Journal of Photochemistry and Photobiology A: Chemistry 213 (2010) 80–86

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photosensitized isomerization of olefin with benzophenone-conjugated amphiphilic graft copolymers

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ARTICLE INFO

Article history:
Received 10 February 2010
Received in revised form 20 April 2010
Accepted 1 May 2010
Available online 9 May 2010

Keywords:
Amphiphilic polymer
Graft copolymer
Photosensitizer
Photoisomerization
Olefin

ABSTRACT

Two kinds of amphiphilic graft copolymers, PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA, consisting of polar poly(acrylic acid) (PAA), less polar poly(methyl methacrylate) (PMMA), and benzophenone (BP) photosensitizing units, have been synthesized. These polymers, when used as a photosensitizer for isomerization of trans-β-methylstyrene, show a sensitization activity controlled by solvents. In benzene and chloroform, P(AA-*co*-BP)-*g*-PMMA forms a micelle structure consisting of aggregated P(AA-*co*-BP) core with dissolved PMMA units at the outer sphere. This suppresses a triplet energy transfer (TET) from the excited state BP units to olefin and, hence, shows lower sensitization activity than a bulk sensitizer (4-methoxybenzophenone: MBP). In methanol, both polymers form a weak aggregate of less polar PMMA units containing dissolved PAA units. The internal cavity of the aggregate is less polar and stabilizes the excited state BP units. This accelerates a TET from the excited state BP units to olefin and shows higher sensitization activity than MBP.

1. Introduction

Design of polymers containing photosensitizing units has attracted much attention in photochemical organic transformation [1] because polymer microenvironment provides various functions [2], such as accumulation of substrates [3], stabilization of excited state sensitizers [4], and enhancement of energy transfer to substrate [5]. Amphiphilic polymers containing both polar and less polar units have attracted a great deal of attention because of their unique properties. Notably, different solubility of the respective units in solvents usually leads to a self-assembly of the polymers [6], forming several kinds of nanostructures such as spheres [7], vesicles [8], and rods [9]. Various kinds of amphiphilic polymers have been proposed such as graft copolymers [10], block copolymers [11], star polymers [12], and hyperbranched polymers [13]. Among them, amphiphilic graft copolymers have been studied extensively because of their synthesis simplicity [14]. These polymers are usually synthesized via one of three methods [15]: (i) "grafting from" reaction involving a growth of side chains from the initiating groups on the polymer backbone; (ii) "grafting onto" reaction involving a coupling of side polymer chains onto the polymer backbone, and (iii) "grafting through" reaction involving a copolymerization of macromonomers. The morphology and structure of amphiphilic graft copolymers in different solvents have been studied extensively [16], and the polymers have been applied to various kinds of functional materials such as solubilizer [17], drug delivery media [18], catalyst [19], and adsorbent [20]. Although some amphiphilic polymers containing photosensitizing units have been used for photoreaction [21], there is no report of amphiphilic graft copolymer containing a photosensitizing unit.

In the present work, we synthesized amphiphilic graft copolymers consisting of less polar poly(methyl methacrylate) (PMMA), polar poly(acrylic acid) (PAA), and photosensitizing benzophenone (BP) units by the grafting through method. Two copolymers containing BP units either in PAA or PMMA unit, PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA, were synthesized (Scheme 1). These copolymers were used as a photosensitizer for isomerization of trans-β-methylstyrene (trans-MS) to cis-MS. We found that the sensitization activity of these copolymers strongly depends on solvents. ^{1}H NMR and dynamic light scattering (DLS) analysis indicate that this is due to the self-assembly of polymers in different solvents, leading to a change in location of BP moieties and polarity around the BP moieties.

2. Experimental

2.1. General

All of the reagents used were supplied from Wako, Aldrich, and Tokyo Kasei and used without further purification. Water was puri-

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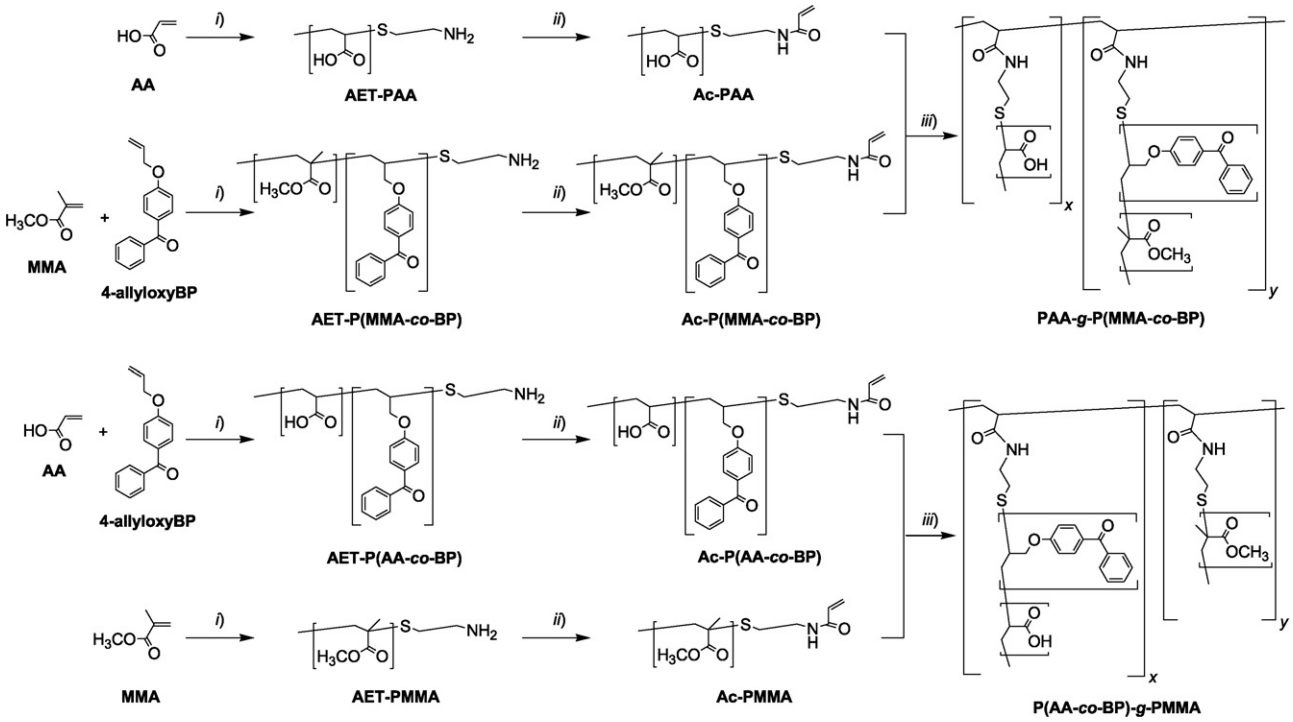
doi:10.1016/j.jphotochem.2010.05.003



Scheme 1. Synthesis of amphiphilic graft copolymers containing a photosensitizing unit. (i) AET, AIBN, toluene, 70 °C; (ii) acryloyl chloride, TEA, DMF, 65 °C; (iii) AIBN, DMSO, 65 °C.

fied by the MilliQ system. PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA were synthesized according to procedure summarized in Scheme 1. A hemicyanine dye (4-(4-dimethylaminostyryl)-1-methylpyridinium iodide) was synthesized according to literature procedure [22].

2.1.1. Synthesis of AET-PAA and AET-P(AA-co-BP)

AET-PAA was synthesized as follows: AA (1.40 g, 20 mmol), aminoethanthiol (AET) (0.5 g, 6.5 mmol), and AIBN (0.09 g, 0.55 mmol) were dissolved in toluene (5 mL), and the solution was degassed by twice freeze–pump–thaw cycles. The solution was kept at 65 °C for 14 h under dry N_2 and added slowly to diethyl ether (100 mL). The precipitate formed was collected by centrifugation and purified by reprecipitation with MeOH (1 mL) and diethyl ether (100 mL), affording AET-PAA as a white solid (1.7 g). AET-P(AA-*co*-BP) was synthesized in a manner similar to that of AET-PAA with 4-allyloxyBP (0.25 g, 1.1 mmol) [23] as a white solid (1.6 g). AET-PAA: ^{1}H NMR (400 MHz; DMSO-d_6; TMS): δ (ppm) = 1.57–1.83 (br, 2H, –CHCH_2–), 2.30 (d, J = 5.12 Hz, 1H, –CHCH$_2$–), 11.6 (br, COOH). AET-P(AA-*co*-BP): ^{1}H NMR (400 MHz; DMSO-d_6; TMS): δ (ppm) = 1.56–1.83 (br, 2H, –CHCH_2–), 2.30 (d, J = 5.25 Hz, 1H, –CHCH$_2$–), 7.02 (br, ArH), 7.60 (br, ArH), 11.6 (br, COOH).

2.1.2. Synthesis of AET-PMMA and AET-P(MMA-co-BP)

AET-PMMA was synthesized as follows: MMA (2.0 g, 20 mmol), AET (0.6 g, 7.8 mmol), and AIBN (0.09 g, 0.55 mmol) were dissolved in toluene (5 mL), and the solution was degassed by twice freeze–pump–thaw cycles. The solution was kept at 65 °C for 14 h under dry N_2 and added slowly to methanol (100 mL). The precipitate formed was collected by centrifugation, affording AET-PMMA (1.3 g) as a white solid. AET-P(MMA-*co*-BP) was synthesized in a manner similar to that of AET-PMMA with 4-allyloxyBP (0.25 g, 1.1 mmol) as a white solid (1.2 g). AET-PMMA: ^{1}H NMR (400 MHz; DMSO-d_6; TMS): δ (ppm) = 0.82–0.98 (br, 3H, C(CH_3)), 1.78–1.85 (d, J = 18.67 Hz, 2H, –CHCH_2–), 3.56 (s, br, 3H, COOCH_3). AET-P(MMA-*co*-BP): ^{1}H NMR (400 MHz; DMSO-d_6; TMS): δ (ppm) = 0.82–0.98 (br, 3H, C(CH_3)), 1.78–1.85 (d, J = 18.72 Hz, 2H, –CHCH_2–), 3.56 (s, br, 3H, COOCH_3), 6.96 (br, ArH), 7.67 (br, ArH).

2.1.3. Synthesis of Ac-PAA and Ac-P(AA-co-BP)

Ac-PAA was synthesized as follows: AET-PAA (1.12 g), triethylamine (TEA) (0.30 g, 3.0 mmol), and acryloyl chloride (0.30 g, 3.3 mmol) were dissolved in DMF (5 mL). The mixture was stirred for 14 h under dry N_2 at room temperature, and a HCl salt of TEA formed was removed by filtration. The resultant was added slowly to diethyl ether (100 mL). The precipitate formed was collected by centrifugation and purified by reprecipitation with MeOH (1 mL) and diethyl ether (100 mL), affording Ac-PAA (1.2 g) as a white solid. Ac-P(AA-*co*-BP) was synthesized in a manner similar to that of Ac-PAA with AET-P(AA-*co*-BP) (1.1 g) as a white solid (0.9 g). Ac-PAA: ^{1}H NMR (400 MHz; DMSO-d_6; TMS): δ (ppm) = 1.60–1.83 (br, 2H, –CHCH_2–), 2.30 (d, J = 5.23 Hz, 1H, –CHCH$_2$–), 5.56 (m, –CH=CH$_2$), 6.08 (m, –CH=CH_2), 11.6 (br, COOH). Ac-P(AA-*co*-BP): ^{1}H NMR (400 MHz; DMSO-d_6; TMS): δ (ppm) = 1.53–1.77 (br, 2H, –CHCH_2–), 2.24 (d, J = 5.44 Hz, 1H, –CHCH$_2$–), 5.56 (m, –CH=CH$_2$), 6.08 (m, –CH=CH_2), 7.05 (br, ArH), 7.63 (br, ArH), 12.1 (br, COOH).

2.1.4. Synthesis of Ac-PMMA and Ac-P(MMA-co-BP).

Ac-PMMA was synthesized as follows: AET-PMMA (1.0 g), TEA (0.30 g, 3.0 mmol), and acryloyl chloride (0.30 g, 3.3 mmol) were dissolved in DMF (5 mL). The mixture was stirred under dry N_2 for 14 h at room temperature, and a HCl salt of TEA formed was removed by filtration. The resultant was added slowly to diethyl ether (100 mL). The precipitate formed was collected by centrifugation and purified by reprecipitation with MeOH (1 mL) and diethyl ether (100 mL), affording Ac-PMMA (1.0 g) as a white solid. Ac-P(MMA-*co*-BP) was synthesized in a manner similar to that of Ac-PMMA with AET-P(MMA-*co*-BP) (1.07 g) as a white solid (1.0 g). Ac-PMMA: ^{1}H NMR (400 MHz; DMSO-d_6; TMS): δ (ppm) = 0.84–0.98 (br, 3H, C(CH_3)), 1.78–1.85 (d, J = 18.34 Hz, 2H, –CHCH_2–), 3.56 (s, br, 3H, COOCH_3), 5.50 (m, –CH=CH$_2$), 6.08 (m, –CH=CH_2). Ac-P(MMA-*co*-BP): ^{1}H NMR (400 MHz; DMSO-

Table 1
Property of polymers.

Polymer	x/y[a]	M_n [b] (g mol^{-1})	M_w [b] (g mol^{-1})	BP unit [c] (μmol g^{-1})	E_S [d] (kJ mol^{-1})	E_T [d] (kJ mol^{-1})
Ac-PMMA		14,500	60,000			
Ac-PAA		17,000	67,100			
Ac-P(MMA-*co*-BP)		15,400	36,000	69.7	329	289
Ac-P(AA-*co*-BP)		11,800	26,100	256	329	288
PAA_x-*g*-P(MMA-*co*-BP)$_y$	65/35	45,700	151,700	18.0	334	289
P(AA-*co*-BP)$_x$-*g*-$PMMA_y$	81/19	27,600	87,500	88.4	332	287

[a] Determined by ^{1}H NMR analysis.
[b] Determined by GPC analysis.
[c] Determined from absorption spectra.
[d] Excited state energies estimated by absorption, fluorescence, and phosphorescence (77 K) analysis.

d_6; TMS): δ (ppm) = 0.84–0.98 (br, 3H, C(CH_3)), 1.78–1.85 (d, J = 18.56 Hz, 2H, –CHCH_2–), 3.56 (s, br, 3H, COOCH_3), 5.50 (m, –C*H*=CH_2), 6.09 (m, –CH=CH_2), 6.97 (br, Ar*H*), 7.67 (br, Ar*H*).

2.1.5. Synthesis of PAA-g-P(MMA-co-BP) and P(AA-co-BP)-g-PMMA

PAA-*g*-P(MMA-*co*-BP) was synthesized as follows: Ac-PAA (0.4 g), Ac-P(MMA-*co*-BP) (0.4 g), and AIBN (0.1 g, 0.6 mmol) were dissolved in DMSO (5 mL), and the solution was degassed by twice freeze-pump-thaw cycles. The solution was kept at 65 °C for 14 h under dry N_2 and added slowly to diethyl ether (100 mL). The precipitate formed was collected by centrifugation and purified by reprecipitation with MeOH (1 mL) and diethyl ether (100 mL), affording PAA-*g*-P(MMA-*co*-BP) (0.40 g) as a white solid. P(AA-*co*-BP)-*g*-PMMA was obtained in a manner similar to that of PAA-*g*-P(MMA-*co*-BP) with Ac-P(AA-*co*-BP) (0.3 g) and Ac-PMMA (0.3 g) as a white solid (0.48 g). PAA-*g*-P(MMA-*co*-BP): ^{1}H NMR (400 MHz; DMSO-d_6; TMS): δ (ppm) = 0.82–0.98 (br, 3H, C(CH_3)), 1.59–1.78 (br, 2H, –CHCH_2–), 1.78–1.85 (d, J = 18.55 Hz, 2H, –CHCH_2–), 2.30 (d, J = 5.02 Hz, 1H, –C*H*CH_2–), 3.56 (s, br, 3H, COOCH_3), 6.97 (br, Ar*H*), 7.67 (br, Ar*H*), 11.7 (br, COO*H*). IR (KBr): ν (cm^{-1}) = 3438, 3001, 2954, 2889, 1730, 1445, 1383, 1273, 1239, 1201, 1151, 987, 835, 747. P(AA-*co*-BP)-*g*-PMMA: ^{1}H NMR (400 MHz; DMSO-d_6; TMS): δ (ppm) = 0.82–0.98 (br, 3H, C(CH_3)), 1.58–1.78 (br, 2H, –CHCH_2–), 1.78–1.85 (d, J = 18.62 Hz, 2H, –CHCH_2–), 2.30 (d, J = 5.13 Hz, 1H, –C*H*CH_2–), 3.56 (s, br, 3H, COOCH_3), 7.03 (br, Ar*H*), 7.59 (br, Ar*H*), 12.1 (br, COO*H*). IR (KBr): ν (cm^{-1}) = 3435, 3000, 2957, 2838, 1730, 1600, 1452, 1397, 1259, 1192, 1152, 989, 800, 752.

2.2. Photoreaction

Each polymer was dissolved in benzene, chloroform, or methanol (5 mL) containing trans-MS within a Pyrex glass tube (capacity: 20 mL). The tube was sealed using a rubber septum cap. Argon gas was bubbled through the solution for 5 min at 5 °C. The tube was photoirradiated with magnetic stirring by a high-pressure Hg lamp (100 W; Eikohsha Co. Ltd., Osaka, Japan), filtered through an aqueous $CuSO_4$ (10 wt%) solution to give light wavelengths of λ > 320 nm. The light intensity at 320–400 nm (through the filter) is 905 mW m^{-2}, and the temperature of the solution is 298 K during photoirradiation. Substrate and product concentrations were measured by a gas chromatography (Shimadzu GC-1700, equipped with FID).

2.3. Analysis

Absorption spectra were recorded on an UV–vis photodiode-array spectrophotometer (Shimadzu; Multispec-1500; resolution, 1 nm; band-path length, 1.5 nm) [24]. The amounts of BP units on the polymers were determined by comparison of absorbance ($A_{290\,nm}$) with 4-methoxybenzophenone (MBP) in DMSO (ε = 1.62 × 10^4 M^{-1} cm^{-1}) at 298 K. ^{1}H NMR spectra were obtained by JEOL JNM-AL400 (400 MHz). Fluorescence and phosphorescence spectra (77 K) were measured on a Hitachi F-4500 fluorescence spectrophotometer (resolution, 1 nm; band-path length, 2.5 nm) [25], with an EtOH/diethyl ether glass (2/1 v/v). Singlet and triplet energy of the polymers were determined according to literature procedure [26]. DLS analysis was performed on a laser light scattering spectrometer (LB-500, HORIBA) [27]. Molecular weight of the polymers was determined by gel permeation chromatography (GPC) using a JASCO HPLC system equipped with a PU-980 pump (JASCO) and refractive index detector RI-930 (JASCO) with KF-806L column (Shodex). Polystyrene standards were used for calibration. The oven temperature was 40 °C, and DMF containing LiBr (0.01 M) was used as a carrier solvent (flow rate: 0.6 mL/min), where the polymers containing PAA units were analyzed after esterification of –COOH units with BF_3/MeOH [28].

3. Results and discussion

3.1. Properties of polymers

Two kinds of amphiphilic graft copolymers containing photosensitizing BP units, PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA, were synthesized via a grafting through method [15], according to procedure depicted in Scheme 1. The properties of the polymers are summarized in Table 1. As shown in Fig. 1, absorption spectra of both polymers show a distinctive absorption band of the BP moieties at 260–330 nm, which is similar to that of 4-methoxybenzophenone (MBP) used as a reference sensitizer (spectrum c). In addition, singlet energy (E_S) and triplet energy (E_T) of the polymers are similar to that of MBP (E_S = 325 and E_T = 289 kJ mol^{-1}).

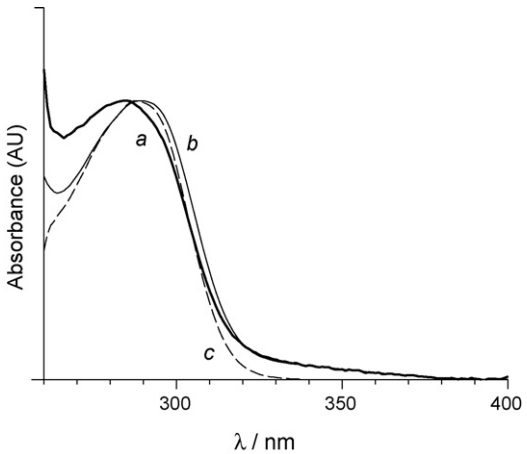


Fig. 1. Absorption spectra of (a) PAA-*g*-P(MMA-*co*-BP) (0.2 g L^{-1}), (b) P(AA-*co*-BP)-*g*-PMMA (0.2 g L^{-1}), and (c) MBP (0.17 μM) measured in DMSO at 298 K.

Table 2
Cis-MS yields obtained by 12 h photoirradiation of trans-MS in (a) benzene, (b) chloroform, and (c) methanol with the respective sensitizers.[a]

Solvent	Sensitizer	cis-MS yield (%)
Benzene	MBP	17.4
	PAA-*g*-P(MMA-*co*-BP)	14.5
	P(AA-*co*-BP)-*g*-PMMA	3.8
Chloroform	MBP	10.4
	PAA-*g*-P(MMA-*co*-BP)	9.2
	P(AA-*co*-BP)-*g*-PMMA	3.8
Methanol	MBP	3.0
	PAA-*g*-P(MMA-*co*-BP)	8.1
	P(AA-*co*-BP)-*g*-PMMA	12.0

[a] The sensitizers are MBP (5.0 μM), PAA-*g*-P(MMA-*co*-BP) (0.56 g L^{-1}), P(AA-*co*-BP)-*g*-PMMA (0.11 g L^{-1}), respectively, where the polymer solutions contain 5.0 μM BP units.

Photosensitization activities of these polymers were estimated with an isomerization of trans-*β*-methylstyrene (trans-MS) to cis-MS, a typical isomerization reaction promoted by a triplet energy transfer (TET) from the excited state BP (^{3}BP*) to trans-MS [29]. The photoreaction was performed by photoirradiation (λ > 320 nm) of different organic solvents such as benzene, chloroform, and methanol containing trans-MS (25 μmol) and the respective polymers (containing 0.025 μmol BP unit) under Ar atmosphere. Photoirradiation of all solutions containing respective polymers gives rise to cis-MS as a sole product, as does MBP. Other products such as oxetanes and olefin dimers are not observed, as is the case with unpolymerized BP sensitizer [29], and the mass balances of the reactions are more than 90%. Table 2 summarizes the cis-MS yields (based on the initial amount of trans-MS) obtained by 12 h photoirradiation. Fig. S1 (Supplementary material) shows the time-dependent change in cis-MS yields. The yields increase with time and are not saturated at 12 h photoirradiation. This indicates that the isomerization does not achieve the photostationary state after 12 h photoirradiation. With MBP, the cis-MS yield lies in the order of benzene > chloroform > methanol. This is because, as reported [30], the n,π^* triplet excited state of BP unit is destabilized in polar solvent. The solvent polarity parameter, Δf, is defined as the following equation [31]:

$$\Delta f = \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \quad (1)$$

where ε is the dielectric constant and n is the refractive index of the solvents, respectively [32]. The Δf values lie in the order of benzene (0.003) < chloroform (0.147) < methanol (0.309), indicating that the solvent polarity increases in this order. These data clearly suggest that isomerization of trans-MS indeed occurs efficiently in less polar solvents. Amphiphilic graft copolymers, however, show different sensitization activity (Table 2). PAA-*g*-P(MMA-*co*-BP) containing BP units in less polar PMMA units shows a cis-MS yield similar to MBP in benzene and chloroform, but shows much higher yield in methanol. In contrast, P(AA-*co*-BP)-*g*-PMMA containing BP units in polar PAA units shows a cis-MS yield much lower than MBP in benzene and chloroform, but shows much higher yield in methanol.

3.2. Photosensitization in benzene and chloroform

The very low sensitization activity of P(AA-*co*-BP)-*g*-PMMA in benzene and chloroform (Table 2) is because, in these solvents, the polymer forms a "micelle" structure consisting of strongly aggregated PAA core with dissolved PMMA units at the outer sphere, as schematically shown in Scheme 2b. The BP units are confined within the aggregate, and the TET from ^{3}BP* to trans-MS is suppressed, resulting in very low cis-MS yield. The aggregation of

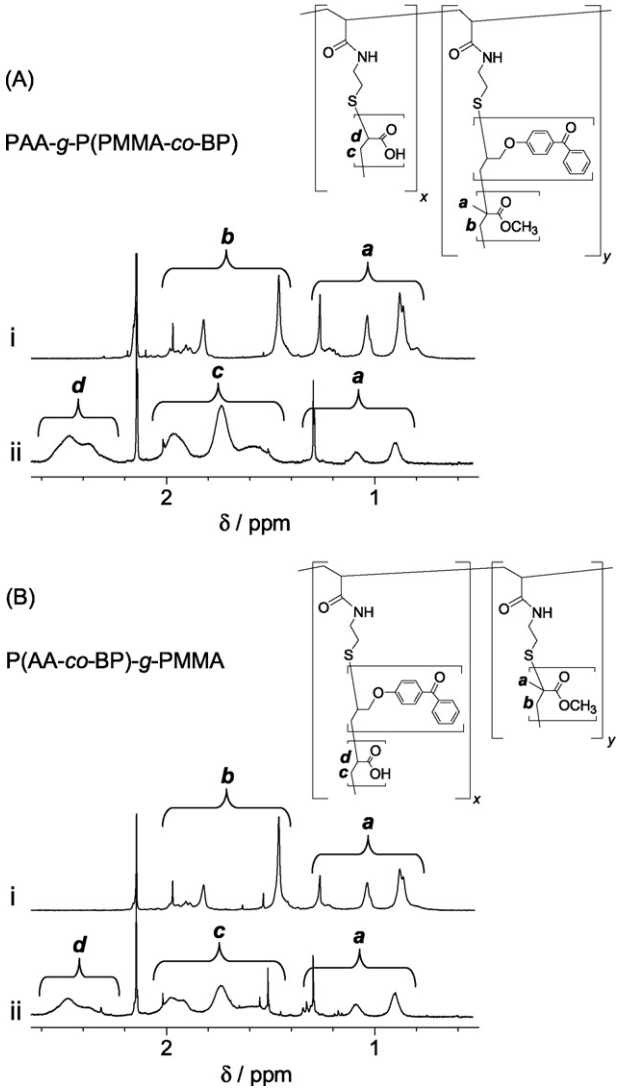
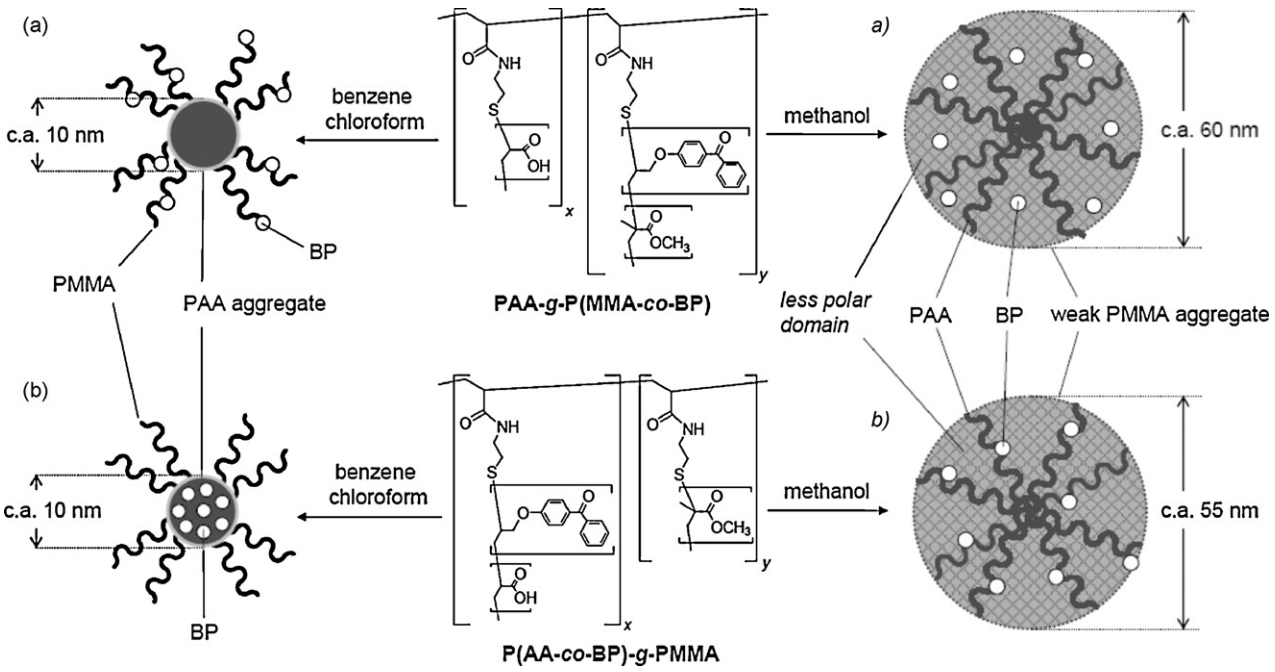


Fig. 2. ^{1}H NMR spectra of (A) PAA-*g*-P(MMA-*co*-BP) and (B) P(AA-*co*-BP)-*g*-PMMA measured in (i) chloroform-*d* and (ii) methanol-d_4.

P(AA-*co*-BP) units and the dissolution of PMMA units are confirmed by ^{1}H NMR analysis of the polymer in chloroform-*d*. As shown in Fig. 2B.i, methyl and methylene signals (*a* and *b*) of the PMMA units appear at 0.8–2.0 ppm [33], whereas the signals of PAA units (*c* and *d*) do not. This suggests that P(AA-*co*-BP) units are indeed aggregated, while PMMA units are dissolved in solution [34]. This is also confirmed by dynamic light scattering (DLS) analysis. As shown in Fig. 3b, P(AA-*co*-BP)-*g*-PMMA in benzene and chloroform shows a formation of polymer particle with 10–20 nm diameter. In contrast, Ac-PMMA polymer with no PAA unit (Scheme 1) does not show scattered light in these solvents (Fig. 3e). This again suggests that P(AA-*co*-BP) units are aggregated, while PMMA units are dissolved. As shown in Fig. 3d, Ac-P(AA-*co*-BP) with no PMMA unit shows polymer particles with 10–20 nm diameter in benzene and chloroform, which is similar to P(AA-*co*-BP)-*g*-PMMA (Fig. 3b). This suggests that, as shown in Scheme 2b, P(AA-*co*-BP)-*g*-PMMA in these solvents indeed forms a micelle structure consisting of the aggregated PAA core with the dissolved PMMA units at the outer sphere. The low cis-MS yield in benzene and chloroform (Table 2) is therefore because strong aggregation of P(AA-*co*-BP) units suppresses TET from ^{3}BP* to trans-MS.

Fig. 2A.i shows ^{1}H NMR spectrum of PAA-*g*-P(MMA-*co*-BP) measured in chloroform-*d*, which contains BP units in less polar PMMA



Scheme 2. Schematic representation of the structure of amphiphilic graft copolymers in different solvents.

units. As is the case for P(AA-*co*-BP)-*g*-PMMA (Fig. 2B.i), methyl and methylene signals for PMMA units (*a* and *b*) appear, whereas the signals for PAA units do not. This indicates that PAA units are aggregated, while P(MMA-*co*-BP) units are dissolved. As shown in Fig. 3a, PAA-*g*-P(MMA-*co*-BP) in benzene and chloroform shows a formation of 10–20 nm polymer particles, which is similar to that of P(AA-*co*-BP)-*g*-PMMA (Fig. 3b). Ac-P(MMA-*co*-BP) in benzene and chloroform does not show particle formation (Fig. 3c), whereas Ac-PAA shows a formation of 10–20 nm particles (Fig. 3f). These indicate that PAA-*g*-P(MMA-*co*-BP) in these solvents forms a micelle structure similar to that of P(AA-*co*-BP)-*g*-PMMA, as shown in Scheme 2a, where the dissolved BP units are located at the outer sphere. The sensitization activity of PAA-*g*-P(MMA-*co*-BP) comparable to that of MBP in benzene and chloroform (Table 2) is therefore due to the dissolution of BP units in a bulk solution.

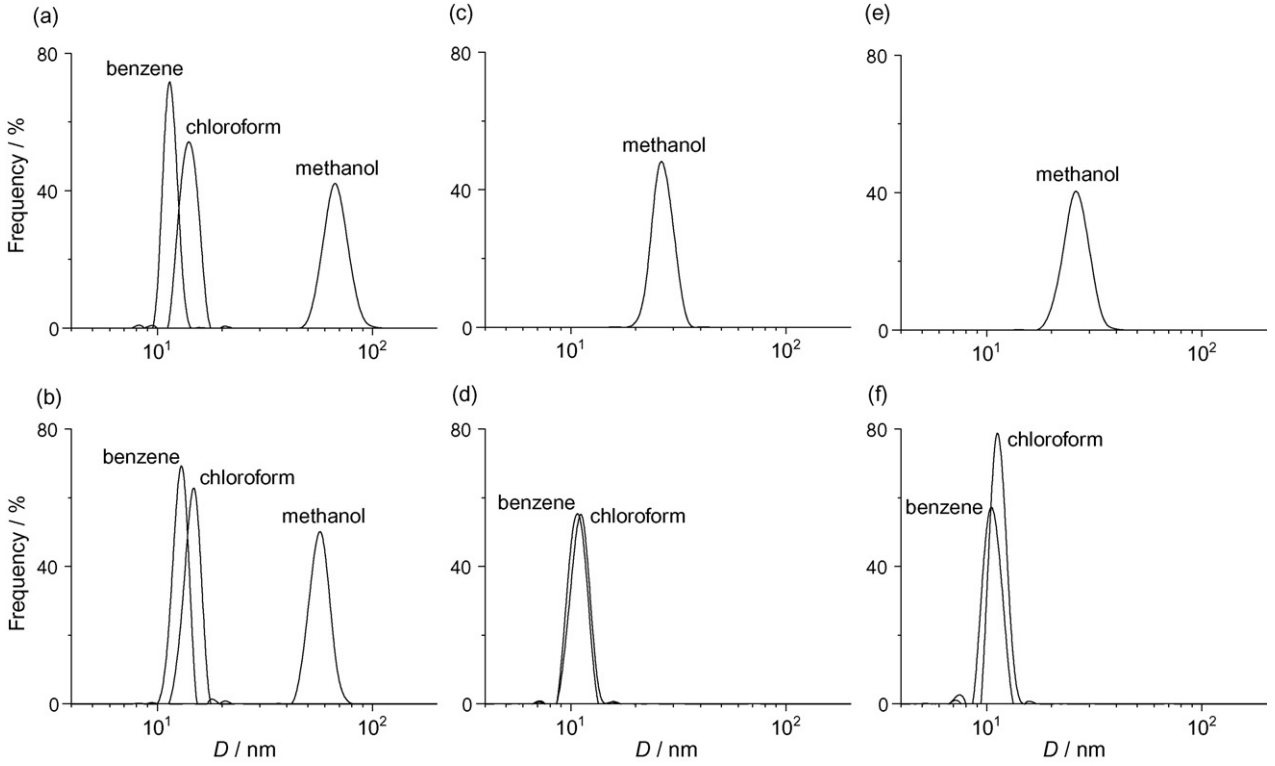


Fig. 3. Hydrodynamic diameter (*D*) of (a) PAA-*g*-P(MMA-*co*-BP) (0.56 g L^{-1}), (b) P(AA-*co*-BP)-*g*-PMMA (0.11 g L^{-1}), (c) Ac-P(MMA-*co*-BP) (0.07 g L^{-1}), (d) Ac-P(AA-*co*-BP) (0.02 g L^{-1}), (e) Ac-PMMA (0.07 g L^{-1}), and (f) Ac-PAA (0.02 g L^{-1}) measured in different solvents.

Table 3
Spectral data of a hemicyanine dye (4-(4-dimethylaminostyryl)-1-methylpyridinium iodide) obtained in methanol.

Polymer	λ_{max} (nm)		
	Absorption	Fluorescence	Stokes shift (cm^{-1})
None	475	588	4000
PAA-*g*-P(MMA-*co*-BP)	476	585	3900
P(AA-*co*-BP)-*g*-PMMA	476	584	3900

3.3. Photosensitization in methanol

As shown in Table 2, in methanol, sensitization activity of both PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA are much higher than that of MBP. This is because these polymers form a weak aggregate containing a "less polar domain" (Scheme 2c and d), which stabilizes the n, π^* triplet excited state BP moieties [30] and enhances TET to trans-MS. The formation of less polar domain is confirmed by absorption and fluorescence analysis with a fluorescent dye. As reported [35], a hemicyanine dye shows a red shift of absorption band and a blue shift of fluorescence band with a decrease in polarity of the media. The Stokes shift (cm^{-1}) between the absorption and fluorescence maxima is therefore correlated with the polarity of media [36]. Table 3 summarizes the spectral data of a hemicyanine dye (4-(4-dimethylaminostyryl)-1-methylpyridinium iodide) measured in methanol without and with polymers. The Stokes shifts obtained with both polymers are lower than that obtained without polymer, indicating that the dye is located in a less polar part formed within the polymers. In the present reaction, accumulation of trans-MS around the BP units is also a possible reason for isomerization enhancement. However, stirring a methanol solution containing the respective polymers and trans-MS (298 K, 12 h) does not show any change in the trans-MS concentration in solution. This suggests that substrate accumulation within the polymer [3] does not contribute to the isomerization enhancement, leaving the formation of less polar domain within the polymer being the major factor.

The less polar domain is formed by a weak aggregation of PMMA units less soluble in methanol. In alcoholic solvents, polar PAA units are soluble, while less polar PMMA units tend to aggregate [37]. Fig. 2ii shows ^{1}H NMR spectra of PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA measured in methanol-d_4. As expected, strong *c* and *d* signals for PAA units appear. In addition, the signal *a* for PMMA units also appears, although at the decreased level. This indicates that less polar PMMA units in both polymers are partly soluble in methanol [34]. As shown in Fig. 3a and b, DLS analysis of PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA in methanol detect polymer particles with 40–100 nm diameter, although smaller particles (10–20 nm) form in benzene and chloroform. This implies that weak aggregation of less polar PMMA units in methanol leads to a formation of large polymer particles with a less polar character.

The formation of weakly aggregated large polymer particles is because the polar PAA units are located within the PMMA aggregate, as schematically shown in Scheme 2c and d. As shown in Fig. 3c and e, Ac-P(MMA-*co*-BP) and Ac-PMMA in methanol show a formation of polymer particles with 20–40 nm diameter, which are much smaller than the particles of PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA polymers in methanol (40–100 nm, Fig. 3a and b). The presence of polar PAA units suppresses the aggregation of less polar PMMA units. This probably leads to a weak aggregation of the PMMA units and results in the formation of large polymer particles. As a result of this, for both P(AA-*co*-BP)-*g*-PMMA and PAA-*g*-P(MMA-*co*-BP), the BP units exist within the less polar domain (Scheme 2c and d), in which their excited states are stabilized. The substrate, trans-MS, is able to diffuse inside the weak aggregate and is isomerized efficiently by TET from ^{3}BP*. The formation of weak aggregate with a less polar domain (Scheme 2c and d) is, therefore, probably the major factor for high photosensitization activity of both PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA polymers in methanol.

4. Conclusion

Effect of solvents on photosensitization activity of amphiphilic graft copolymers containing a BP photosensitizing unit, PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA, has been studied for isomerization of trans-MS, with the following results:

(1) In benzene and chloroform, P(AA-*co*-BP)-*g*-PMMA shows much lower sensitization activity than a bulk MBP sensitizer. The polymer forms a micelle structure consisting of strongly aggregated P(AA-*co*-BP) core with dissolved PMMA units at the outer sphere. The confinement of the BP units within the core suppresses the triplet energy transfer from ^{3}BP* to trans-MS and, hence, results in lower sensitization activity.
(2) In methanol, both PAA-*g*-P(MMA-*co*-BP) and P(AA-*co*-BP)-*g*-PMMA show higher sensitization activity than MBP. These polymers form a weak aggregate of less polar PMMA units, which contains dissolved PAA units. The less polar domain formed within the aggregate stabilizes the excited state BP moieties. This enhances the TET from ^{3}BP* to trans-MS and, hence, results in isomerization enhancement.

Acknowledgments

This work was supported by the Grant-in-Aid for Scientific Research (No. 19760536) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.05.003.

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