Synthesis and Fluorescence in Solution of Polybenzimidazolylphenylenephthalamides

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ABSTRACT: Six polybenzimidazolylphenylenephthalamides (PBIPPA), two meta/para isomers, and four meta/para isomers that had different distances between a benzimidazolyl and the adjacent benzimidazolyl in a polymer chain were synthesized. They were soluble in *N,N*-dimethylacetamide. In addition to the fluorescence from the $\pi \rightarrow \pi^*$ transition of isolated phenylbenzimidazole, a fluorescence from a chromophore complex in the grand state appeared in the fluorescence spectra, which was observed at higher concentrations. The concentration dependence of the intensity of the fluorescence was investigated in order to learn whether the chromophore complex was intermolecular or intramolecular. It was concluded that the chromophore complex is intramolecular, a conclusion supported by the viscometric results. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1412–1416, 2003

Key words: polybenzimidazolylphenylenephthalamides; fluorescence in solution; chromophore complex; intra- and intermolecular complexes; viscometry

INTRODUCTION

Several investigators[1–4] have reported success in the synthesis of poly(phenylene phthalamide) (PPPA) with a bulky pendent substituent such as phenyl, thiazolyl, or oxazolyl for the improvement of solubility with retention of excellent thermal stability. Lozano et al.[2,3] reported on oxazolyl- and thiazolyl-substituted PPPA derived from 2-(3,5-dimethylphenyl benzothiazole) or 2-(3,5-dimethylphenyl benzoxazole). Mikroyannidis[4] reported on syntheses using 2-(3,5-diaminophenyl) benzothiazole or benzoxazole, prepared from 3,5-dinitrobenzoyl chloride and 2-aminothiol or 2-aminophenol. We have succeeded in deriving benzimidazolyl-substituted aromatic polyamides, polybenzimidazolylphenylenephthalamides (PBIPPA), from 2-(3,5-diaminophenyl benzimidazole) **2**, synthesized according to the synthetic route (Scheme 1, similar to Mikroyannidis's route. Moreover, we succeeded in synthesizing two new diamines, **4m** and **4p**, obtained by reduction of the NO_2 of **3m** and **3p**, derived from **2** (Scheme 2). One objective in this article is to detail the synthesis of these novel polymers.

These polymers have excellent thermal stability[5,6] and are soluble in aprotic polar solvents. The solutions emit fluorescence in solution. Fluorescence from a polymer reflects the intra- and intermolecular aggregations in solids[7–9] and in solutions[10–12] because fluorescence involves fluorescence from an excimer, an exciplex, and/or a chromophore complex (chromophores stacked in the grand state) as a probe of molecular aggregation. Frank and Gashgari[9] reported that the ratio of the intensity of excimer fluorescence to that of monomer fluorescence (I_D/I_M) decreased with decreasing difference in solubility parameters between the polymers for blends of poly(2-vinylnaphthalene) with poly(alkyl methacrylate). Tazuke and Matsuyama[11] reported that the weaker the intensity of excimer fluorescence, the better was the solvent. One[12] of this article's authors reported that the intensity of chromophore-complex fluorescence of a polybenzimidazole in formic acid is very weak because of the formation of a polyelectrolyte. In all these articles the arguments about whether the complex fluorescence was emitted intermolecularly or intramolecularly was ambiguous. We expected the fluorescence behavior of PBIPPA, which varied depending on the distance between chromophores (benzimidazolyls), mentioned above, to provide us with evidence for this argument because fluorescence from an intramolecular complex depends on the molecular conformation. The presentation of this evidence is the other objective in this article.

EXPERIMENTAL

Monomer synthesis

2-(3,5-Dinitrophenyl)benzimidazole (**1**)—a solution of 1,2-diaminophenylene (11.7 g, 108.0 mmol) in *N,N*-dimethylacetamide (DMA) (20 mL) was added to a solution of 2-(3,5-dinitrobenzoyl) chloride (25.0 g, 108.5 mmol) in DMA (20 mL) at room temperature.

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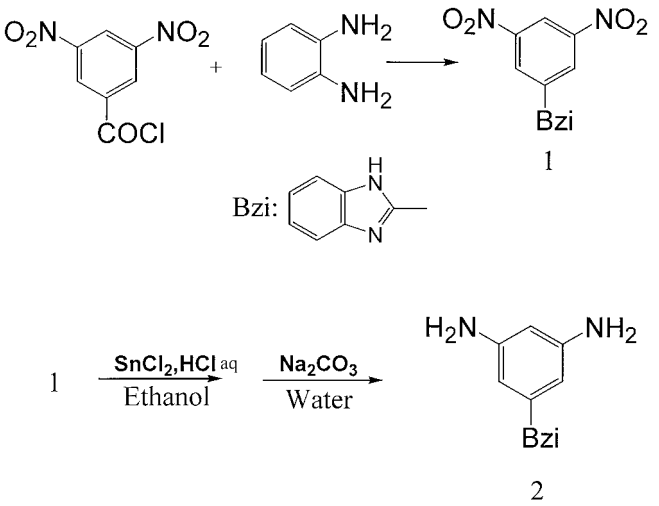
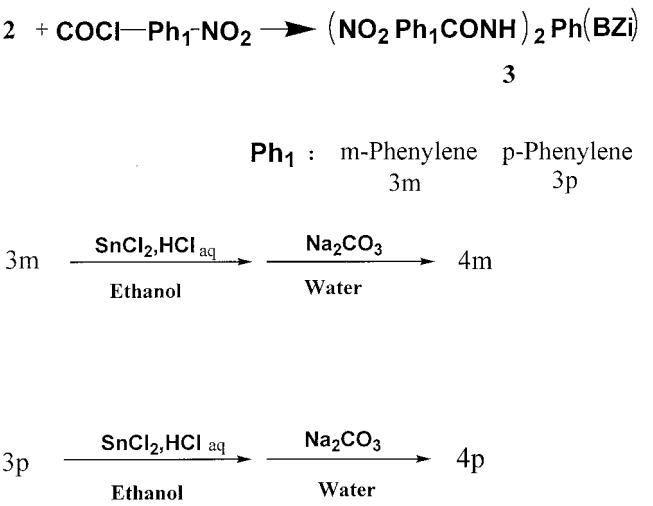


Scheme 1



Scheme 2

The dark brown mixed solution was heated to reflux for 1 h and then cooled to room temperature. The precipitate was removed by suction filtration and naturally dried. The product was purified by recrystallization from ethanol.

Fine yellow needlelike crystal (yield: 30 mol % per 1,2-diaminophenylene). IR (KBr, cm^{-1}): 3336 (NHCN), 3104 (aromatic CH), 1525 (NO_2), 1348 (NO_2). ^{1}H-NMR (DMSO-d_6, δ): 13.8 (1H, NHCN), 9.47 (2H, dinitrophenyl), 8.85 (1H, dinitrophenyl), 7.70–7.68 (2H, benzimidazolyl), 7.31–7.29 (2H, benzimidazolyl).

2-(3,5-Diaminophenyl)benzimidazole (**2**)—To 6.72 g (30 mmol) of **1** placed in 400 mL of an eggplant flask at 333 K was added 90 mL of absolute ethanol. To the resulting yellow product, 45.0 g of $SnCl_2$ dihydrate was added. The solution was heated to reflux for 1 h after the addition of 60 mL concentrated HClaq. The product was purified by recrystallization from concentrated HClaq.

Light purple needlelike crystal (dihydrochloride, yield: 50 mol %). IR (KBr, cm^{-1}): 3426 (NHCN), 3324 (NHCN), 3000–2700 (NH^{3+}, aromatic CH): 1625 (NH_2), 1488 (NH_2). ^{1}H-NMR (DMSO-d_6, δ): 7.86–7.84 (2H, benzimidazolyl), 7.58–7.56 (2H, benzimidazolyl), 7.37 (2H, diaminophenyl), 6.97 (1H, diaminophenyl), 6.3 (6H, ammonio).

3m and **3p**—A mixed solution of **2** (2.24 g, 10.0 mmol) neutralized by Na_2CO_3aq and 3- or 4-nitrobenzoyl chloride (4.00 g, 21.5 mmol) in 30 mL of DMA was heated to reflux for 1 h and then was filtered after cooling at room temperature. The purification was conducted by recrystallization from DMA.

3m, brown powder (yield: 50 mol % per **2**). IR (KBr, cm^{-1}): 3324–3056 (NHCN, NHCO, aromatic CH), 1682 (NHCO), 1616 (NHCO), 1529 (NO_2), 1349 (NO_2), 1297 (NHCO). ^{1}H-NMR (DMF-d_7, δ): 11.10 (2H, NHCO), 10.35 (1H, NHCN), 9.00 (2H, substituted phenylene), 8.87 (1H, substituted phenylene), 8.63–8.51 (6H, nitrophenyl), 7.92 (2H, nitrophenyl), 7.73 (2H, benzimidazolyl), 7.32 (2H, benzimidazolyl). **3p**, brown powder (yield: 30 mol %). IR (KBr, cm^{-1}): 3324–3056 (NHCN, NHCO, aromatic CH), 1671 (NHCO), 1602 (NHCO), 1523 (NO_2), 1348 (NO_2), 1280 (NHCO). ^{1}H-NMR (DMF-d_7, δ): 10.99 (2H, NHCO), 10.33 (1H, NHCN), 8.64 (2H, substituted phenylene), 8.57 (1H, substituted phenylene), 8.45 (4H, nitrophenyl), 8.41 (4H, nitrophenyl), 7.69 (2H, benzimidazolyl), 7.28 (2H, benzimidazolyl). **3m** and **3p** were reduced in a method similar to reduction of **1** (**4m** and **4p**). **4m**, light gray powder (dihydrochloride, yield: 12 mol % of **3m**). ^{1}H-NMR (DMF-d_7, δ): 10.82 (2H, NHCO), 8.86 [2H, **3** of benzimidazolyl phenylene (BIP)], 8.72 (1H, **2** of BIP), 7.60 (2H, **5** of BIP), 7.21 (2H, **6** of BIP), 7.11 (4H, iminobenzoyl), 6.68 (4H, iminobenzoyl), 6.60 (broad, 6H, ammonio). ANAL. Calcd for $C_{27}H_{24}N_6O_2Cl_2$: C,

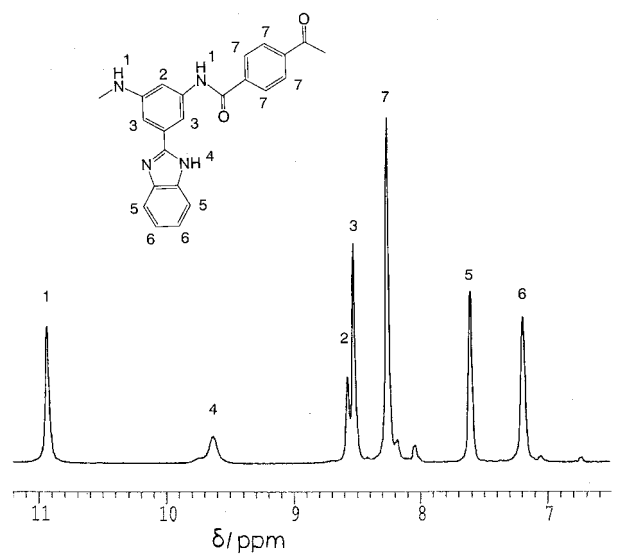


Figure 1 ^{1}H-NMR spectrum of **2p**.

60.56%; H, 4.51%; N 15.70%. Found: C, 58.26%; H, 4.82%; N, 15.10%. **4p**, light gray powder (dihydrochloride, yield: 10 mol % of **3p**). ^{1}H-NMR (DMF-d_6, δ): 10.72 (2H, NHCO), 8.53 (2H, **3** of BIP), 8.42 (1H, **2** of BIP), 7.56 (2H, **5** of BIP), 7.17 (2H, **6** of BIP), 7.12 (4H, p-iminobenzoyl), 6.51 (4H, *p*-iminobenzolyl), 6.20 (broad, 6H, ammonio). ANAL. Calcd for $C_{27}H_{24}N_6O_2Cl_2$: C, 60.56%; H, 4.51%; N 15.70%. Found: C, 57.87%; H, 4.78%; N, 15.00%, where number of hydrogens of BIP is denoted in Figure 1. The dihydrochloride salts of 2, 4m, and 4p were characterized because of easiness in purification.

Polymer synthesis

Equimolar amounts (30.0 mmol) of a diamine (**2**, **4m**, or **4p**) and a phthaloyl chloride (tere- or iso-) were dissolved separately in DMA, whose amount was appropriate for the solubility concentration, and then were mixed with each other. The reaction was purged with nitrogen and stirred for 2 h at room temperature. Filtration yielded the precipitate.

2m, dark brown solid. ^{1}H-NMR (DMA-d_9, δ): 10.81 (2H, NHCO), 9.63 (**4** of BIP), 8.58 (**2** of BIP), 8.56 (**3** of BIP), 8.31 (3H, isophthaloyl), 7.93 (1H, isophthaloyl), 7.62 (**5** of BIP), 7.30 (**6** of BIP). **2p**, dark brown solid. ^{1}H-NMR is shown in Figure 1. **4mm**, dark brown solid. ^{1}H-NMR (DMA-d_9, δ): 10.75 (2H, NHCO), 10.66 (2H, NHCO), 10.38 (1H, **4** of BIP), 8.78 (1H, **2** of BIP), 8.68 (2H, **3** of BIP), 8.31 (3H, isophthaloyl), 7.93 (1H, isophthaloyl), 8.17 (3H, *m*-iminobenzoyl), 7.76 (1H, *m*-iminobenzoyl), 7.66 (2H, **5** of BIP), 7.23 (2H, **6** of BIP). **4mp**, dark brown solid. ^{1}H-NMR (DMA-d9, δ): 10.8 (2H, NHCO), 10.7 (2H, NHCO), 10.4 (1H, **4** of BIP), 8.8 (1H, **2** of BIP), 8.7 (2H, **3** of BIP), 8.25 (4H, terephthaloyl), 8.2 (3H, *m*-iminobenzoyl), 7.8 (1H, *m*-iminobenzoyl), 7.7 (2H, **5** of BIP), 7.2 (2H, **6** of BIP). **4pm**, dark brown solid. ^{1}H-NMR (DMA-d9): 10.8 (2H, NHCO), 10.7 (2H, NHCO), 10.4 (1H, **4** of BIP), 8.8 (1H, **2** of BIP), 8.7 (2H, **3** of BIP), 8.3 (3H, isophthaloyl), 7.9 (1H, isophthaloyl), 8.16 (4H, *p*-iminobenzoyl), 7.7 (2H, 5 of BIP), 7.2 (2H, 6 of BIP). **4pp**, dark brown solid. ^{1}H-NMR (DMA-d9, δ): 10.8 (2H, NHCO), 10.7 (2H, NHCO), 10.4 (1H, **4** of BIP), 8.8 (1H, **2** of BIP), 8.7 (2H, **3** of BIP), 8.3 (4H, terephthaloyl), 8.16 (4H, *p*-iminobenzoyl), 7.7 (2H, **5** of BIP), 7.2 (2H, **6** of BIP).

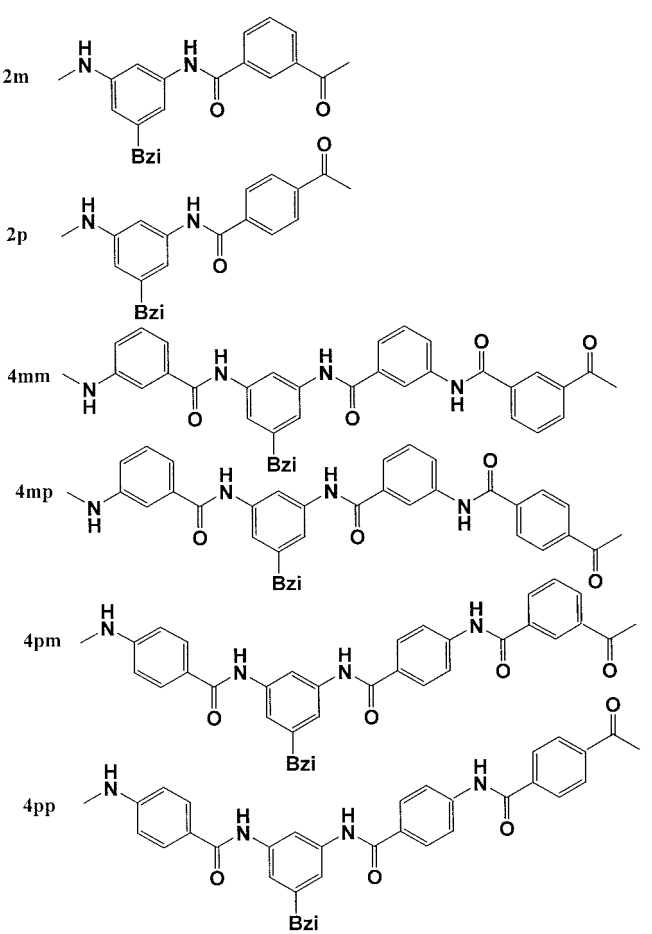


Chart 1

TABLE I
Yield and Viscometric Parameters of Prepared PBIPPA

PBIPPA	Yield[a] (wt %)	[η] (dl/g)	Huggins const[b]
2m	82.2	0.63	0.38
2p	88.3	0.83	0.34
4mm	70.1	0.21	0.40
4mp	74.1	0.28	0.38
4pm	60.1	0.21	0.41
4pp	70.4	0.32	0.38

[a] per iso- or terephthalic acid.
[b] Summation of Huggins and Kraemer constants is equal to 0.50.

Instruments

A JASCO FTIR 230 infrared spectrometer, a Bruker DMX 500 nuclear magnetic resonance spectrometer, and a JASCO V520 fluorescence spectrometer were used for recording IR, ^{1}H-NMR, and fluorescence spectra, respectively. An Ubbelohde viscometer was used at 303 K for measurement of viscosity.

RESULTS AND DISCUSSION

Synthesis

The polymerization products were identified as the expected PBIPPA (**2m**, **2p**, **4mm**, **4mp**, **4pm**, and **4pp**) with structures in Chart 1, according to the NMR and IR spectra and the elemental analysis data. The elemental analysis data were not effective for the identification of these polymers because we could not obtain any PBIPPA without DMA. For example, a representative elemental analysis data on **2p** is—Calcd for

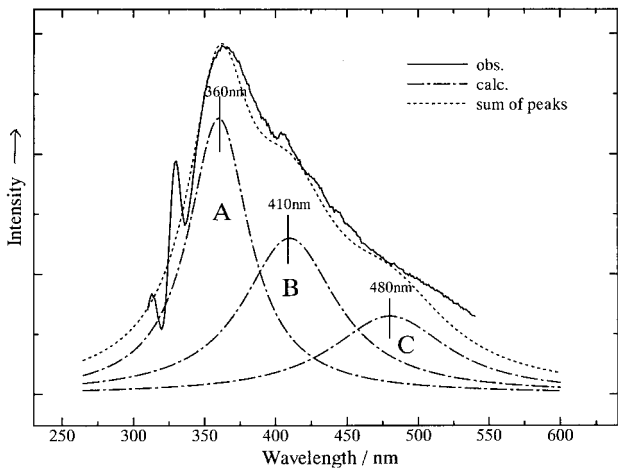


Figure 2 Fitting of three Lorentzian equations to an observed fluorescence spectrum of **4pp**.

$C_{21}H_{14}N_4O_2$ (354.36): C, 71.18; H, 3.98; N, 15.81. Found: C, 70.79; H, 4.21; N, 15.83. This would suggest that about 12 wt% of DMA is contained in the polymer **2p**. On the contrary, the NMR spectra were effective for identification because the sharp and distinct absorption peaks appears selectively. A representative ^{1}H-NMR spectrum (**2p**) is shown in Figure 1. The ^{1}H-NMR spectra of these polymers were consistent with the assignment of those of other aromatic polyamides reported on in the literature.[2,3,13] The IR spectra of these polymers were too complicated to confirm the structure of the individual polymers, though the spectra showed absorption peaks due to amide bonds.

The yield and viscometric data of the resulting polymers are also shown in Table I. It was found that the larger the para-phenylene content, the larger was the molecular weight of the polymer. This can be explained by the steric effect. On the contrary, the reaction acceleration effect,[4,14] which occurs with the addition of triethylamine, did not appear.The reaction retardation effect did occur, however, perhaps because of the lowering of solubility of the produced polymer because of the addition of triethylamine. The Huggins and Kraemer constants were somewhat smaller than those of common polymers, though the viscosity-concentration curves were regular. The thermogravimetry of these polymers is reported elsewhere.[5,6] The TG curves showed two stages of onset temperature, 523 and 763 K. The latter stage is in agreement with that of nonsubstituted aromatic polyamides reported in the literature.[15–17]

Fluorescence spectroscopy

For the fluorescence spectroscopy results, the concentration of all solutions is expressed in chromophore (BI) concentration. The wavelengths at the maximum intensity of fluorescence, λ_{max}, of all the polymers in DMA were in the vicinity of 360 nm, which is within the Lambert–Beer concentration region. This is the same emission wavelength as that associated with the $\pi \rightarrow \pi^*$ transition of phenylbenzimidazole (PhBI). Accordingly, the major emission of all the polymers was emission from the PhBI unit. The major emission exhibited strong concentration quenching, and a broad emission peak appeared in the wavelength region of about 400–550 nm, particularly above a concentration of about 10^{-5} mol L^{-1} of chromophore (PhBI unit). This broad emission peak also appeared in the fluorescence spectrum of the benzimidazole quasi-concentrated solution.

These fluorescence spectra were analyzed by trial-and-error contraction using Lorentzian as shown in Figure 2:

$$f(\lambda) = \sum k_i a_i/(a_i^2 + (\lambda - \lambda_{\max i})^2)$$

$$\lambda_{\max 1} = 360,\ \lambda_{\max 2} = 410,\ \lambda_{\max 3} = 480$$

TABLE II
Peak Areas of Emission Separated by Trial-and-Error Contraction Using Lorentzian

	Concentration (mol/L)														
	$1.69\ 10^{-9}$			$1.69\ 10^{-7}$			$1.69\ 10^{-6}$			$1.69\ 10^{-4}$			$1.69\ 10^{-2}$		
	Peak area[b] (%)			Peak area[b] (%)			Peak area[b] (%)			Peak area[b] (%)			Peak area[b] (%)		
PBIPPA	A_{360}	A_{410}	A_{480}	A_{360}	A_{410}	A_{480}	A_{360}	A_{410}	A_{480}	A_{360}	A_{410}	A_{480}	A_{360}	A_{410}	A_{480}
2m	63.5	31.3	5.2	30.0	56.7	13.3	12.6	8.2	79.2	7.6	3.8	88.6	u	u	u
2p	67.5	26.5	6.0	23.5	56.7	19.8	14.1	7.6	78.3	9.2	5.0	85.8	u	u	u
4mm	67.1	23.2	9.7	64.4	25.6	10.0	40.7	37.0	22.3	5.4	56.1	38.5	u	u	u
4mp	67.9	24.4	7.7	59.7	25.1	15.2	55.8	26.8	17.4	3.6	72.6	23.8	u	u	u
4pm	63.1	37.9	u	57.2	42.8	u	37.5	61.3	1.2	7.5	2.1	90.4	u	u	u
4pp	67.0	33.0	u	53.4	46.6	u	34.2	62.7	3.1	5.7	4.2	90.1	u	u	u
PhBI[c]	99.9	u	u	99.9	u	u	99.9	u	u	97.2	2.8	u	72.2	u	27.8

u, undetectable.
[a] Chromophore concentration;
[b]Divided by (A_{360} + A_{410} + A_{480}).
[c]Phenylbenzimidazole.

The results are summarized in Table II. What is the broad emission attributable to? It is different from that of the solution within the Lambert–Beer concentration region, and it is not an excimer or exciplex because the excitation spectra monitored at 410 and 480 nm showed that the λ_{max} was 340 nm, which is different from 300 nm, the maximum excitation wavelength associated with the $\pi \rightarrow \pi^*$ transition of phenylbenzimidazole or all the polymers and PhBI. The broad emission may be associated with chromophores in the molecular aggregation. Chromophore complexes are considered multiply stacking chromophores because emission from free chromophore a result of the $\pi \rightarrow \pi^*$ transition. The emission from the aggregates is pronounced in the spectra of the PhBI solutions above about 10^{-2} mol L^{-1} and the PBIPPA solutions above about 10^{-6} mol L^{-1}. This suggests that the chromophore complexes occurred because of intramolecular interaction. Because PBIPPA solutions of concentrations below 10^{-5} mol L^{-1} showed a regular viscosity-concentration behavior, PBIPPA molecules may be molecularly distributed in solutions below 10^{-5} mol L^{-1}. This also supports the conclusions that the broad emission resulted from intramolecular chromophore complexes and that the broad emission from PBIPPA with a larger PhBI content per repeating unit detectable at lower concentrations.

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