimers and the different dielectric constant of the environment [29]. The block copolymer is also of good water-solubility, indicating the presence of PEG chain. Fig. 4(b) gives the emission spectra in THF and in water, which are similar in shape, the band is slightly broadened in the latter case with a small blue-shift from 416 to 413 nm, and the block copolymer in H_2O exhibited lower quantum efficiency (20%) than that in THF (100%). We propose that the aggregation in water is dominated by the interchain hydrophobic interactions, which lead to lower emission intensities due to $\pi-\pi$ interactions, but the aggregates break in the THF solution. Although reduced PF interchain contacts lead to reduced self-quenching (higher emission intensities) and lower emission frequencies, yet a new aggregate structure forms, which is dominated by the interactions of PEG coil chains intertwisted together and also consistent with ^{1}H NMR spectroscopy results measurements [30]. Therefore, the blue-shifted emission band and decreased quantum efficiency in water are in agreement with the existence of interchain interactions for PF blocks.

The photo-luminescence quantum yield of the prepared copolymer thin film is quite high and *ca*. 52% measured by the integrate sphere [31] comparable to that (40%) of the precursor **3** (PF) in the solid state [32]. It indicates that the presence of a long PEG chain has little effect on the photo-luminescent properties but also succeeds preventing the aggregate formation in the block copolymer and decreasing PL quenching through non-specific interactions [33].

4. Conclusions

A highly luminescent water-soluble rod–coil block copolymer was prepared by the polycondensation method with PF as the rod segment and PEG as the coil segment. A series of measurement techniques, including ^{1}H NMR, GPC, TEM, PL, fluorescence and polarizing.microscopy were used to characterize the as-prepared copolymer. Due to ease of synthesis, its good solubility in water and its excellent PL, this kind of copolymer is expected to have great potential as a fluorescent marker for various purposes by further molecular design to perform such functions.

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References

[1] L.H. Chen, D.W. McBranch, H.L. Wang, R. Helgeson, F. Wudl, G. Whitten, Proc. Natl. Acad. Sci. 96 (1999) 12287.

[2] J. Wang, D.L. Wang, E.K. Miller, D. Moses, G.C. Bazan, A.J. Heeger, Macromolecules 33 (2000) 5153.

[3] S. Abe, L.H. Chen, J. Polym. Sci., B, Polym. Phys. 41 (2003) 1676.

[4] M. Yan, L.J. Rothberg, E.W. Kwock, T.M. Miller, Phys. Rev. Lett. 75 (1995) 1992.

[5] C.Y. Tan, M.R. Pinto, K.S. Schanze, Chem. Commun. (2002) 446.

[6] L.F. Zhang, A. Eisenberg, Science 268 (1995) 1728.

[7] L.F. Zhang, A. Eisenberg, J. Am. Chem. Soc. 118 (1996) 3168.

[8] S.A. Jenekhe, X.L. Chen, Science 279 (1998) 1903.

[9] J.S. Liu, E. Sheina, T. Kowalewski, R.D. McCullough, Angew. Chem., Int. Ed. 41 (2002) 329.

[10] H.B. Wang, H.H. Wang, V.S. Urban, K.C. Littrell, P. Thiyagarajan, L.P. Yu, J. Am. Chem. Soc. 122 (2000) 68553.

[11] D. Neher, Macromol. Rapid Commun. 22 (2001) 1366.

[12] M. Leclerc, J. Polym. Sci., A, Polym. Chem. 39 (2001) 2867.

[13] U. Scherf, E.J.W. List, Adv. Mater. 14 (2002) 477.

[14] D.A. Herold, K. Keil, D.E. Bruns, Biochem. Pharmacol. 38 (1989) 73.

[15] A. Rosler, G.W.M. Vandermeulen, H.A. Klok, Adv. Drug Deliv. Rev. 53 (2001) 95.

[16] G.N. Tew, L.M. Li, S.I. Stupp, J. Am. Chem. Soc. 120 (1998) 5601.

[17] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.

[18] J.A. Osaheni, S.A. Jenekhe, J. Am. Chem. Soc. 117 (1995) 7389.

[19] Yilgor, B.D. Mather, S. Unal, E. Yilgor, T.E. Long, Polymer 45 (2004) 5829.

[20] D. Marsitzky, T. Brand, Y. Geerts, M. Klapper, K. Mullen, Macromol. Rapid Commun. 19 (1998) 385.

[21] S.Y. Kim, I.L.G. Shin, Y.M. Lee, C.S. Cho, Y.K. Sung, J. Control. Release 51 (1998) 13.

[22] H.A. Klok, S. Lecommandoux, Adv. Mater. 13 (2001) 1217.

[23] S. Jain, F.S. Bates, Science 300 (2003) 460.

[24] T.A.T. Lee, A. Cooper, R.P. Apkarian, V.P. Conticello, Adv. Mater. 12 (2000) 1105.

[25] L. Zhai, R.D. McCullough, Adv. Mater. 14 (2002) 901.

[26] T.R. Hebner, C.C. Wu, D. Marcy, M.H. Lu, J.C. Sturm, Appl. Phys. Lett. 72 (1998) 519.

[27] L.T. Hsiue, C.C.M. Ma, H.B. Tsai, J. Polym. Sci., A, Polym. Chem. 33 (1995) 1153.
[28] W. Zhao, T. Cao, J.M. White, Adv. Funct. Mater. 14 (2003) 783.
[29] F.I. Wu, R. Dodda, D.S. Reddy, C.F. Shu, J. Mater. Chem. 12 (2002) 2893.
[30] S. Wang, G.C. Bazan, Chem. Commun. (2004) 2508.
[31] W.J. Lin, W.C. Chen, W.C. Wu, Y.H. Niu, A.K.Y. Jen, Macromolecules 37 (2004) 2335.
[32] X.Z. Jiang, S. Liu, H. Ma, A.K.Y. Jen, Appl. Phys. Lett. 76 (2000) 1813.
[33] S. Setayesh, A.C. Grimsdale, T. Weil, V. Enkelmann, K. Mullen, F. Meghdadi, E.J.W. List, G. Leising, J. Am. Chem. Soc. 123 (2001) 946.