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Temperature- and pH-responsive photosensitization activity of polymeric sensitizers based on poly-*N*-isopropylacrylamide

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ABSTRACT

We previously reported that a copolymer consisting of *N*-isopropylacrylamide (NIPAM) and benzophenone (BP) units, behaves as a photosensitizer showing temperature-controlled oxygenation activity in water (*J. Am. Chem. Soc.* **2006**, *128*, 8751). This polymer shows a heat-induced oxygenation enhancement at low temperature region (5–20 °C), while showing a heat-induced oxygenation suppression at high temperature region (20–60 °C), resulting in an *off-on-off* activity profile against the temperature window. This is driven by a heat-induced phase transition of the polymer from *coil* to *micelle* and then to *globule* states. In the present work, effects of adding an amine component (*N*-[3-(dimethylamino)propyl]acrylamide: DMAPAM) to the polymer on the sensitization activity were studied, where the relationship between the phase transition behavior and the activity was clarified by several spectroscopic analyses. The polymers, poly(NIPAM$_x$-*co*-BP$_y$-*co*-DMAPAM$_z$), show activity controlled by temperature and pH. The off-on-off activity profile shifts to higher temperature with a pH decrease. This is because protonation of the DMAPAM units leads to an increase in the polymer polarity and, hence, the polymer aggregates at higher temperature. In addition, increase in the DMAPAM content of the polymer leads to further shift of the activity profile. In contrast, at pH < 8, no activity enhancement is observed because complete protonation of the DMAPAM units suppresses polymer aggregation.

1. Introduction

The design of polymers containing photosensitizing units has attracted a great deal of attention in photochemical organic transformation [1], because polymer microenvironment provides various functions [2] such as accumulation of substrates [3], stabilization of photoexcited sensitizers [4], and enhancement of energy transfer to substrates [5]. In an earlier work [6], we synthesized a polymeric photosensitizer showing temperature-controlled oxygenation activity by singlet oxygen ($^1O_2$) in water. The poly(NIPAM$_x$-*co*-BP$_y$) (**P0** polymer) has a structure consisting of *N*-isopropylacrylamide (NIPAM) and benzophenone (BP) units (Scheme 1a). The **P0** polymer in water promotes a heat-induced oxygenation enhancement at low temperature region (5–20 °C), while promoting a heat-induced oxygenation suppression at high temperature region (20–60 °C). It is well known that polyNIPAM in water shows a reversible phase transition associated with hydration/dehydration of the polymer chain by temperature [7]. PolyNIPAM has a polar structure at low temperature (*coil* state), but a rise in temperature leads to weak aggregation, leading to a formation of less polar domain inside the polymer (*micelle* state). Further increase in temperature leads to strong aggregation and produces polymer particle (*globule* state). The temperature-controlled $^1O_2$ oxygenation by **P0** polymer is triggered by this phase transition sequence (Scheme 2). The less polar domain formed inside the micelle state polymer lengthens $^1O_2$ lifetime, leading to heat-induced oxygenation enhancement at <20 °C. In contrast, the globule state polymer expels the substrate to bulk solution, leading to oxygenation suppression at >20 °C.

It is well known that the aggregation property of polyNIPAM, when containing ionizable groups such as carboxylic acids or amine groups, strongly depends on the pH of the solution. The polarity of these ionizable groups changes significantly upon protonation/deprotonation by changes in pH, thus leading to drastic change in the aggregation properties of the polymer [8]. In the present work, the effects of adding an ionizable amine group (*N*-[3-(dimethylamino)propyl]acrylamide: DMAPAM) [9] to the polymer on the sensitization activity were studied in order to add a new functionality to the temperature-responsive polymeric sensitizer. We synthesized two polymers, poly(NIPAM$_x$-*co*-BP$_y$-*co*-DMAPAM$_z$)

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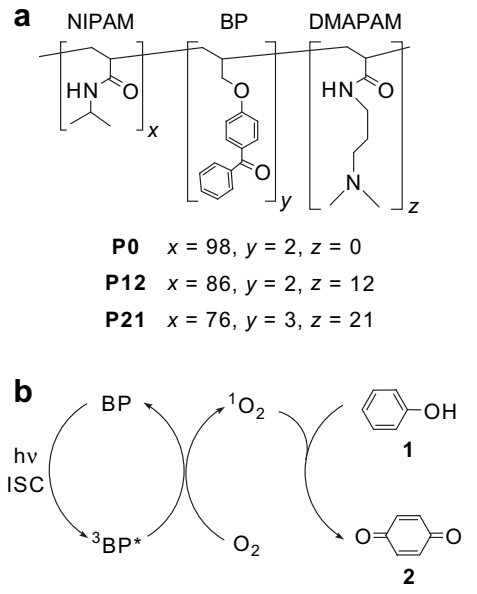


Scheme 1. (a) Structure of poly(NIPAM$_x$-*co*-BP$_y$-*co*-DMAPAM$_z$) and (b) sensitized $^1O_2$ oxygenation of phenol (**1**) to *p*-benzoquinone (**2**), where ISC denote the intersystem crossing.

($x/y/z = 76/3/21$, **P21** polymer; $x/y/z = 86/2/12$, **P12** polymer), containing different amounts of DMAPAM units (Scheme 1a, Table 1). We found that the incorporated DMAPAM units strongly affect the aggregation property and the sensitization activity of the polymers; these polymers show sensitization activity controlled by temperature and pH. We describe here the detailed relationship between the aggregation behavior and the sensitization activity of the polymers by means of absorption, dynamic light scattering, and ^{1}H NMR analyses.

2. Experimental

2.1. Materials

NIPAM monomer (Wako, ≥98%) was purified by recrystallization from *n*-hexane. AIBN (Wako, 98%) was recrystallized from methanol before use. DMAPAM monomer (Wako, ≥97%), 4-hydroxybenzophenone (TCI, ≥98%), acryloyl chloride (TCI, ≥95%), toluene (Wako, ≥99%), methanol (Wako, ≥99.8%), diethyl ether (Wako, ≥99%), D_2O (Merk, 99.9%), and phenol (Wako, ≥99%) were used as received. Water was purified by the Milli Q system. Compositions of buffered aqueous solutions are as follows: pH 8 (0.05 M KH_2PO_4 and 0.047 M NaOH), pH 9 (0.05 M H_3BO_3, 0.05 M KCl, and 0.021 M NaOH), pH 10 (0.025 M $NaHCO_3$ and 0.011 M NaOH), and pH 11 (0.025 M $NaHCO_3$ and 0.023 M NaOH).

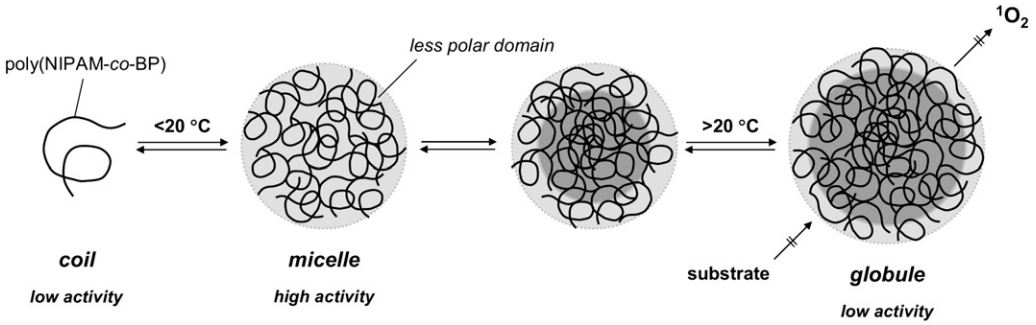
Poly(NIPAM$_x$-*co*-BP$_y$-*co*-DMAPAM$_z$). Required amounts of NIPAM, 4-allyloxyBP [10], DMAPAM, and AIBN (Table 1) were dissolved in toluene (5 mL) and degassed by twice freeze-pump-thaw cycles. The solution was kept at 60 °C for 18 h under dry N_2. The resultant was poured into diethyl ether (100 mL). The precipitate formed was collected by centrifugation and purified by reprecipitation with MeOH (1 mL) and diethyl ether (100 mL), affording poly(NIPAM-*co*-BP-*co*-DMAPAM) as a fluffy brown solid: ^{1}H NMR (400 MHz; $CDCl_3$; TMS): δ (ppm) = 1.07 (s, br, –C(CH_3)$_2$), 1.2–2.2 (m, –$CHCH_2$– and –$CH_2CH_2CH_2$–), 3.22 (s, br, –NHCH_2CH_2– and –CH_2N(CH_3)$_2$), 3.88 (s, br, –CH–), 6.72 (br, –NH–), 7.65 (br, Ar–H). The BP amount of the respective polymers was determined by comparison of absorbance (A_{290}) with 4-methoxyBP ($\epsilon = 7.98 \times 10^3$ M^{-1} cm^{-1} methanol, 298 K).

2.2. Photoreaction

Each polymer was dissolved in a buffered aqueous solution (5 mL) containing phenol (**1**) within a Pyrex glass tube (capacity: 20 mL). Each tube was sealed using a rubber septum cap, and O_2 was bubbled through the solution for 5 min in an ice bath to avoid evaporation of the materials. The sample 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 $\lambda > 320$ nm. The light intensity at 320–400 nm (through the filter) is 905 mW m^{-2}. Substrate and product concentrations were measured by GC-FID (Shimadzu GC-14B).

2.3. Analyses

Absorption spectra were recorded on an UV-visible photodiode-array spectrophotometer (Shimadzu; Multispec-1500) [11] with a temperature controller (Shimadzu; S-1700) with a 10 mm path length quartz cell. ^{1}H NMR spectra were obtained by JEOL JNM-AL400 spectrometer (400 MHz). Fluorescence and phosphorescence spectra (77 K) were measured on a Hitachi F-4500 fluorescence spectrophotometer using an ethanol/diethyl ether glass (2/1 v/v) within a 4 mm cylindrical quartz tube. The singlet energy (E_S) and triplet energy (E_T) of the sensitizers were determined according to a literature procedure [12]. Dynamic light scattering (DLS) measurement was carried out with a laser scattering spectrometer (LB-500, HORIBA) [13], where the light source was a 5 mW semiconductor laser ($\lambda = 650$ nm) and the scattering angle was 90°. The molecular weights of the polymers were 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) [14]. The oven temperature



Scheme 2. Temperature-dependent change in structure and sensitization activity of **P0** Polymer.

Table 1
Property of Poly(NIPAM$_x$-*co*-BP$_y$-*co*-DMAPAM$_z$)

	$x/y/z$ (mol%) [a]	Feed composition (g)[b]			M_n[c]	M_w/M_n[c]	BP content (μmol g^{-1})[d]	E_S (E_T) (kJ mol^{-1})[e]
		NIPAM	AlloxyBP	DMAPAM				
P21	76/3/21	0.60	0.13	0.21	28600	4.79	237	336 (289)
P12	86/2/12	0.60	0.20	0.11	48000	3.10	185	330 (289)
P0	98/2/0	0.60	0.13		84700	4.47	189	329 (289)

[a] Determined by ^{1}H NMR analysis.
[b] Amounts used for synthesis.
[c] Determined by GPC.
[d] Determined by absorption spectra (Fig. 1).
[e] Excited-state energies estimated by absorption, fluorescence, and phosphorescence (77 K) measurements in ethanol/diethyl ether (2/1 v/v).

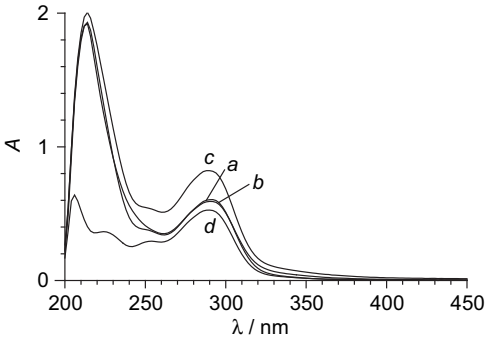


Fig. 1. Absorption spectra of (a) **P0**, (b) **P12**, (c) **P21** polymers (0.4 g L^{-1}), and (d) 4-methoxyBP (0.66 μM) measured in methanol at 298 K.

was 40 °C and DMF containing LiBr (0.01 M) was used as the carrier solvent (flow rate: 0.6 mL min^{-1}). Potentiometric pH titration was carried out on a COMTITE-550 potentiometric automatic titrator (Hiranuma Co., Ltd.) with a glass electrode GE-101 [15].

3. Results and discussion

3.1. Effects of DMAPAM content

Two kinds of polymeric photosensitizers with different DMAPAM content, poly(NIPAM$_x$-*co*-BP$_y$-*co*-DMAPAM$_z$) ($x/y/z = 76/3/21$, **P21**; $x/y/z = 86/2/12$, **P12**), were synthesized by copolymerization of NIPAM, 4-allyloxyBP, and DMAPAM with AIBN as an initiator (see Experimental section). Fig. 1 shows absorption spectra of the polymers. Both polymers show distinctive BP absorption at 270–350 nm, as does the DMAPAM-free **P0** polymer. In addition, as shown in Table 1, singlet energy (E_S) and triplet energy (E_T) of both polymers are similar to that of **P0**. Effects of DMAPAM content on the sensitization activity were studied first in comparison to that of **P0**. The activity was tested by $^1O_2$ oxygenation of phenol (**1**) to *p*-benzoquinone (**2**) (Scheme 1b) [16]. The reaction was performed by photoirradiation ($\lambda > 320$ nm, 3 h) to an O_2-saturated aqueous solution of pH 10 containing phenol (**1**) with the respective polymers at constant polymer concentration (0.08 g L^{-1}). At all tested temperatures, **2** was produced as the sole product [6]. Fig. 2 shows a temperature-dependent change in turnover number (TON) for **2** formation [=(**2** yield)/(BP amount in solution)] [17]. With **P0**, the activity increases with a rise in temperature at <20 °C, but decreases at >20 °C, showing an "*off-on-off*" activity profile against the temperature window. **P12** and **P21** polymers also show an

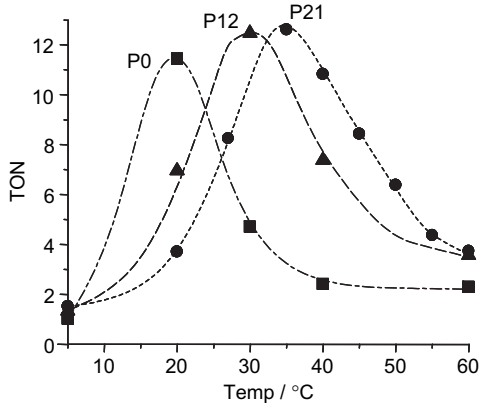


Fig. 2. Temperature-dependent change in turnover number (TON) for **2** formation during reaction ($\lambda > 320$ nm, 3 h) of **1** (2 mM) in O_2-saturated aqueous solution (pH 10, 5 mL) with respective polymers (0.08 g L^{-1}).

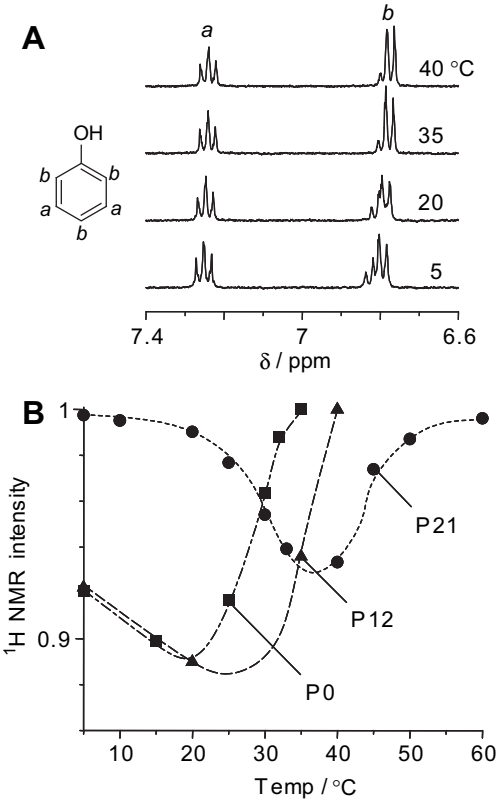


Fig. 3. (A) ^{1}H NMR spectra of **1** measured in D_2O with **P12**. (B) Intensity of ^{1}H NMR signals of **1** measured with the respective polymers. The intensity was determined by integration of all *CH* resonances of **1**, where the intensity measured at each temperature without polymer is set as 1.

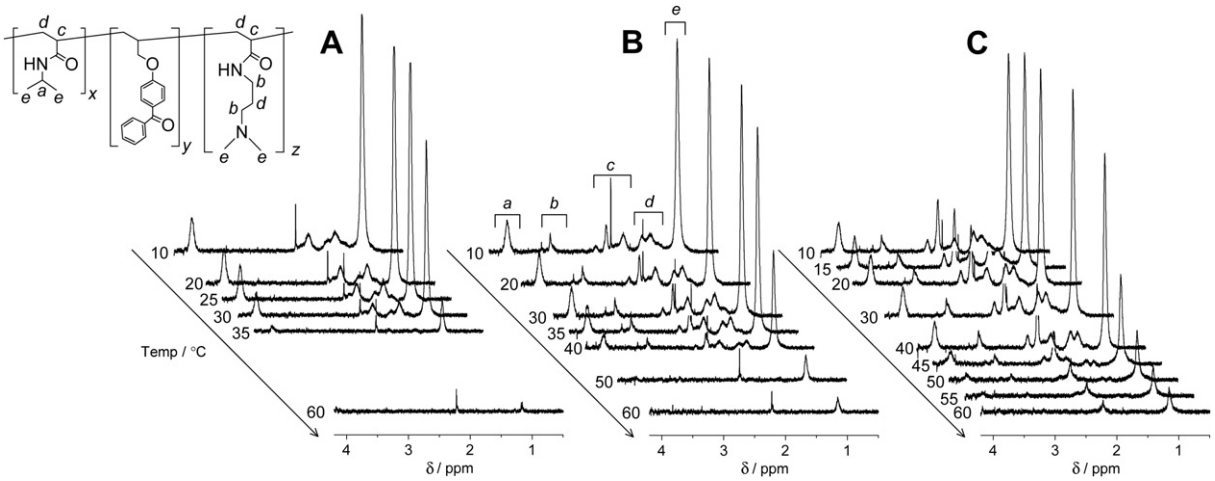


Fig. 4. ^{1}H NMR spectra of (A) **P0**, (B) **P12**, and (C) **P21** measured in D_2O (pH 10) at different temperature.

off-on-off profile; however, the profile shifts to higher temperature regions with an increase in the DMAPAM content of the polymer.

As described previously for the **P0** polymer [6], the off-on-off activity is due to the phase transition of the polymer (Scheme 2). PolyNIPAM has a polar structure at low temperature (*coil* state), but a rise in temperature leads to a weak aggregation through an intrapolymer interaction (*n*-cluster formation) [18] and results in a formation of less polar domain inside the weakly aggregated polymer (*micelle* state). Further increase in temperature leads to strong aggregation and produces polymer particle (*globule* state).

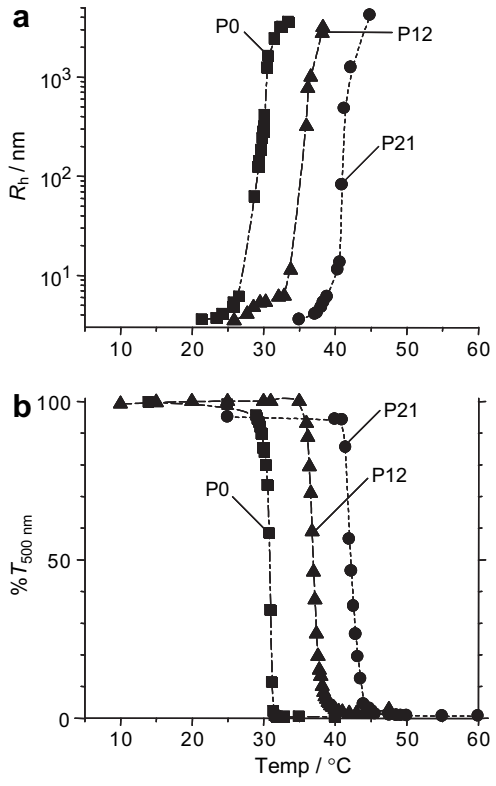


Fig. 5. (a) Temperature-dependent change in hydrodynamic radius (R_h) of polymer particles. (b) Change in transmittance (%T_{500nm}) of the respective polymer solutions. The measurement was performed with 0.08 g L^{-1} polymer.

The heat-induced oxygenation enhancement at 5–20 °C is due to the formation of the less polar domain within the micelle state polymer. The less polar domain formation is confirmed by ^{1}H NMR analysis of **1** with polymer in D_2O (Fig. 3). Fig. 3B (square) shows a change in signal intensity of the *CH* resonance of **1** determined by integration of the signals. The intensity decreases with a rise in temperature up to 20 °C, meaning that **1** exists within the less polar domain and the polarity of the domain decreases as the temperature rises. The $^1O_2$ lifetime is lengthened within the less polar domain [19] and, therefore, the reaction between $^1O_2$ and **1** is accelerated, resulting in heat-induced activity enhancement at <20 °C (Fig. 2). In contrast, the decrease in the sensitization activity at >20 °C is due to the phase transition of the polymer from micelle to globule state, leading to a removal of **1** from the globule state polymer particles (Scheme 2). The globule formation is confirmed by ^{1}H NMR, dynamic light scattering (DLS), and transmittance analyses of the polymer. Fig. 4A shows ^{1}H NMR spectra of the **P0** polymer measured in D_2O. The signals decrease at >20 °C, indicating that the polymer becomes insoluble associated with the phase transition from micelle to globule state. As shown in Fig 5a, DLS analysis of the **P0** polymer solution detects a scattered light at >20 °C, indicative of a formation of polymer particles [20]. The size of the polymer particles increases as the temperature rises. In addition, as shown in Fig. 5b, transmittance of the **P0** polymer solution (%T_{500nm}) starts to decrease at >20 °C. These data clearly indicate that the globule formation takes place at >20 °C (Scheme 2). The removal of **1** from the globule state polymer is confirmed by

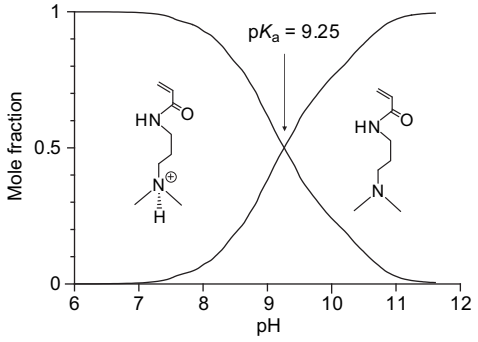
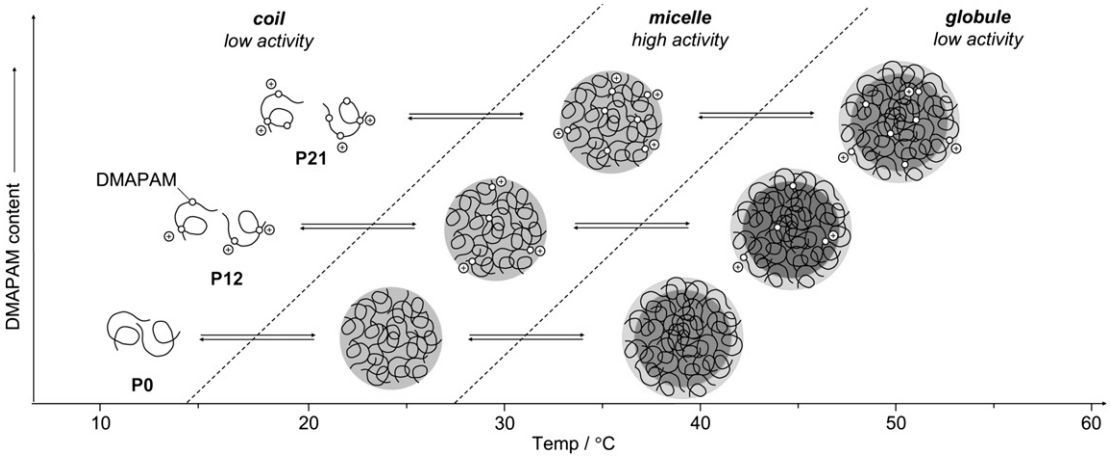


Fig. 6. Mole fraction distribution of the protonated/deprotonated states of DMAPAM (6.0 mM) determined by potentiometrical titration at 25 °C.



Scheme 3. Temperature-dependent changes in structure of polymers in a buffered aqueous solution with pH 10.

^{1}H NMR analysis of **1** with the polymer (Fig. 3B, square). The intensity of **1** increases at >20 °C, indicating that **1** is indeed removed from the globule polymer. At this temperature range, the reaction of **1** with $^1O_2$ must therefore occur in bulk solution. Within the globule polymer, O_2 can diffuse and form $^1O_2$ [21]. However, the $^1O_2$ diffusion to bulk solution is suppressed by the rigid globule polymer [22]. This suppresses the reaction of **1** with $^1O_2$, resulting in oxygenation suppression at >20 °C (Fig. 2).

As shown in Fig. 2, the off-on-off activity profile shifts to higher temperature with an increase in the DMAPAM content of the polymer. This is due to the protonation of DMAPAM moiety. Fig. 6 shows mole fraction distribution of the protonated/deprotonated states of a DMAPAM monomer determined by potentiometrical titration. At this pH (10), about 25% of the DMAPAM molecules are protonated. As reported [9], highly polarized ionic moieties suppress the polyNIPAM aggregation. The protonation of the DMAPAM moieties may lead to an upward shift of the aggregation temperature of the polymer and, hence, results in an activity shift to higher temperature (Scheme 3). The shift of the aggregation temperature is confirmed by DLS analysis (Fig. 5a). With an increase in the DMAPAM content of the polymer, particle formation occurs at higher temperature (>36 °C,

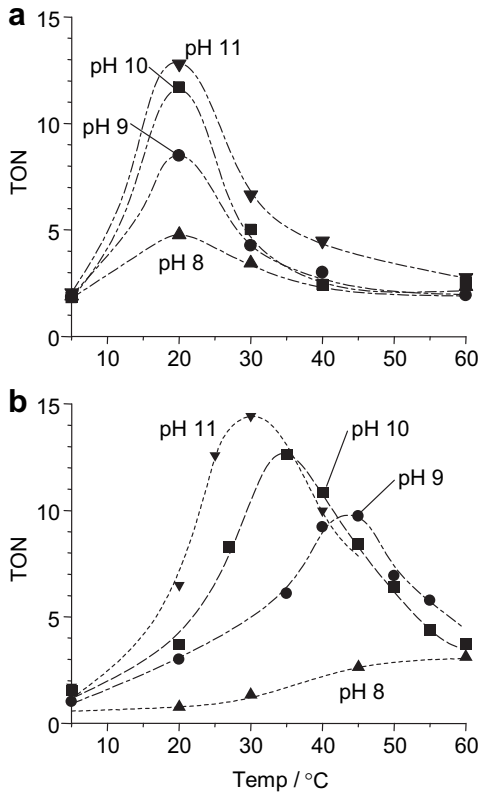


Fig. 7. Temperature-dependent change in TON for **2** formation during reaction of **1** ($\lambda > 320$ nm, 3 h) with (a) **P0** and (b) **P21** polymers (0.08 g L^{-1}) in O_2-saturated aqueous solution of different pH.

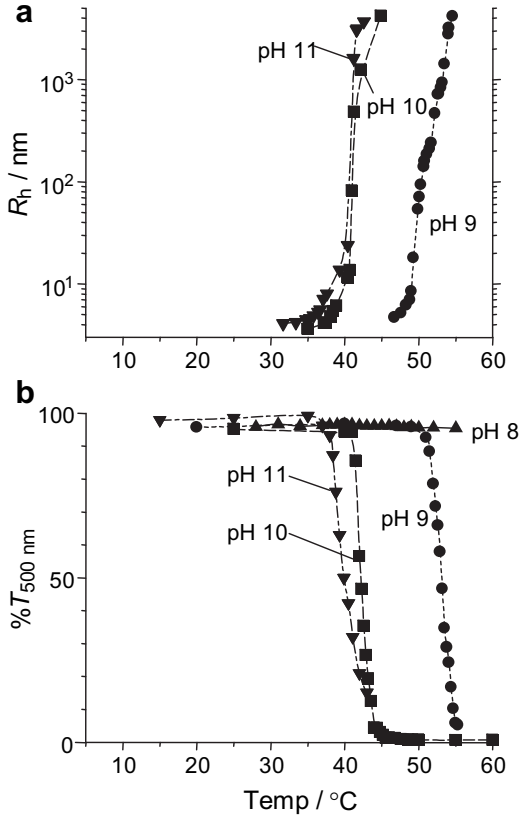


Fig. 8. (a) Temperature-dependent change in hydrodynamic radius (R_h) of **P21** polymer particles (0.08 g L^{-1}) in an aqueous solution of different pH. (b) Change in transmittance (%T_{500nm}) of **P21** solution.

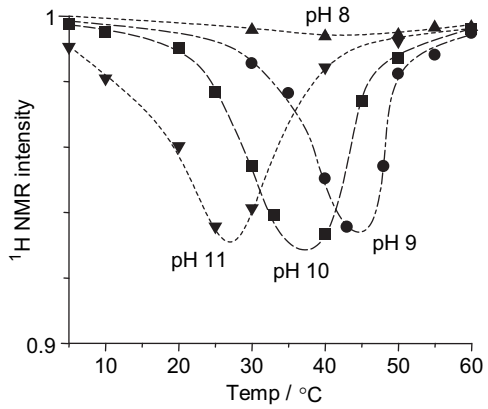


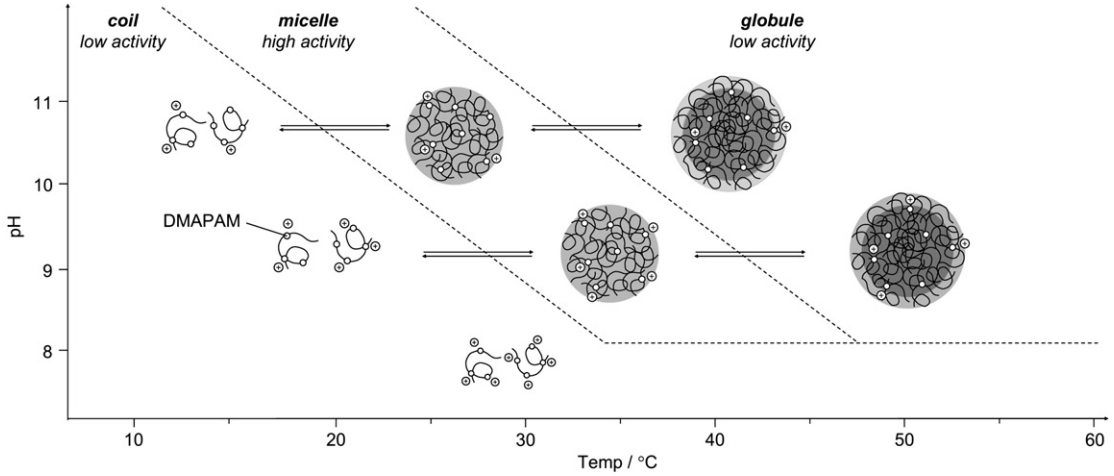
Fig. 9. ^{1}H NMR signal intensity of **1** (2 mM) measured with **P21** at different pH. The intensity was determined by integration of all C*H* resonances of **1**, where the intensities measured at each temperature without **P21** are set as 1.

P21; >26 °C, **P12**; >20 °C, **P0**). In addition, as shown in Fig. 5b, decrease in the transmittance of the polymer solution takes place at higher temperature with the DMAPAM content increase. Furthermore, as shown in Fig. 4, ^{1}H NMR intensity of **P12** and **P21** polymers decreases at higher temperature relative to **P0**. These data clearly indicate that the increase in the DMAPAM content of the polymer leads to an upward shift of the aggregation temperature. Further confirmation is made by ^{1}H NMR analysis of **1** with polymers (Fig. 3B). The decrease in the ^{1}H NMR intensity of **1** occurs at higher temperature with the DMAPAM content increase, suggesting that the formation of the less polar domain indeed occurs at higher temperature. The above findings indicate that the DMAPAM units within the polymer controls the aggregation temperature and, hence, controls the sensitization activity.

3.2. pH effects

To clarify the effect of DMAPAM units in more detail, pH effects on the sensitization activity were studied with **P21** polymer. Fig. 7a and b show TON for **2** formation during reaction of **1** with **P0** and **P21**, respectively at different pH. With **P0** and **P21**, the maximum sensitization activity increases with an increase in pH. This is because, at higher pH, deprotonation of **1** produces a phenoxide anion ($pK_a = 9.98$), which is more reactive for $^1O_2$ oxygenation than the protonated form of **1** [23]. As reported [24], the lifetime of the excited state BP at pH > 6 is almost constant (ca. 2×10^{-4} s), indicating that the excited state BP lifetime is not affected by pH. With **P0**, the maximum activity temperature (20 °C) does not change at the entire pH range. This is because phase transition temperature of the unmodified polyNIPAM is insensitive to pH [25]. In contrast, for **P21**, the off-on-off activity profile shifts to higher temperature with a pH decrease. In addition, at pH 8, activity enhancement is scarcely observed. The no activity enhancement at pH 8 is because polymer aggregation does not occur at this pH. As shown in Fig. 6, pK_a of the DMAPAM unit is 9.3, meaning that, at pH 8, almost all of the DMAPAM units are protonated. This may lead to a polarization of the DMAPAM units within the polymer and, hence, suppresses the polymer aggregation at the entire temperature range. At pH 8, DLS analysis of the **P21** solution does not detect the polymer particle formation (detection limit, 3 nm) at the entire temperature range. In addition, as shown in Fig. 8b, transmittance of the **P21** solution does not decrease. Further confirmation was made by ^{1}H NMR analysis of **1** measured with **P21** polymer (Fig. 9). At pH 8, the C*H* resonance intensity of **1** scarcely changes at any temperature. These clearly indicate that, at pH 8, polymer aggregation does not occur (Scheme 4), leading to no activity enhancement over the entire temperature range (Fig. 7b).

As shown in Fig. 7b, at pH 9–11, the off-on-off activity profile is observed because deprotonation of the DMAPAM units allows polymer aggregation. The shift of the activity profile to lower temperature with a pH increase is because the deprotonation of the DMAPAM unit leads to a decrease in the polymer polarity and, hence, allows polymer aggregation at lower temperature [9]. As shown in Fig. 8a, polymer particles form at lower temperature with a pH increase. In addition, as shown in Fig. 8b, decrease in the transmittance of the polymer solution takes place at lower temperature with a pH increase. These data indicate that the protonation states of DMAPAM units critically control the aggregation temperature of the polymer (Scheme 4). Further confirmation of the mechanism is made by ^{1}H NMR analysis of **1** with **P21** polymer. As shown in Fig. 9, at pH 9–11, decrease in the *CH* resonance intensity of **1** occurs at lower temperature with a pH increase, indicating that the less polar domain also forms at lower temperature with a pH increase. These results agree well with the activity data (Fig. 7b); the protonation states of the DMAPAM units control the aggregation behavior of the polymer and, hence, allow photosensitization activity control.



Scheme 4. pH- and temperature-dependent change in structure of **P21** in buffered aqueous solutions with different pH values.

4. Conclusions

Photosensitization properties of polymeric sensitizers, poly-(NIPAM$_x$-*co*-BP$_y$-*co*-DMAPAM$_z$), have been studied in water. These polymers show sensitization activity controlled by temperature and pH. At basic pH (>9), the polymer shows an off-on-off activity profile against the temperature window. The activity increase at lower temperature is due to the phase transition of the polymer from coil to micelle, and the decrease at higher temperature is due to the transition from micelle to globule. With a pH decrease, the off-on-off activity profile shifts to higher temperature because protonation of the DMAPAM units leads to an increase in the polymer polarity and, hence, the polymer aggregates at higher temperature. In contrast, no activity enhancement occurs at pH < 8 because complete protonation of the DMAPAM units suppresses the polymer aggregation. These findings suggest that pH-sensitivity can be added to the thermoresponsive polymeric photosensitizer. The results presented here will provide useful information to the development of more efficient and functional photosensitizers for organic transformations.

Acknowledgments

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