Effects of Dilution with PMMA and Network Formation on Fluorescence from Benzimidazolylphenylenes Linked to PMMA Network

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ABSTRACT: N,N'-5-(2-benzimidazolyl)-1,3-phenylenebis(-methacrylamide) (BIPBMA) was synthesized and copolymerized with methyl methacrylate (MMA) by changing feed BIPBMA/MMA molar ratio. The swelling experiments suggest that these cross-linked copolymers (c-copolymers) have a polymer network structure. To compare with c-copolymers, synthesized 3-(2-benzimidazolyl) phenylmethacrylamide (BIPMA) was copolymerized with MMA by changing feed BIPMA/MMA molar ratio. These linear copolymers (l-copolymers) were dissolved in N,N-dimethylacetamide (DMA). The fluorescence spectra of c-copolymers were well fitted by trial-and-error contraction with sums of five or less of Lorentzian equations. The fluorescence spectra of l-copolymers were so distributed that only the initial peak was fitted to a single Lorentzian equation. The fluorescence spectra of BIPBMA/DMA solutions with various concentrations were also fitted to sums of five or less of Lorentzian equations. The fitted coefficients were used to quantify dilution effect. The fluorescence intensity of c-copolymers is higher than that of l-copolymers in a same chromophore concentration. A relation between the intensity and the chromophore concentration shows a concentration quenching owing to chromophore aggregating for c-copolymer, l-copolymer, and the solution. A critical concentration point before which the intensity increases appeared in the plots of intensity against concentration for the c-copolymer and the solution. The critical point of the c-copolymer is higher than that of the solution and that of the l-copolymer (if observed). This suggests that the network formation and the dilution break up the chromophore aggregates. The fluorescence spectra of c-copolymers (1/200) adjusted by varying AIBN concentrations suggest that the fluorescence is independent of the extent of cross-linking. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1841–1845, 2010

Key words: PMMA; PMMA network; fluorescence; concentration dependence

INTRODUCTION

There are several studies[1–6] on syntheses of poly(phenylenephthalamide)s (PPPA) soluble in organic solvent because of facility in fabrication of available goods. In our previous study,[6] a poly(benzimidazolylphenylenephthalamide) (PBIPPA) soluble in aprotic polar solvents was successfully synthesized. In the fluorescence spectra of PBIPPA, red-shift and decrease in intensity were observed with increasing polymer concentration.[6] So far such concentration quenching was explained by chromophore aggregation,[6–10] interaction between polymers,[11] etc in solution. Red-shifts of the fluorescence in solid were also reported for a bilayer[12] of a conjugated ring polymer with an aromatic donor molecule, a copolymer[13] of a chromophore monomer linked by an aliphatic side chain with another chromophore, and a copolymer[14] of a chromophore monomer with methyl methacrylate (MMA), with decreasing the concentration of donor molecule, side chain, and MMA, respectively. This means that the fluorescence in solid emits from chromophore aggregates and therefore, the quantum yield is low. It is obstacles to practical application to light emitting device such as diode.[15]

In concentrated solution, efforts were conducted to obtain photoemission of better quantum yield as follows: cooling temperature,[16] lowering pH,[17] addition of a surfactant,[18] substitution of a surfactant,[19] copolymerization,[20–22] end-capping polymer,[23,24] etc. To our knowledge, there is no report on efforts to break up chromophore aggregates in polymer solid.

The object of the present article is to give studies of dilution and network formation effects of fluorescence from chromophore aggregates. N,N'-5-(2-benzimidazolyl)-1,3-phenylenebis(methacrylamide) (BIPBMA) was synthesized to use as a cross-linker and as a monomer (see Fig. 1). Copolymers of BIPBMA with MMA were synthesized at the various feed molar ratios. To compare with BIPBMA/MMA cross-linked copolymers (c-copolymers), N-3-(2-benzimidazolyl)phenylmethacrylamide (BIPMA) (see Fig. 1) was synthesized and BIPMA/MMA linear
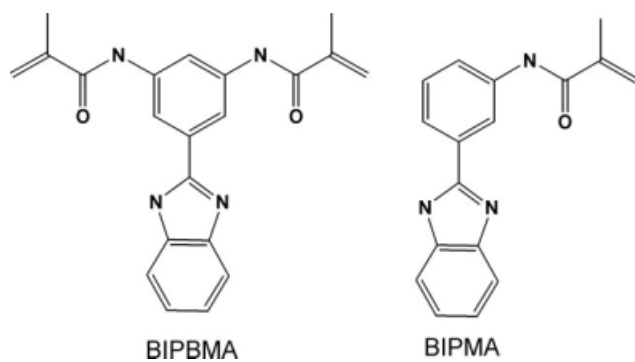
Figure 1 BIPBMA and BIPMA.

copolymers (*l*-copolymers) were synthesized. The extent of cross-linking of *c*-copolymers of 1/200 feed BIPBMA/MMA molar ratio was adjusted by various azobisisobutyronitrile (AIBN) concentration.

EXPERIMENTAL

Materials

2-(3,5-Dinitrobenzoyl) chloride (DNBC, from ALDRICH), 2-(3-nitrobenzoyl) chloride (NBC, from ALDRICH), 1,2-diaminophenylene (OPD) (from WAKO), anhydrous tin(II) chloride (from WAKO), aquaous hydrogen chloride (36%, from WAKO), ethanol (99.5%, from WAKO), sodium carbonate (99.5%, from WAKO), methacryloyl chloride (MAC) (from WAKO), triethylamine (from WAKO), and activated charcoal powder (from WAKO) were used as received. MMA (from WAKO) was distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) (from WAKO) was recrystallized from ethanol. *N,N*-dimethylacetamide (DMA) (from WAKO) was used after addition of molecular sieves for dehydration.

Monomer synthesis

2-(3,5-Diaminophenyl)benzimidazole (DAPBI)

The synthesis is described in detail elsewhere.[6] The product of reaction of DNBC (108.5 mmol) in DMA with OPDA (108.0 mmol) in DMA was heated to reflux after stirring at room temperature. The product was reduced to DAPBI hydrochloride by use of tin(II) chloride and hydrochloric acid after recrystallization from ethanol and then drying. DAPBI hydrochloride was used after neutralization with sodium carbonate.

2-(3-aminophenyl)benzimidazole (APBI)

The synthesis was conducted in a manner similar to DAPBI, using NBC (135 mmol) and OPDA (130 mmol).

N,N′-5-(2-benzimidazolyl)-1,3-phenylenebis(methacrylamide)

In a 50 mL eggplant flask were placed DAPBI (0.98 g, 4.38 mmol), DMA (3 mL), triethylamine (1.5 mL, 10.8 mmol), and MAC (3.5 mL, 35.8 mmol). The mixture was stirred for 1 h. The reaction mixture was poured into 50 mL of hot water. The precipitate was collected by filtration and dried under vacuum. The product was purified twice by washing with ethanol and water.

^{1}H-NMR (DMSO-d, ppm): 10.36 (s, 2H), 8.32 (s, 2H), 8.24 (s, 1H), 7.82 (d, 2H), 7.55 (d, 2H), 5.94 (s, 2H), 5.60 (s, 2H), 1.98 (s, 6H). Yield: 80%.

N-3-(2-benzimidazolyl)phenylmethacrylamide (BIPMA)

The synthesis was conducted in a manner similar to BIPBMA, using APBI (3.925 mmol), DMA (2 mL), triethylamine (1.5 mL), MAC (3 mL).

^{1}H-NMR (DMSO-d, ppm): 10.36 (s, 1H), 8.32 (s, 2H), 8.24 (s, 1H), 7.82 (d, 2H), 7.62(s, 1H), 7.55 (d, 2H), 7.52 (s, 1H), 5.94 (s, 1H), 5.60 (s, 1H), 1.98 (s, 3H). Yield: 75%.

Copolymerization

Linear copolymers (*l*-copolymers)

In a glass-tube (entry 1) of six glass-tubes with 12 mm diameter and flame-sealed one end side, BIPMA (0.75 mmol) was dissolved in DMA (3.6 mL). In each of another two glass-tubes (entries 2 and 3) was placed 1.2 mL of the solution. In another glass-tube (entry 4) was placed 0.6 mL of the one solution (entry 3) of the two solutions (entries 2 and 3). The solution (entry 4) was diluted with DMA (0.6 mL). In another glass-tube (entry 5) was placed 0.6 mL of the solution (entry 4). After the solution (entry 5) was diluted with DMA (0.6 mL), 0.6 mL of the solution (entry 5) was placed in another glass-tube (entry 6). After the solution (entry 6) was diluted with DMA (0.6 mL), 0.6 mL of the solution (entry 6) was thrown away. After that, the open end side of six glass-tubes was flame-sealed, after addition of a proper amount of MMA. Feed amount of BIPMA, MMA, and DMA is shown in Table I. The reactants in the sealed glass-tube were irradiated by a UM-452 high pressure mercury lamp (USHIO) at 303 K for 7 h. The rod-like product taken out of the grass-tube was dried under vacuum till the weight became constant. Decrease in weight was about 90% weight of fed DMA. The linear copolymers with lower concentrations were not be synthesized, because of difficulty in dissolution of MMA in DMA.

Cross-linked copolymers (*c*-copolymers)

The synthesis of *c*-copolymers was conducted in same manner as the synthesis of *l*-copolymers except

TABLE I
Preparation of BIP Linked to Linear PMMA

Entry	BIPMA/ MMA	BIPMA/ mmol	MMA/ mmol	DMA/mL
1	1/100	0.25	25	1.2
2	1/200	0.25	50	1.2
3	1/400	0.125	50	0.6
4	1/800	0.0625	50	0.6
5	1/1600	0.0313	50	0.6
6	1/3200	0.0156	50	0.6

that BIPBMA was used instead of BIPMA. To estimate the extent of cross-linking, the degree of swelling (S_w) of products was obtained as the ratio of the weight of a given copolymer in initial state to the weight of it swollen as follows: about 12 mm diameter and about 2 mm thickness disk of copolymer precisely weighed was immersed in DMA at 298 K. The swollen copolymer was immersed again in fresh DMA after surface-dried and weighed. This procedure was repeated till the weight became constant. The S_w values of the products are shown in Table II.

c-Copolymers (BIPB MA/MMA = 1/200) with various amounts of AIBN

Cross-links are formed by linkage of cross-linkers to active chain ends propagating from cross-linkers. Chains growing from decomposed initiators have an active and an inactive ends. Therefore, cross-links decrease with amount of initiators. To obtain copolymers (BIPBMA/MMA = 1/200) with various S_w values, copolymerization was conducted in the presence of AIBN. The S_w values of the products are shown in Table II.

Fluorescence measurement

The fluorescence spectra of copolymers were measured after drying at 373 K for a week under evacuation. The longitudinal edge of a sample rod and the beam from the tip of glass fiber attachment of a Fluorog τ3 spectrometer (SPEX), which has the outlet of incident light and the inlet of emission light, were hold at 45° angle and 5 mm length for all fluorescence spectrum measurements. The excitation wave-

TABLE II
The S_w Values of *c*-Copolymers

BIPBMA/MMA[a]	1/100	1/200	1/400	1/800–1/3200
S_w		1.85	1.91	5.88	unknown[b]
BIPBMA/AIBN[c]	1/0.25	1/0.50	1/1.00	
S_w		2.4	4.6	11.0	

[a] Without AIBN.
[b] Swollen to vessel size.
[c] BIPBMA/MMA = 1/200.

length of 310 nm was used. The fluorescence spectra of BIPBMA in DMA were obtained by using a quartz cell of rectangular (5 × 10 mm: the incident light path length is 5 mm) prism.

RESULTS AND DISCUSSION

Figure 2 shows fluorescence spectra of *l*-copolymers. The spectra have two peaks at λ_{max} of 405 and 515 nm. The peak at 405 nm is close to λ_{max} of emission characteristic of benzimidazolyl-phenyl or -phenylene (BIP), which appears in fluorescence spectra of BIPBMA in dilute solution (Fig. 3). The emission with 515 nm λ_{max} is associated with BIP aggregates, because of increase in intensity and red-shift of λ_{max} with increasing BIP concentration. The emission from chromophore aggregates in film or concentrated solution was shown for some of conjugated polymers.[6–11] To obtain effective information on individual emission bands from such a distributed spectrum, trial-and-error contraction using Lorentzian equations is convenient and certain.

$$I(\lambda) = \Sigma a_i/(b_i + (\lambda - \lambda_i)^2)$$

The spectra in Figure 2 are too distributed to analyze by use of some Lorentzian equations. Therefore, a Lorentzian equation was fitted to only an initial peak with an upward slope. This emission shows a concentration quenching. The existence of S_w values for *c*-copolymers suggests formation of a PMMA
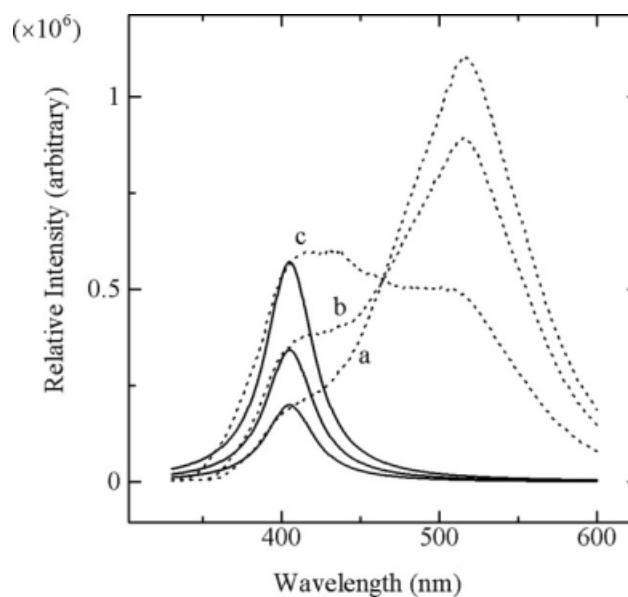

Figure 2 Fluorescence spectra of *l*-copolymers: BIPMA/MMA = 1/400 (a), 1/800 (b), 1/3200 (c). Solid lines are drawn by Lorentzian equations with $b_i = 350$, $\lambda_i = 405$, and $10^{-7}a_i = 7$ (a), 12 (b), 20 (c). The relative intensity is given by actually acquired photon count.
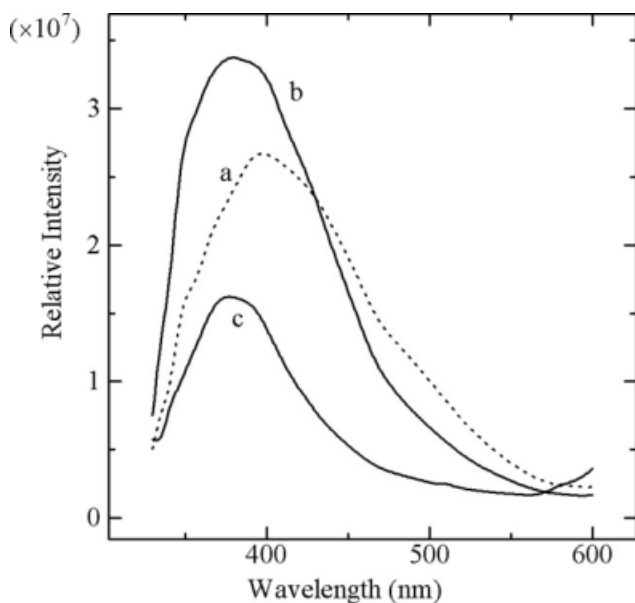
Figure 3 Fluorescence spectra of BIPBMA/DMA solutions: concentration/10^{-5} M = 156 (a), 26.1 (b), 2.61 (c). The relative intensity is given by actually acquired photon count.
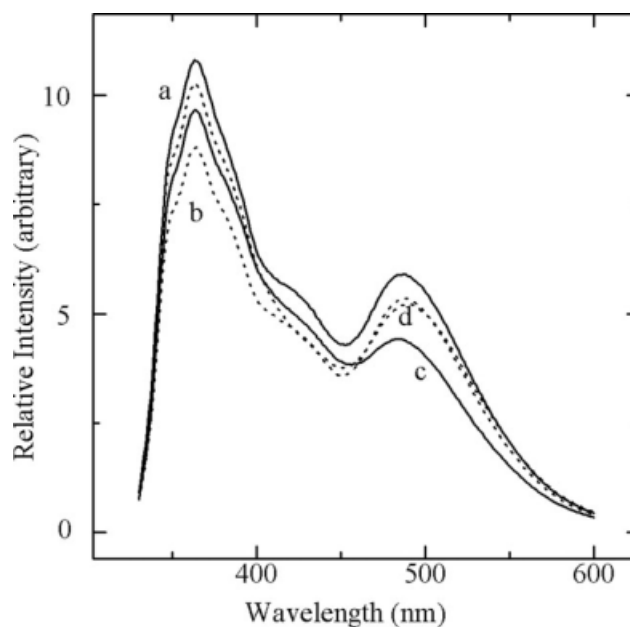

Figure 5 Fluorescence spectra of *c*-copolymers (1/200) with various AIBN amounts: AIBN feed amount/mmol = 0 (a), 0.064 (b), 0.128 (c), and 0.256 (d).

network. Figure 4 shows fluorescence spectra of *c*-copolymers. The emission of BIP aggregates is very weak. The BIP concentrations of *c*-copolymers are same as those of *l*-copolymers in Figure 2. Therefore, this suggests that the cross-links break up BIP aggregates. Figure 5 shows influence of the extent of cross-linking on the emission. The emission seems to be independent of the extent of cross-linking. The
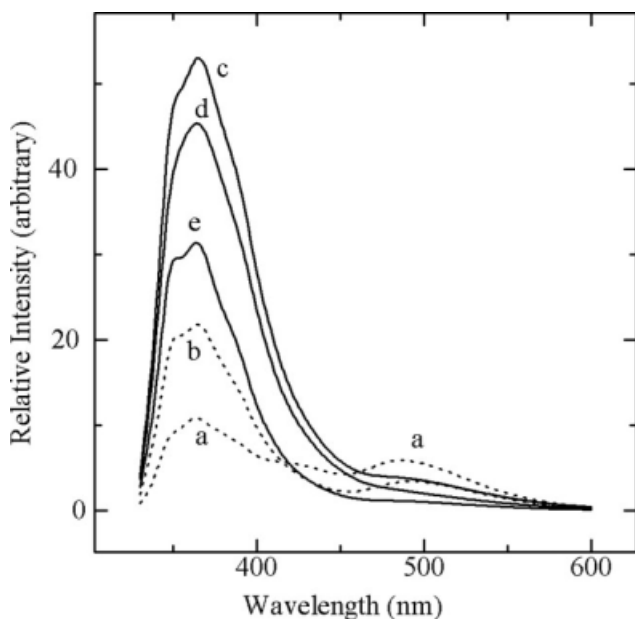

Figure 4 Fluorescence spectra of *c*-copolymers: BIPBMA/MMA = 1/100 (a), 1/400 (b), 1/800 (c), 1/1600 (d), 1/3200 (e). The relative intensity is given by actually acquired photon count.

emissions in Figures 2–4 show concentration-quenching and that the intensity for *c*-copolymers is about 20 times that for *l*-copolymers. A sum of five or less of Lorentzian equations was well fitted to the spectra in Figure 4. The coefficients are shown in Table III. With increasing BIP concentration, the intensity of bands 1, 2, and 3, decreases, on the contrary, the intensity of bands 4and 5, increases. This means that the bands 1, 2, and 3 are the bands characteristic of BIP and the bands 4 and 5 are the band associated with BIP aggregates. Emission peaks for BIPBMA/DMA solutions were also separated to five or less of Lorentzian equations with λ_{max} values similar to those for *c*-copolymers. The bands 1, 2, and 3 are considered to be the bands characteristic of BIP because these show concentration quenching. Figure 6 shows plots of the intensity of emission characteristic of BIP against BIP concentration for *l*-copolymers, *c*-copolymers, and the solutions. Where the intensity was evaluated by integration of the Lorentzian equation from 330 nm through 600 nm:

$$I_i = (a_i/b_i)\{\arctan((600 - \lambda_i)/b_i^{1/2})$$
$$- \arctan((330 - \lambda_i)/b_i^{1/2})\}$$

The upward slope (no concentration quenching) region under a critical concentration is the Lambert-Bear emission region,[7] where chromophore aggregates are broken up. The critical concentration of the *c*-copolymer is higher than that of the *l*-copolymer (if observed) and the solution. This suggests that formation of polymer network and dilution contributes

TABLE III
Coefficients of Lorentzian Equations Fitting to Fluorescence Spectra of the *c*-Copolymers

| Band	Coefficient	BIPBMA/MMA					
		1/100	1/200	1/400	1/800	1/1600	1/3200
1	$10^{-7}a_i$	17	19	90	135	110	78
	b_i	75	75	75	75	75	75
	λ_i	348	348	348	348	348	348
2	$10^{-7}a_i$	245	255	450	1400	1100	200
	b_i	350	350	350	350	350	350
	λ_i	362	362	362	365	365	362
3	$10^{-7}a_i$	200	200	550	1300	1700	1450
	b_i	530	530	530	600	900	600
	λ_i	384	384	380	390	390	370
4	$10^{-7}a_i$	230	221	0	0	0	0
	b_i	800	800	0	0	0	0
	λ_i	423	420	0	0	0	0
5	$10^{-7}a_i$	780	630	280	200	0	0
	b_i	1500	1200	1000	1000	0	0
	λ_i	494	492	498	498	0	0
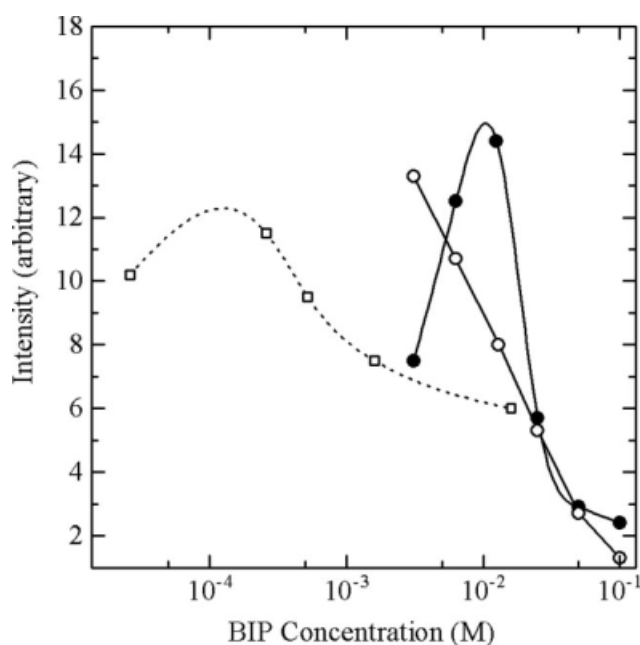
Figure 6 Concentration quenching of fluorescence from BIP in PMMA network (black circle), linear PMMA (white circle), and DMA (white rectangle).

to breaking up chromophore aggregates. The fluorescence spectrum of *l*-copolymer with 3.12×10^{-3} *M* is similar to that of *c*-copolymer with 0.1 *M*, as shown in (c) in Figure 2 and (a) in Figure 4. This suggests that the *l*-copolymer has the critical point around $3 \times 10^{-4}M$ close to that of solution.

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