JOURNAL OF MATERIALS SCIENCE **39** (2004) 2717–2726

Random conjugated polybenzazole copolymers: Synthesis, characterization, and exciton confinement effects in photophysical properties

SHANFENG WANG[†], PINGPING WU, ZHEWEN HAN[*]
Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China
E-mail: shanfeng_wang@yahoo.com
E-mail: zhwhan@ecust.edu.cn

New conjugated random copolymers of poly(*p*-phenylene benzobisoxazole) (PBO) and poly(2,5-benzoxazole) (ABPBO) with various compositions have been synthesized and characterized by Fourier transform infrared (FTIR), wide-angle X-ray diffraction (WAXD), UV-absorption, and photoluminescence spectra. The side-to-side distance between two neighboring PBO-ABPBO chains can be modulated by the composition ratio. The absorption, excitation, and emission peaks for the copolymers in methanesulfonic acid can also be regulated by the copolymer composition from the homopolymer ABPBO solution to homopolymer PBO solution. However, the emission peaks of copolymers in solid state are quite different from those of their homopolymers. The copolymers showed blue shifted, structured emission spectra centered with higher quantum efficiency at 470 nm compared with the parent homopolymer PBO, indicating the effects of exciton confinement in the random copolymers. The relationship between the structure and properties for the random copolymers can be interpreted roughly by the sequence length distribution of the different segments estimated from the copolymerization statistics.
© *2004 Kluwer Academic Publishers*

1. Introduction

Conjugated polymers have been explored in solid state electronic and optoelectronic devices such as light-emitting diodes (LEDs) and thin film transistors because of their semiconducting and luminescent properties [1, 2]. Compared with the traditional inorganic LEDs, the conjugated polymer-based LEDs have many advantages such as color-controllability, bendability, and easy-fabrication. Among all the existing conjugated polymers, the poly(benzazole) family including poly(*p*-phenylene benzobisoxazole) (PBO), poly(*p*-phenylene benzobisthiazole) (PBZT), and poly(2,5-benzoxazole) (ABPBO) has been studied since the early 1980s initially for the purpose of the mechanical applications [3–6]. As shown in Fig. 1, the π-conjugated and rigid structures of these polymers bring about many outstanding photoluminescence as well as mechanical properties and thermal stability. The benzoxazole group in these polymers has a strong chromophoric effect on the fluorescence of conjugated systems because it enhances the emission quantum yield via a decrease in the nonradiative decay rate constant [7]. The poly(benzazole) family is favorably considered to be superior electron-transport and hole-blocking materials in polymer light-emitting diodes (LED) [8] and thin film transistors with relatively high mobility have been made from PBZT and PBZT blends [9].

Generally speaking, there are two major challenging problems [10] in developing conjugated polymers for LEDs, (1) achieving high fluorescence quantum efficiencies and (2) obtaining spectrally pure blue luminescent polymers. Intense efforts have been performed on discovering the origin of low fluorescence quantum efficiencies [11–16] in solid-state film of conjugated polymer and obtaining spectrally pure blue luminescent polymers [10, 17]. It is believed that emission in these polymers arises from interchain and intrachain excitons. Normally the luminescence quantum efficiency is greatly suppressed and a featureless, red-shifted emission spectrum occurs upon turning from dilute solutions or blends to solid films. The formation of aggregates for the polybenzazoles in methanesulfonic acid was also reported in our earlier paper [18].

Jenekhe and his colleagues have studied on the photophysical properties of poly(benzazole) family in detail. They synthesized the rod-coil copolymers

---

[*] Corresponding author.

[†] *Present address*: Department of Polymer Science, The University of Akron, Akron, Ohio 44325, USA.

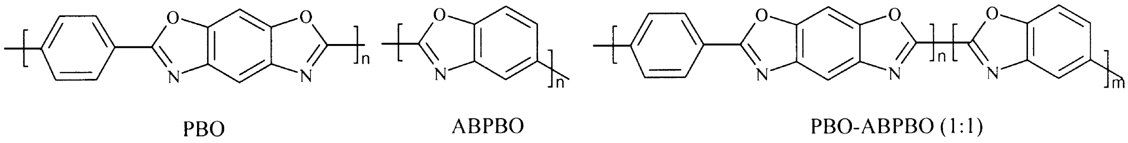


Figure 1 Chemical structures of polymers discussed herein.

consisting of such electroactive and photoactive segments [8, 19–22] and found that the luminescence quantum yield varied with copolymer composition, reaching over 6- and 7-fold enhancements compared to the "bulk" pure conjugated polymers with the formation of nanocomposites [22]. The block conjugated copolymers are expected to have novel photoluminescence and electroluminescence properties due to *quantum confinement effect* [23], which is believed not to be existent in homopolymers, random copolymers, and alternating copolymers. Jenekhe *et al.* studied the ABA triblock conjugated copolymer, poly(2,5-benzoxazole)-*block*-poly(benzobisthiazole-2,6-diyl-1,4-phenylene)-*block*-poly(2,5-benzoxazole) (TBA-4) and observed evidence for spatial confinement of excitons as well as microphase separation [24–26].

Previously the work was mainly done on the block copolymers and the blends of homopolymer and the block copolymer [24–26]. Random copolymerization is a very simple way to obtain copolymers having different structures and different properties from their parent homopolymers. In order to investigate the photoluminescence properties of random copolymers, the random copolymer PBO-ABPBO with different compositions have been synthesized and characterized, the UV and photoluminescence properties are detailed in the present paper.

2. Experimental

2.1. Materials

One monomer of PBO, 2,4-diamino-1,5-benzenediol dihydrochloride (DABDO) was prepared through a three-step reaction from resorcin in our laboratory according to Ref. [27].

The monomer of ABPBO, 3-amino-4-hydroxybenzoic acid hydrochloride (AHBAH) was also prepared through a two-step reaction from *p*-hydroxylbenzoic acetate in our laboratory according to the modified method discussed in Ref. [28].

Terephthalic acid (TPA) was purchased from Beijing Xudong Chemical Co. and it was ground fine before using as the second monomer for polymerizing PBO.

The polymerization medium, poly(phosphoric acid) (PPA) with a P_2O_5 content of 80.8% was newly prepared using 85% phosphoric acid (purchased from Suzhou Jincheng Chemical Co.) and phosphorus pentoxide (P_2O_5) (obtained from Shanghai 1st Chemical Co.).

2.2. Synthesis

The synthesis and characterization of the conjugated homopolymers PBO and ABPBO were reported in the literature [3–6]. The modified synthesis methods were also reported in our previous papers [27, 28].

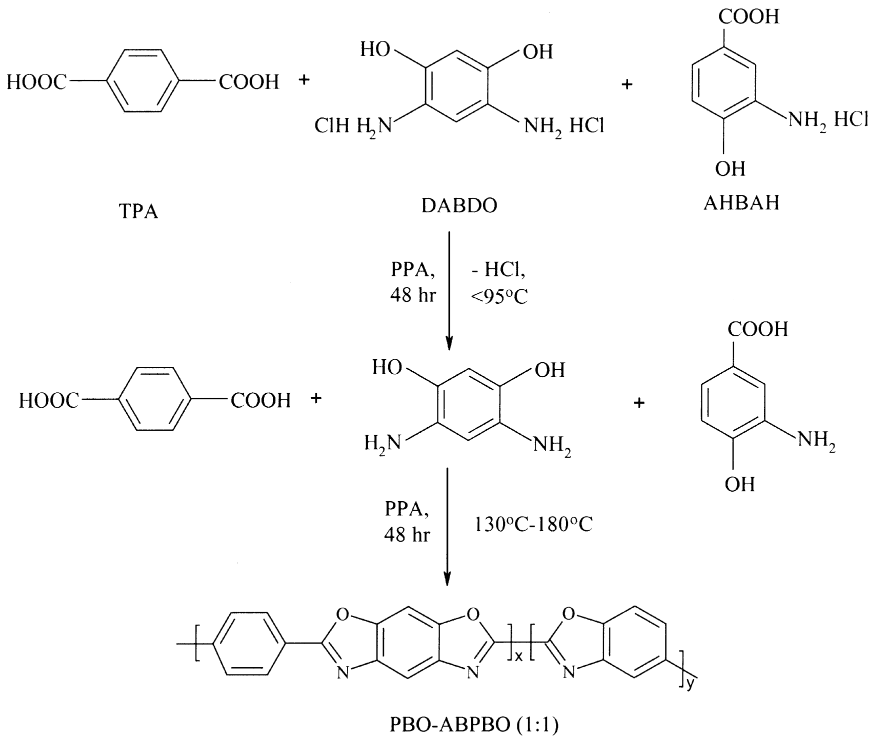
The following procedure shown in Scheme 1 exemplifies the synthesis of the three different compositions of the PBO-ABPBO random copolymers. In the polymerization of PBO-ABPBO (1:1), a total of 10.0 g (52.7 mmol) AHBAH, 11.2373 g (52.7 mmol) DABDO and 8.7621 g (52.7 mmol) TPA were mixed together with the calculated weight of 73.65 g newly prepared 80.8% PPA in a glass reactor vessel installed with a mechanical stainless stirrer described in Ref. [29], two gas ports and one port for feeding fresh P_2O_5 during the polycondensation. The reaction vessel was purged with argon for one hour, and dehydrochlorination (i.e., removal of HCl from AHBAH and DABDO) was performed at 90°C for at least 20 h with argon atmosphere. During the dehydrochlorination, interval vacuum was applied to speed up the process until the gas flowing from the reaction mixture did not show acidity. After complete dehydrochlorination, 44.66 g fresh P_2O_5 was added into the reaction vessel under positive argon pressure after the vessel cooled down to 50°C. The reaction mixture was stirred for 30 min and the temperature was progressively raised to 130°C in 2 h and maintained at that temperature for 10 h. When the reaction mixture showed stir opalescence, the temperature was raised to 160°C for 12 h and finally to 180°C and held at this temperature for 12 h. The final P_2O_5 content of PPA became 84% and the concentration of the polymer in PPA became 13%.

We modified the polymerization so that the monomers can be mixed together at the very beginning in order to ensure that TPA and DABDO are molar equivalent instead of adding TPA later after complete dehydrochlorination. High molecular weight polymers can also be obtained through this modified procedure and it is convenient for operators.

The highly viscous polymerization dope was extracted on a heated glass board and then immersed in a large volume of cold water for at least 3 days to remove polymer medium PPA completely. The water bath was examined with pH paper till it became neutral. Then the polymer films were dried in air. The polybenzazole samples were washed again by acetone and deionized water and then dried sufficiently to minimize the absorbed moisture before doing measurements.

Heat treatment of the polymer film samples was carried out in a muffle oven at different temperatures, such as 200, 350, 450, and 550°C for 10 min. The polymer films were fixed in a copper clamp in order to be oriented by the tension during the heat treatment. Anal. Calcd for PBO-ABPBO: C, 71.80; N, 2.58; H, 11.90. Found: C, 69.62; N, 2.65; H, 11.45.

The synthesis of the other two copolymers with different compositions was similar to that of PBO-ABPBO (1:1). The difference was in the mole ratio of DABDO (or TPA) to AHBAH. All the calculations for



Scheme 1 Random copolymerization of PBO and ABPBO.

the weights of the monomers and P_2O_5 were based on the final concentration of polymer and the P_2O_5 content in PPA. Both are required that a proper concentration of the polymers in the medium in order to get a nematic phase and a proper final P_2O_5 content to get the optimal medium for polymerization. The formulae used for calculations are deduced in the way similar to the previous report [6].

2.3. Characterization

The molecular weights of PBO, ABPBO are 14000, and 46000 g mol^{-1}, respectively, which were estimated by Mark-Houwink equations [3] and intrinsic viscosities obtained. PBO-ABPBO (1:1) has an intrinsic viscosity of 670 cm^3/g in methanesulfonic acid (MSA) at 25°C. The intrinsic viscosities of the polymers and copolymers were determined by using a modified device containing a dilution Ubbelohde capillary viscometer (MC 0.8–0.9 mm) described in Ref. [30]. MSA was obtained from Aldrich-Sigma Chemical Co. Polymer solutions were prepared in MSA in the glove box. The polymer solution used in the absorption and photoluminescence measurements has a concentration of 4.4 g/m^3, which corresponds to 3.14×10^{-7} M for PBO given the molecular weight of 14000 g mol^{-1}. The polymer thin films used in solid-state photoluminescence determination were prepared using the method [31, 32] proposed by Jenekhe *et al.*, i.e., the solution cast from the polybenzazoles in the mixture of nitromethane (NM) and aluminum chloride ($AlCl_3$) with a polymer concentration of about 3 wt%. The thin films were dried at 80°C in a vacuum oven for 12 h after complete decomplexation in deionized water for at least 3 days. Fourier transform infrared (FTIR) spectra were taken on freestanding films of the polymers at room temperature using Nicolet Magna-IR 550 FTIR spectrometer.

Wide-angle X-ray diffraction (WAXD) 2θ scans were collected in a range of 5–60° on a Rigaku D/max-rB rotating anode X-ray generator with Ni-filtered Cu K_α ($\lambda = 0.15401$ nm) radiation operated at 100 mA and 40 kV.

Absorption spectra and photoluminescence spectra of the polymer solutions of MSA were recorded at room temperature on a Shimadzu UV-365 UV-visible spectrophotometer and on a Hitachi 850 fluorescence spectrophotometer, respectively. Photoluminescence spectra of the polymer thin films were recorded on a Hitachi F-3000 fluorescence spectrophotometer at room temperature in Institute of Chemistry, Academia Sinica in Beijing.

3. Results and discussion

3.1. New random copolymer PBO-ABPBO: molecular structure

A comparison of the FTIR spectra of ABPBO, PBO, and their copolymer PBO-ABPBO (1:1) is shown in Fig. 2. Because the structure of ABPBO is similar to that of PBO, the FTIR spectra of those three polymers share many absorption peaks, such as 1058, 1012 (=C—O—C); 852, 819, 705 (C=CH on the substituted phenyl rings); 1230 (C=CH), 1268 (—C—O—C, asymmetric); 1618 (C=N and C=C); 3448 (—OH) cm^{-1}. The comparison shows that FTIR spectrum of the copolymer PBO-ABPBO is almost identical to that of PBO except there are two groups of characteristic peaks standing for ABPBO. The strong peak at 885–870 cm^{-1} indicates the absorption for 1,2,4 substitution in phenyl rings. The other absorption peak for $\beta_{C=C}$ appears at 1230 cm^{-1}. PBO-ABPBO's FTIR spectrum contains the information for both components in the copolymer. It suggests that the copolymer consists of two components, PBO and ABPBO.

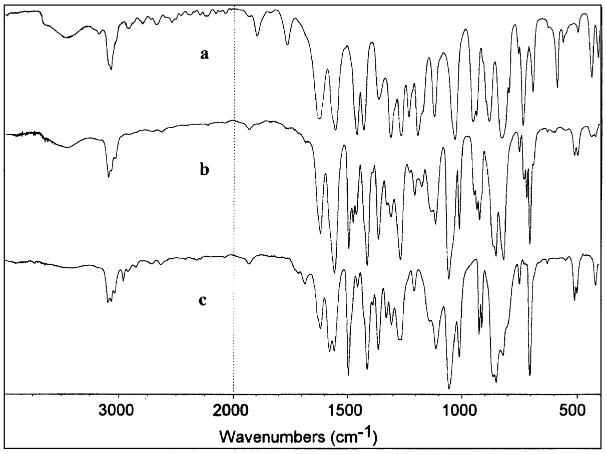


Figure 2 FTIR spectra of ABPBO (a), PBO-ABPBO (1:1) copolymer (b), and PBO (c).

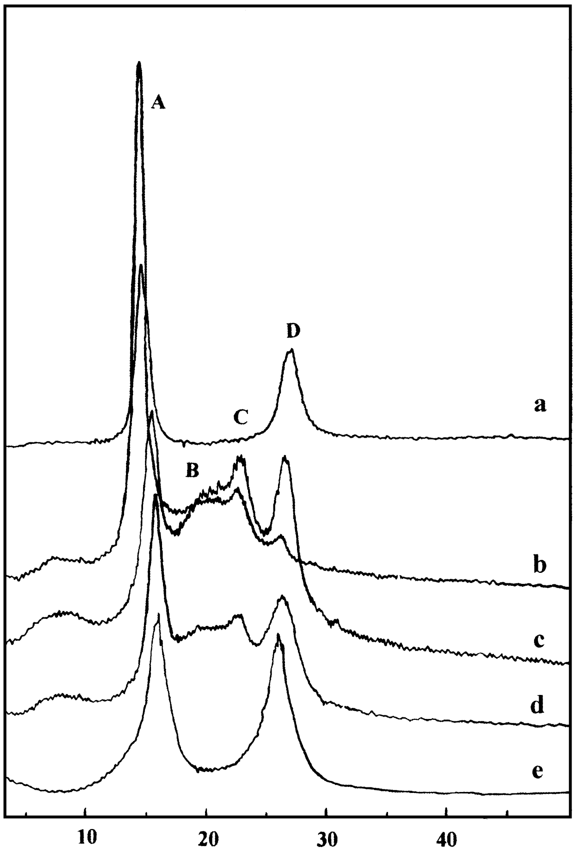


Figure 3 WAXD patterns for ABPBO (a), PBO (e), and PBO-ABPBO copolymers (b: 1:3, c: 1:1, d: 3:1).

The concentration to form liquid-crystalline phase in the PBO-ABPBO (1:1) copolymerization dope lies between 6.5 and 16 wt% roughly. It was reported that PBO's concentration range for nematic phase is 5 to 14 wt% and ABPBO's is 14.5 to 16 wt% [6]. When the copolymerization was designed to have a final polymer concentration of 7 wt%, the intrinsic viscosity was only 262 cm^3/g. It increased to 343 cm^3/g when the copolymer concentration was 10 wt% and leveled off to 665 cm^3/g for 13 and 15 wt%. The concentration range for the nematic phase of PBO-ABPBO (1:1) copolymer is broader than both of the components and the final copolymer concentration in the polymerization is vital to get the high molecular weight copolymers.

The ordered structure of the copolymers with different compositions of PBO and ABPBO can be displayed by wide angle X-ray diffraction (WAXD) as shown in Fig. 3 and all the related information is listed in Table I. All the samples were heat treated under tension in a muffle oven at 550°C before the WAXD measurements. The diffraction peak positions stand for the periodicity of ordered array of the copolymer chains. The interplanar distance of the copolymers, calculated from the angle of the diffraction peak by using the following Bragg's equation as a function of a number of units:

$$2d \sin\theta = n\lambda \qquad (1)$$

where d is the interplanar distance, θ is the scattering angle, n is the order of the reflection, and λ is the wavelength of the X-ray used. In the present case, n is 1 and λ is 0.15418 nm for nickel-filtered Cu K_α radiation.

All the polymers shown in Fig. 3 have two strong peaks at the interplanar spacing corresponding to around $2\theta = 15°$ (~0.6 nm, labeled as peak A) and 26° (~0.34 nm, labeled as peak D). As to copolymers, there are two weak peaks at around $2\theta = 20°$ and 23° between the two strong peaks. They are marked in Fig. 3 and Table I as peak B and peak C. It can be observed that the corresponding interplanar distance at peak A increases with the content of ABPBO. The periodicity here stands for the side-to-side distance between two neighboring polybenzazole rigid chains. For pure PBO, its side-to-side distance is 0.549 nm as shown in Table I, corresponding to (200) plane [33]. While the value for pure ABPBO is slightly larger than that with 0.607 nm due to a catenation angle of 162°, which is less than the value of 180° for PBO [6]. The interplanar distance at the peak A for ABPBO was reported to be the response to (100) plane [34]. When the ABPBO content in the copolymers increases, it can be expected that the side-to-side distance of two original neighboring PBO chains be raised by the addition of nonfully linear ABPBO segments. It should be noted that PBO and ABPBO crystalline cells belong to different

TABLE I WAXD results of ABPBO, PBO, and their copolymers PBO-ABPBO

	2θ(°)				d (nm)			
Sample	A	B	C	D	A	B	C	D
a: ABPBO	14.6	/	/	26.6	0.607	/	/	0.335
b: PBO-ABPBO (25%:75%)	14.2	21.0	22.5	26.1	0.623	0.423	0.396	0.341
c: PBO-ABPBO (50%:50%)	15.2	20.0	22.4	26.1	0.583	0.443	0.396	0.341
d: PBO-ABPBO (75%:25%)	15.6	19.2	22.5	26.1	0.567	0.462	0.394	0.341
e: PBO	16.1	/	/	26.5	0.549	/	/	0.336

crystalline systems. PBO is monoclinic [33] while ABPBO is pseudo-orthorhombic [34]. Both crystalline systems were interfered by each other to some content and some disordered morphology of the copolymers showed up in WAXD patterns as peak B and peak C. The peak positions of B and C do not change much with the composition of the copolymers, whereas B peak corresponds to a distance of 0.42–0.46 nm and C peak corresponds to a distance of 0.395 nm. They can be interpreted as the distances in the connection domain or defects of the two components in the copolymers. The diffraction peak D at $2\theta = 26^\circ$ for all the polymers shown in Fig. 3 stands for the face-to-face distance between two neighboring polymer chains. The face-to-face distance for PBO is 0.336 nm, corresponding to (010) plane [33] and that for ABPBO is 0.335 nm, corresponding to (010) and (110) planes [34]. These two are quite close to each other, while the face-to-face distances of the copolymers are slightly larger than 0.335 nm and almost identical to each other for different compositions. The peak D in WAXD patterns indicates that the rings of PBO and ABPBO are still coplanar with a small angle between two consecutive ring axes. The addition of ABPBO segments to the PBO chain mainly changes the side-to-side distance between two neighboring chains.

It should be noted that the copolymer PBO-ABPBO with an ABPBO composition of 75% has a unique WAXD pattern. As shown in curve b in Fig. 3, the intensity of peak A is almost 5 times larger than those of other two copolymers and 10 times larger than that of peak C, which is the second strongest peak in the WAXD pattern. Meanwhile, it was very difficult to dissolve the copolymer PBO-ABPBO (1:3) in $AlCl_3$/NM to form a homogeneous solution like other copolymers, which indicates the relationship between the solubility and the crystalline structure. The similar solvent resistance was also reported in vinylene-linked PBZT due to the nature of chain packing and strong intermolecular interactions [20]. It needs further studies to know how the chain packing and therefore intermolecular interactions affect the solubility of the conjugated polymers.

Heat treatment of polybenzazoles has a significant effect on their polymer structures and mechanical properties as it gets rid of P_2O_5 and advances further the reaction of cyclization [35]. After heat treatment, the chain regularity and the conjugation length in these polymers were improved and the packing of the polymer chains became more compact. Our previous results showed that the WAXD patterns for ABPBO and poly(2,5-benzothiazole) (ABPBT) became stronger and sharper with a slight decrease in the interplanar distance after heat treatment, indicating more compact chain arrangements and longer conjugation lengths [35]. In electron paramagnetic resonance (EPR) studies [36], the spin centers were observed to be delocalized over more conjugation units in PBO-ABPBO copolymers and other polybenzazoles, which resulted in the decrease of the EPR line-width, i.e., "motion narrowing". In the EPR studies, PBO-ABPBO have electron Zeeman g-factor values around 2.0045, which is a typical nitrogen-participated g-value [36]. The PBO-ABPBO (1:1) copolymer samples were heat treated in a muffle oven at different temperatures for 10 min and the WAXD patterns are shown in Fig. 4. The interplanar distances were calculated using Bragg equation (Equation 1) and listed in Table II.

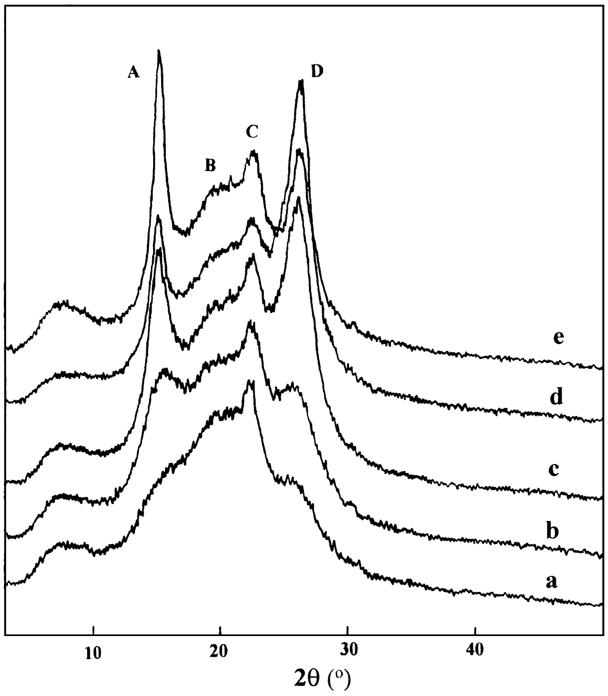


Figure 4 WAXD patterns for PBO-ABPBO (1:1) films heat-treated at different temperatures (a: as received; b, c, d, e: 200, 350, 450, 550°C for 10 min).

It can be observed that the untreated polymer film shows a broad diffraction peak representing a disordered and amorphous morphology. With increasing the heat treatment temperature, the peak A and the peak D showed up gradually in WAXD patterns and the intensities of them increased dramatically. The half-peak width of the peaks also decreases, which means that the regularities in side-to-side direction and

TABLE II WAXD results of PBO-ABPBO (1:1) heat-treated at different temperatures

	$2\theta(^\circ)$				d (nm)			
Sample	A	B	C	D	A	B	C	D
a: as-received	/	19.2	22.7	25.7	/	0.461	0.392	0.346
b: 200°C, 10 min	15.6	20.0	22.7	25.7	0.566	0.443	0.392	0.346
c: 350°C, 10 min	15.3	19.8	22.6	26.2	0.578	0.448	0.393	0.340
d: 450°C, 10 min	15.1	20.8	22.4	26.0	0.588	0.426	0.397	0.342
e: 550°C, 10 min	15.2	20.0	22.4	26.1	0.583	0.443	0.396	0.341

face-to-face direction of those polymer chains were enhanced efficiently by heat treatment. The peak B and peak C did not change much with the heat treatment temperature. Even after heat treatment at 550°C, both peaks were still at the same positions with the same intensities, meaning the connection domains of the two components PBO and ABPBO are the permanent defects in the ordered structure of the copolymers.

3.2. Chain sequence length distribution in copolymer

Jenekhe *et al.* [22] applied copolymerization statistics to predict the sequence length distribution of the conjugated rod-like segments and the prediction was indeed consistent with the ^{1}H NMR results. In this paper, the two components in the random copolymers are both rigid-rod like and similar in structure. Moreover, PBO-ABPBO copolymers are difficult to be dissolved in ordinary solvents. So, the rough estimation of the sequence length distribution of the two segments is presented here without ^{1}H NMR analysis.

In Jenekhe's work, 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT), the monomer of PBZT, reacted to both terephthalic acid (TPA) and 1,10-decanedicarboxylic acid in PPA to form rod-coil copolymers [22]. In the copolymerization of PBO and ABPBO, the reaction was more complicated because there was one monomer AHBAH having both acid (short as A) and basic (short as B) functional groups on itself. To our knowledge, it is the first attempt to apply copolymerization statistics to the present system containing three different components. If we first denote DABDO as BB, TPA as AA, and AHBAH as BA, then we can see that the segmented PBO-ABPBO copolymer chain architecture in Scheme 1 can be denoted as (BB-AA)$_x$(BA)$_y$ where the segment chain lengths x and y are statistical in nature. So the overall composition of PBO f is $\sum x/(\sum x + \sum y)$ and the distribution of the segmental lengths x and y is determining to the chain packing, conformations, and other physical properties of the copolymers. There are two assumptions for doing the copolymerization statistics of this system [37]. One is that copolymerization is expected to be irrelevant of the reactivities of the monomers [37], another is that functional groups react with other completely. In the polycondensation, it is necessary to realize the second assumption in order to obtain the copolymers with high molecular weights [37].

Let p be the probability that a condensation reaction occurs between the acid functional group A of TPA and the basic functional group B of DABDO; $1 - p$ is the probability that a condensation reaction occurs between A of TPA and B of AHBAH. Then the probability that a condensation reaction occurs between the basic functional group B of DABDO and the acid functional group A of TPA is p; $1 - p$ is the probability that a condensation reaction occurs between B of DABDO and A of AHBAH. Also, the probability for an acid group A (or a basic group B) of AHBAH to react with B of DABDO (or A of TPA) is p; while the probability for it to react with a basic group B (or an acid group A) of itself is $1 - p$. The value of p is related to the fraction of the functional groups forming PBO segments in the total functional groups. For example, when PBO:ABPBO = 1:1, 3:1, and 1:3, $p = 2/3$, 6/7, and 2/5 respectively. The probability $P_{\mathrm{I}}(x)$ that the sequence –BB– in (BB-AA)$_x$ is:

$$P_{\mathrm{I}}(x) = (1-p)^2[2xp^{2x-1} + (2x+1)p^{2x}],$$
$$0 < p < 1; \quad \sum_{x_i}^{\infty} P_{\mathrm{I}}(x) = 1 \qquad (2)$$

The details for deducing the probability $P_{\mathrm{I}}(x)$ are described in Appendix.

Fig. 5 shows the probability of block size of –BB– for three different compositions of PBO in copolymers using this probability model. The probability of –AA– in (BB-AA)$_x$ is identical to that of –BB–. Similarly, one can calculate the probability of –AB– in the polymer chains. The probability of –AB– in BB-(AB)$_y$-AA is

$$P_{\mathrm{II}}(y) = y(1-p)^{y-1}p^2 \qquad (3)$$

One can see in Fig. 5, the block size distribution of –AB– at different compositions of PBO in the copolymers. The most possible sequence length can

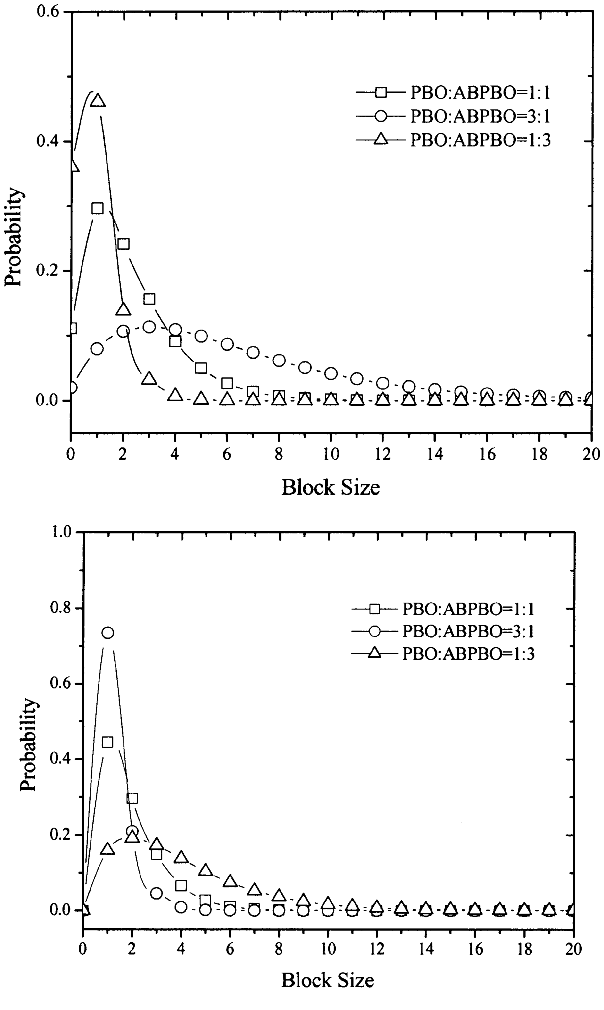


Figure 5 Probability distribution of –BB– (top) and –AB– (bottom) block sizes according to Equations 2 and 3, respectively.

be obtained for –BB– (or –AA–) and –AB–.

$$\begin{aligned} x_{\max} &= -\frac{1+p+p\ln p}{2(\ln p + p\ln p)}, \\ y_{\max} &= -\frac{1}{\ln(1-p)}; \quad 0 < p < 1 \end{aligned} \tag{4}$$

When PBO:ABPBO is 1:1, 1:3, and 3:1, $x_{\max}$ is 1.003, 0.403, and 3.013, respectively, while $y_{\max}$ is 0.910, 1.958, and 0.514. It can be seen that the statistical results show that the most possible block size of (BB-AA) is one and that for (AB) is also one when PBO:ABPBO = 1:1, which means that the copolymerization is close to an alternating copolymerization in this case. When the composition of one segment in the copolymer is dominant, the sequence of another segment is liable to be interrupted by the dominant segments and difficult to be long. In the case of PBO:ABPBO = 1:3, it can be observed in Fig. 5 that the probability of the block size of 1 for PBO segment is about 45%, while it decreases dramatically to 13 and 4% for block size 2 and block size 3. It means that the acid groups of TPA more easily reacted with the basic groups of AHBAH instead of DABDO because it was statistically favored when the amount of AHBAH was dominant in the reaction mixture. Meanwhile, the basic groups of DABDO were also liable to react with the acid groups of AHBAH. Then the crystalline structure of PBO was almost broken in the copolymer chains while it remained in other two cases, which can be considered as a possible reason for the extremely high intensity of diffraction peak A for PBO-ABPBO (1:3) mentioned in Section 3.1.

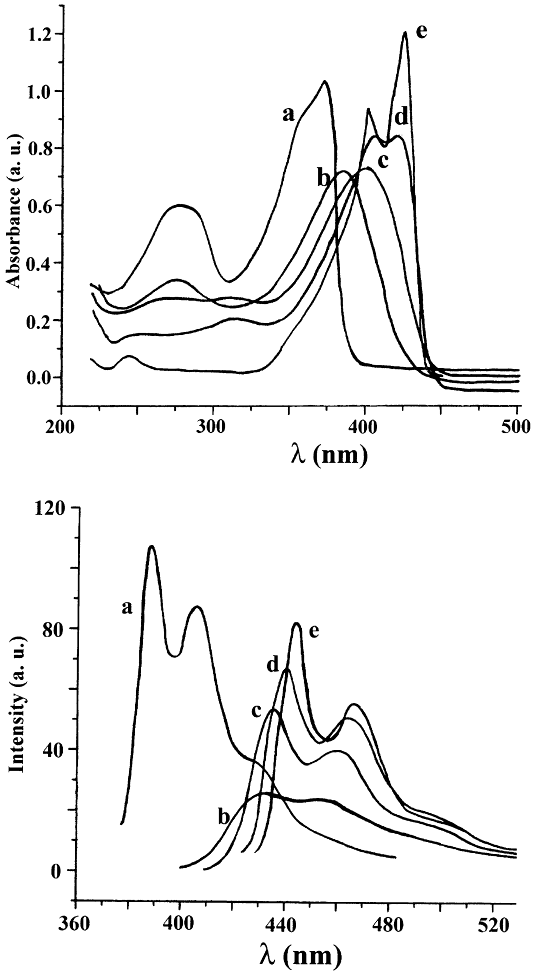


Figure 6 UV absoption spectra (top) and photoluminescence emission spectra (bottom) of ABPBO (a), PBO (e), and PBO-ABPBO (b: 1:3, c: 1:1, d: 3:1) in MSA (C = 4.4 g/m^3).

3.3. UV absorption spectra and PL spectra of copolymers in MSA and in solid state

The detailed investigation of the absorption spectra and PL spectra of copolymers in MSA at various concentrations was presented in our earlier paper [18]. In this section, we want to make a comparison between the results for the copolymers in MSA dilute solution and in solid state. Fig. 6 shows the UV-absorption spectra and the corresponding emission spectra of the polymer solutions with a concentration of 4.4 g/m^3. It is evident that the UV-absorption spectra for copolymers have their own characteristic bands and the UV-absorption peak of the polymer shifts to longer wavelength with the increase of PBO composition in the copolymers, from 373 nm for the pure ABPBO solution to 425 nm for the pure PBO solution. This result is expected considering that the coplanarity of protonated PBO rigid chain in the dilute solutions is better than that of ABPBO because ABPBO adopts both *trans* and *cis* conformations and *cis*-conformation can induce the coil-like array in ABPBO solution and then deteriorate the coplanarity of the polymer chain in dilute solutions [6].

Fig. 6 also shows the emission spectra and the peak positions for excitation spectra and emission spectra are listed in Table III. The peaks appearing in the emission spectra can be divided into three groups, as shown in Table III as Em1, Em2, and Em3. Similar to absorption spectra, the emission spectra also show the red shift of the peak with the increase of PBO fraction in PBO-ABPBO copolymers. It should be noted that the emission curve of ABPBO at the concentration of 4.4 g/m^3 is quite displaced from other polymers at the same concentration while the difference is not that large for the concentration of 1200 g/m^3 [18]. As mentioned above, ABPBO can assume *cis*-conformation when the concentration is low enough and PBO is a rigid-rod polymer at any concentration [6]. So the larger difference at the lower concentration may suggest that the PBO segments can efficiently give the hindrance to the *cis*-conformation of ABPBO chain. At higher concentrations, the formation of aggregates in the polymer molecules reduced the quantum efficiency and brought some new featureless emission bands at longer wavelengths [18, 39].

Fig. 7 shows the PL excitation and emission spectra of thin films of PBO and two PBO-ABPBO copolymers with composition ratios of 3:1 and 1:1 for PBO:ABPBO. It was mentioned in the previous discussion that PBO-ABPBO (1:3) was very difficult to be dissolved in AlCl$_3$/NM to fabricate thin films. So here we just present the results for the other two PBO-ABPBO copolymers. It should be noted that the PL spectra of solid thin films were obtained from different fluorescence spectrophotometers; the intensity here in Fig. 7

TABLE III Excitation and emission bands of polymers in MSA at 4.4 g/m^3 and solid thin films

Sample	State	Ex^a (nm)	I_x^{b} (a.u.)	Em$_1$^{c} (nm)	I_1 (a.u.)	Em$_2$ (nm)	I_2 (a.u.)	Em$_3$ (nm)	I_3 (a.u.)
ABPBO	Solution	376	63	388	107	406	87	/	/
PBO-ABPBO (1:3)	Solution	382	65	432	25	452	23	/	/
PBO-ABPBO (1:1)	Solution	399	85	438	53	461	39	/	/
	Solid	415	11	/	/	469	11	/	/
		431	10						
PBO-ABPBO (3:1)	Solution	424	100	440	67	466	50	/	/
	Solid	316	14			472 (491, 502)	18 (13, 13)	/	/
		346	18						
		415	19						
PBO	Solution	430	102	442	72	466	55	/	/
	Solid	415	7	/	/	/	/	544	8

^{a}Excitation wavelength.
^{b}Intensity.
^{c}Emission wavelength.

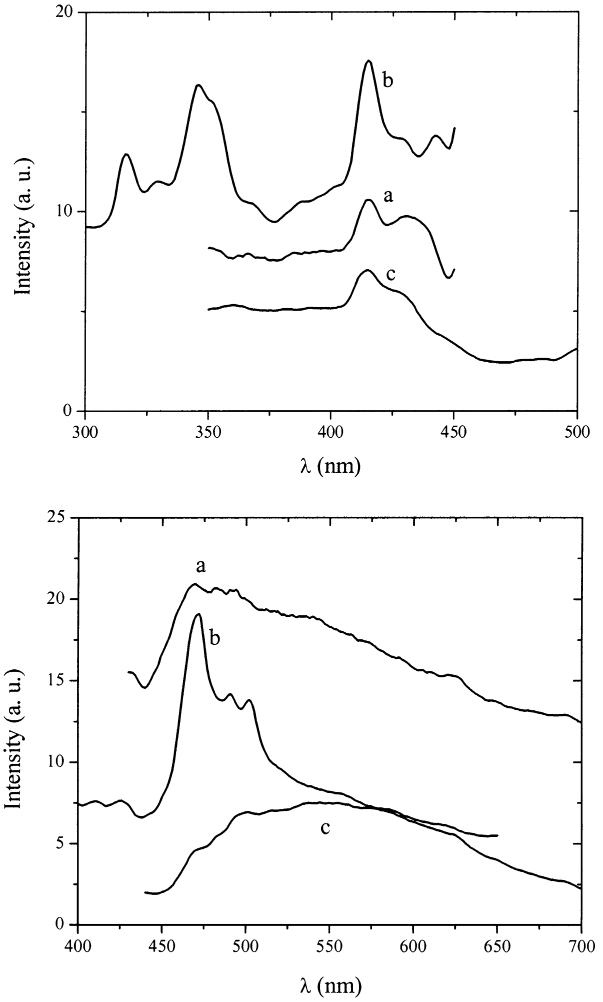


Figure 7 Photoluminescence excitation spectra (top) and emission spectra (bottom) of PBO-ABPBO (a: 1:1, b: 3:1), and PBO (c) thin films after heat-treatment at 80°C.

cannot be directly compared with that of solutions. The excitation and emission spectra were vertically shifted arbitrarily to separate from each other; the intensities are shown in Table III. When the molecules with lower emission energy are introduced to organic one-dimensional (1-D) semiconductors, they would form the discontinuous delocalized quantum well state in energy band, which are well-like PL emission centers [23]. Jenekhe [24, 25] synthesized some triblock copolymers using PBZT and ABPBO with different segmental lengths because of a large potential barrier can be expected ($\Delta E_g = E_g^A - E_g^B = 0.76$ eV). The energy band gaps for two parent homopolymers PBO and ABPBO are 2.76 eV [38] and 3.24 eV [25]. The difference between the two energy gaps is 0.48 eV, which is less than that between PBZT and ABPBO and the copolymers were synthesized by random polymerization.

Although the absorption and emission peaks of the copolymers in solutions can be modulated by the composition, the solid samples are quite different from the parent homopolymers in their emission spectra. The excitation and emission peak positions for thin films are also listed in Table III. From the excitation spectra, one cannot observe the additive spectra of the excitation spectra of two parent components as being reported for the triblock copolymer TBA4 [24, 25]. The main excitation peaks for all the polymer samples here are around 415 nm and the emission spectra were recorded when the thin films were excited at 415 nm. The emission peak position for homopolymer PBO is at 544 nm and the spectrum is structureless and broad (in the 450–700 nm region). It was also reported that ABPBO has a relatively weak emission in the 380–430 nm region [25]. After random copolymerization, the emission peaks blue shifted from 544 nm for PBO to 472 nm and 469 nm for PBO:ABPBO = 1:3 and 1:1, respectively. It reflects that the copolymers are spectrally pure blue luminescent polymers since the emission wavelengths lie in the blue emission wavelength region of 440–495 nm. For PBO-ABPBO (3:1), the quantum efficiency is also enhanced compared to PBO homopolymer and the emission spectrum shows a structured curve in a narrower wavelength region of 450–550 nm. This result is striking because it is similar to the two-dimensional (2-D) spatial confinement of PBZT quantum wires as TBA4 was diluted in the matrix of ABPBO [25, 26]. In that case, a blue shift from the pure PBZT and band narrowing were observed upon increasing dilution of TBA4 in ABPBO matrix [25, 26]. Generally speaking, the structured PL spectra shows that the copolymers are related to some isolated polymer chains, for example, the polymer chains in dilute solution or dispersed in some other polymer matrix without any interchain interactions to form aggregates [18, 39]. The same effect can be achieved in the present random polymers because PBO segments were diluted in ABPBO segments, which is similar to Jenekhe's blending method [25, 26]. It should be noted that the thin films in Fig. 7 were dried at 80°C in a vacuum oven for 12 h after complete decomplexation, the polymer thin films were disordered and amorphous according to the morphology study in Figs 3 and 4. The disordered microstructure also deduced the intermolecular interaction and therefore the interchain and intrachain excimer or aggregation formation [22, 39] in solid state due to the ordered array of the rigid-rod molecules could be further suppressed.

In comparison with the previous work [24–26] on block-copolymers and blends based on PBZT and ABPBO, it is a more convenient way to produce such conjugated copolymers without introducing any non-conjugated components, which may cause poor charge transport and ruin the original outstanding mechanical properties of polybenzazoles [26]. Further studies are going to be done in order to better the understanding about the quantum confinement effect and the application of such conjugated copolymers.

4. Conclusions

Novel conjugated random copolymers of poly(*p*-phenylene benzobisoxazole) (PBO) and poly(2,5-benzoxazole) (ABPBO) with different compositions were synthesized through a rather simple way and characterized by Fourier transform infrared (FTIR), wide-angle X-ray diffraction (WAXD), UV-absorption, and photoluminescence spectra. This kind of PBO-ABPBO copolymer has a larger concentration range ($\sim$6.5 to $\sim$16 wt%) to form nematic phase than their parent homopolymers. The addition of ABPBO segments into the PBO polymer chain increased the side-to-side distance between the neighboring polymer chains without affecting the face-to-face distance much. The heat treatment can enhance the regularity of the copolymer chains and make the copolymer chains pack more closely. Two disordered WAXD peaks are found in the copolymers and those two peaks do not change with composition and heat treatment. The absorption, excitation, and emission peaks for the copolymer dilute solutions in methansulfonic acid can be regulated by the copolymer composition from the homopolymer ABPBO solution to homopolymer PBO solution. But the PL emission peaks for copolymer thin films are quite different from those for the parent homopolymers. Such random copolymers showed the blue shifted, structured emission spectra centered at 472 nm with higher quantum efficiency due to exciton confinement effects. The relationship between the structure and properties for the random copolymers can be roughly interpreted by the sequence length distribution of the different segments estimated from the copolymerization statistics.

Acknowledgement

We gratefully acknowledge the financial support granted by the National Natural Science Foundation of China (No. 29774007) and the National High Technology Plan.

Appendix

The probability $P_{\mathrm{I}}(x)$ that the sequence –BB– in (BB-AA)$_x$ can be divided into four possibilities.

(1) BA-[BB-AA]$_x$-BA
(2) AB-[AA-BB]$_x$-AB
(3) BA-[BB-AA]$_x$-BB-AB
(4) AB-AA-[BB-AA]$_x$-BA

The probabilities for these four cases are $P_1(x) = xp^{2x-1}(1-p)^2$, $P_2(x) = xp^{2x-1}(1-p)^2$, $P_3(x) = (x+1)p^{2x}(1-p)^2$, and $P_4(x) = xp^{2x}(1-p)^2$, where p is be the probability that a condensation reaction occurs between the acid functional group A on TPA and the basic functional group B on DABDO.

The total probability $P_{\mathrm{I}}(x)$ of the sequence –BB– in (BB-AA)$_x$ is

$$P_{\mathrm{I}}(x) = (1-p)^2\left[2xp^{2x-1} + (2x+1)p^{2x}\right],$$
$$0 < p < 1; \quad \sum_{x_i}^{\infty} P_{\mathrm{I}}(x) = 1.$$

The probability $P_{\mathrm{II}}(y)$ of –AB– in (AB)$_y$ is simpler. There is only one possibility, i.e., (AB)$_y$ segment is in BB-(AB)$_y$-AA. The probability $P_{\mathrm{II}}(y)$ is

$$P_{\mathrm{II}}(y) = y(1-p)^{y-1}p^2, \quad 0 < p < 1;$$
$$\sum_{y_i}^{\infty} P_{\mathrm{II}}(y) = 1.$$

References

1. R. H. FRIEND, R. W. GYMER, A. B. HOLMES, J. H. BURROUGHES, R. N. MARKS, C. TALIANI, D. D. C. BRADLEY, D. A. DOS SANTOS, J. L. BREDAS, M. LOGDLUND and W. R. SALANECK, *Nature* **397** (1999) 121.
2. H. E. KATZ and Z. BAO, *J. Phys. Chem.* **104** (2002) 671.
3. J. F. WOLFE, in "Polybenzaothiazole and Polybenzoxazoles," edited by H. F. Mark, "Encyclopedia of Polymer Science and Technology," 2nd ed. (Wiley, New York, 1988) Vol. 11, p. 601.
4. J. F. WOLFE and F. E. ARNOLD, *Macromolecules* **14** (1981) 909.
5. J. F. WOLFE, B. H. LOO and F. E. ARNOLD, *ibid.* **14** (1981) 915.
6. A. W. CHOW, S. P. BITLER, P. E. PENWELL, D. J. OSBORNE and J. F. WOLFE, *ibid.* **22** (1989) 3514.
7. Y.-H. SO, J. M. ZALESKI, C. MURLICK and A. ELLABOUDY, *ibid.* **29** (1996) 2783.
8. M. M. ALAM and S. A. JENEKHE, *Chem. Mater.* **14** (2002) 4775.
9. A. BABEL and S. A. JENEKHE, *J. Phys. Chem.* B **106** (2002) 6129.
10. J. A. OSAHENI and S. A. JENEKHE, *Macromolecules* **27** (1994) 739.
11. I. D. W. SAMUEL, G. RUMBLES and C. J. COLLINS, *Phys. Rev.* B **52** (1995) R11573.
12. J. W. BLATCHFORD, T. L. GUSTAFSON, A. J. EPSTEIN, D. A. VANDEN BOUT, J. KERIMO, D. A. HIGGINS, P. F. BARBARA, D. K. FU, T. M. SWAGER and A. G. MACDIARMID, *ibid.* **54** (1996) R3683.
13. J. W. BLATCHFORD, S. W. JESSON, L.-B. LIN, T. L. GUSTAFSON, D. K. FU, H. L. WANG, T. M. SWAGER and A. G. MACDIARMID, *ibid.* **54** (1996) 9180.

14. U. LEMMER, S. HEUN, R. F. MAHRT, U. SCHERF, M. HOPMEIER, U. SIEGNER, E. O. GOBEL, K. MULLEN and H. BASSLER, *Chem. Phys. Lett.* **240** (1995) 373.
15. T.-Q. NGUYEN, V. DOAN and B. J. SCHWARTZ, *J. Chem. Phys.* **110** (1999) 4068.
16. R. JAKUBIAK, C. J. COLLISON, W. C. WAN, L. J. ROTHBERG and B. R. HSIEH, *J. Phys. Chem.* A **103** (1999) 2394.
17. D. D. GEBLER, Y. Z. WANG, J. W. BLATCHFORD, S. W. JESSEN, L. B. LIN, T. L. GUSTAFSON, H. L. WANG, T. M. SWAGER, A. G. MACDIARMID and A. J. EPSTEIN, *J. Appl. Phys.* **78** (1995) 4264.
18. S. WANG, P. WU and Z. HAN, *Macromolecules* **36** (2003) 4567.
19. J. A. OSAHENI and S. A. JENEKHE, *ibid.* **26** (1993) 4726.
20. *Idem.*, *Chem. Mater.* **4** (1992) 1282.
21. *Idem.*, *ibid.* **6** (1994) 1906.
22. *Idem.*, *J. Amer. Chem. Soc.* **117** (1995) 7389.
23. R. RUCKH, E. SIGMUND, C. KOLLMAR and H. SIXL, *J. Chem. Phys.* **85** (1986) 2797.
24. X. L. CHEN and S. A. JENEKHE, *Macromolecules* **29** (1996) 6189.
25. *Idem.*, *Appl. Phys. Lett.* **70** (1997) 487.
26. *Idem.*, *Synt. Met.* **85** (1997) 1431.
27. P. WU, X. ZHANG and Z. HAN, *Funct. Polym.* **5** (1992) 169.
28. Z. HAN, Z. LU, X. SHI and P. WU, *Acta Polym. Sin.* **2** (1997) 141.
29. D. L. VANDERHART, E. W. WANG, R. K. EBY, B. M. FANCONI and K. L. DEVRIES, AFWAL-TR-85-4137 'Exploration of Advanced Characterization Techniques for Molecular Composites'.
30. S. WANG, G. BAO, P. WU and Z. HAN, *Eur. Polym. J.* **36** (2000) 1843.
31. S. A. JENEKHE, P. O. JOHNSON and A. K. AGRAWAL, *Macromolecules* **22** (1989) 3216.
32. S. A. JENEKHE and P. O. JOHNSON, *ibid.* **23** (1990) 4419.
33. A. V. FRATINI, P. G. LENHERT, T. J. RESCH and W. W. ADAMS, *Mater. Res. Soc. Symp. Proc.* **134** (1989) 431.
34. A. V. FRATINI, E. M. CROSS, J. F. O'BRIEN and W. W. ADAMS, *J. Macromol. Sci.-Phys.* B **24** (1985–1986) 159.
35. S. WANG, G. BAO, Z. LU, P. WU and Z. HAN, *J. Mater. Sci.* **35** (2000) 5873.
36. S. WANG, P. WU and Z. HAN, *Polymer* **42** (2001) 217.
37. G. ODIAN, "Principles of polymerization," 2nd ed. (Wiley-InterScience, New York, 1981) p. 143.
38. S. A. JENEKHE, J. A. OSAHENI, J. S. METH and H. VANHERZEELE, *Chem. Mater.* **4** (1992) 683.
39. S. A. JENEKHE and J. A. OSAHENI, *Science* **265** (1994) 765.

Received 17 July 2003
and accepted 15 January 2004