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Synthesis and Characterization of Star Polyacrylamides Using Poly(ethylene imine) as a Core via Photopolymerization in Water

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Water-soluble thioxanthone-terminated poly(ethylene imine) (PEI 600, PEI 1800, PEI 3000 and PEI 10000; 600, 1800, 3000 and 10000 are the weight-average molecular weights of the above PEIs, respectively). Macrophotoinitiators were synthesized by introducing a certain amount of thioxanthone (TX) moieties into the periphery of PEI, and the products were confirmed by ^{1}H-NMR, FT-IR, and elemental analysis. Star polyacrylamides (PAMs) were prepared using the obtained macrophotoinitiator as a core via photopolymerization. The effect of the molecular weight of the macrophotoinitiator on photoinitiation efficiency of the resulting polymers was investigated. The result shows that the choice of the macrophotoimitator has no influence on the rate of polymerization. In addition, three plots of characteristic properties with the star polymer were studied to confirm the existence of arms in the resulting star PAM.

Keywords: Water-soluble photoinitiator, photopolymerization, star polyacrylamide

1 Introduction

Photopolymerization science has become an increasingly interesting subject because of its widespread applications (1, 2). In the development of this technology, the photoinitiator systems play a very important role. In order to form photoinitiator systems with high performance, one of the effective ways is to develop macrophotoinitiators, which is more advantageous relative to low-molecular weight molecules due to the macromolecular nature (3–6). At the same time, water-soluble photoinitiator systems have been receiving more attention primarily because of their prominent superiority in environmental protection (7–9). Water-soluble photoinitiators derived from thioxanthone (TX) used as H-abstraction type initiators are widely used in processes such as printing inks, coatings, microelectronics and photoresists (10–12). Therefore, it is of much interest to prepare water-soluble polymeric photoinitiator systems.

Star polymers have usually been synthesized via living polymerizations, including anionic (13), ring-opening (ROP) (14), atom transfer radical (ATRP) (15) and reversible addition fragmentation transfer polymerization (RAFT) (16). However, anionic and cationic polymerization suffers from rigorous requirement, and many functional monomers cannot be used by the ATRP and RAFT methods.

Recently, photopolymerization has been used to prepare star polymers using H-abstraction type initiators such as benzophenone and thioxantone in the presence of dendrimers containing a number of tertiary amine groups as hydrogen donors. Tasdelen et al. described the synthesis of dendrimer/star poly(methyl methacrylate) via phtotoinitiatied free radical polymerization using thioxantone plus poly(propylene imine) dendrimers (PPI) (17). Modified PPI containing thioxathone was used as a macrophotoinitiator in the preparation of the dendrimer/star polyacrylamides (PAMs) in the DMSO and H_2O solution (18, 19). However, star characterization was not discussed in the study.

In the current study, we report the preparation of star PAMs with poly(ethylene imine) (PEI) as core moieties. The reason PEIs are chosen is that they are commercially available at a fair cost and have many properties associated with monodispersed PPI, such as, highly branched,

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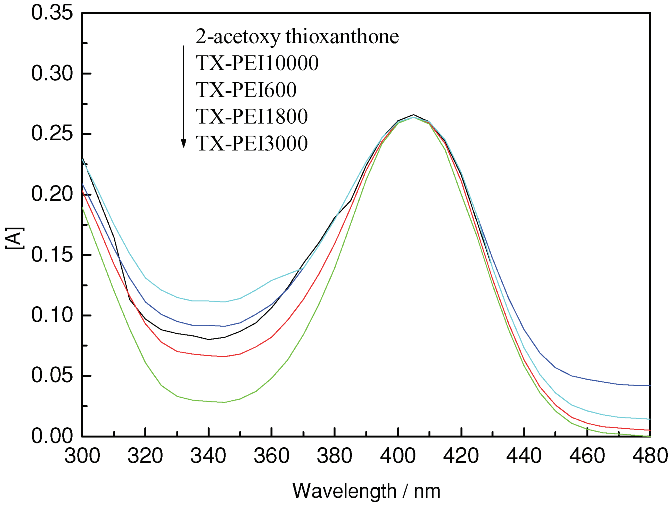


Fig. 1. UV spectra of thioxanthone-terminated PEIs in water and $CHCl_3$ and 2-acetoxy thioxanthone in $CHCl_3$ (concentration = 0.05 mmol/L measured in thioxanthone moieties).

water-soluble and high in amino groups. With their structures shown in Figure 1, thioxanthone-terminated PEI macrophotoinitiators were synthesized by introducing a certain amount of TX into the periphery of PEIs.

The use of PEI, as opposed to a true dendrimer, carries some disadvantages, including an inherent initial polydispersity — an irregular structure that is difficult to analyze (discussed later). However, we believe that the easy availability of PEI outweighs the more difficult product (i.e., multifunctional TX moieties) analysis compared to true dendrimers.

In addition, three relationships including radius of gyration (R_g) vs. weight average molecular weight (M_w), the second virial coefficient A_2 vs. M_w and intrinsic viscosity $[\eta]$ vs. number molecular weight (M_n) were plotted and studied to confirm the existence of arms in the resulting star PAM.

2 Experimental

2.1 Materials

Poly(ethylene imine) (PEI 600, PEI 1800, PEI 3000 and PEI 10000, where 600, 1800, 3000 and 10000 are the weight-average molecular weight of the PEIs, respectively) from Aladdin-reagent Corporation. 2-Acetoxy thioxanthone (20) and 2-(2, 3-epoxy) propoxyl-thioxanthone (10) were synthesized according to literature procedures. Other chemicals are of analytical grade except as noted.

2.2 Synthesis of Water-Soluble Macrophotoinitiators

A mixture of 1.0 g (3.52 mmol) 2-(2,3-epoxy) propoxylthioxanthone, 0.42 g PEI, and 10 mL of chloroform was stirred at 60°C for 24 h. After cooling to room temperature, the chloroform solution was poured into 10-fold petroleum ether. The formed precipitate was filtered to give a crude product, which was dried in vacuum to yield the macrophotoinitiator.

Thioxanthone-terminated PEI 600 (TX-PEI 600): ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.59-7.22 (aromatic), 4.14-4.00 ($-OCH_2$),3.67-2.67 (NH_2-CH_2, $NH-CH_2$, $N-CH_2$), 1.49-0.82 (CH_2); FT-IR (KBr): 3353 cm^{-1}(O–H, N–H), 2933cm^{-1}(C–H), 1632 cm^{-1}(C=O); UV: $\lambda_{max} = 406$ nm, in water and $CHCl_3$; Elemental analysis: C 50.61, H 6.58, N 8.78, S 6.21.

Thioxanthone-terminated PEI 1800 (TX-PEI 1800): ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.46-7.20 (aromatic), 4.13-3.86 ($-OCH_2$), 3.68-2.67 (NH_2-CH_2, $NH-CH_2$, $N-CH_2$), 1.26-0.82 (CH_2); FT-IR (KBr): 3369 cm^{-1}(O–H, N–H), 2936 cm^{-1}(C–H), 1632 cm^{-1}(C=O); UV: $\lambda_{max} = 406$ nm, in water and $CHCl_3$; Elemental analysis: C 53.59, H 6.42, N 9.49, S 6.88.

Thioxanthone-terminated PEI 3000 (TX-PEI 3000): ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.60-7.18 (aromatic), 4.33-3.85 ($-OCH_2$), 3.70-2.65 (NH_2-CH_2, $NH-CH_2$, $N-CH_2$), 1.52-0.81 (CH_2); FT-IR (KBr); 3362 cm^{-1}(O–H, N–H), 2934 cm^{-1}(C–H), 1632 cm^{-1}(C=O); UV: $\lambda_{max} = 406$ nm, in water and $CHCl_3$; Elemental analysis: C 53.62, H 6.35, N 8.90, S 6.48.

Thioxanthone-terminated PEI 10000 (TX-PEI 10000): ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.30-6.91 (aromatic), 4.76-3.90 ($-OCH_2$), 3.73-2.66 (NH_2-CH_2, $NH-CH_2$, $N-CH_2$), 1.49-0.82 (CH_2); FT-IR (KBr): 3365 cm^{-1}(O–H, N–H), 2935 cm^{-1}(C–H), 1632 cm^{-1}(C=O); UV: $\lambda_{max} = 406$ nm, in water and $CHCl_3$; Elemental analysis: C 52.27, H 6.80, N 9.19, S 6.31.

2.3 Photopolymerization

Photopolymerization studies were performed in a quadrate beaker by irradiating about 20 mL of 25% wt acrylamide (AM) water solution at 40°C. The concentration of TX was 5×10^{-3}mol L^{-1}in water. The light source was a high-pressure Hg lamp (500 W) and was passed through a light filter with cut-off wavelength of 360 nm, and the lamp was placed at a distance of 15 cm from the sample (5.20 mW cm^{-2}at the top of the reaction mixtures, where the thickness is 1 cm). The light intensity was measured by a Sentry Optronics Corporation 513UVAB Radiometer. At the end of irradiation, the reaction mixture was precipitated in excess methanol. After being collected by filtration, the polymer was kept in a vacuum oven for drying. Conversions were determined gravimertrically.

2.4 Analysis

^{1}H-NMR spectra were recorded on a Bruker 300 MHz spectrometer with $CDCl_3$ as a solvent. FT-IR spectra were recorded on a ThermoFisher Nicolet 6700 FTIR spectrometer. The samples were prepared either as KBr pellets or as liquid films between KBr discs. UV-Vis spectra were recorded in aqueous solutions and $CHCl_3$ by a Shimadzu UV1700 PharmaSpec UV-Vis spectrophotometer. Elemental analysis was conducted on an Elementar Vario El III apparatus.

Size exclusion chromatography (SEC) analysis was conducted using a Water 515 liquid chromatograph instrument connected with a Waters 2410 refractive index detector at 30°C. The gel permeation column was linear ultrahydrogel (7.8×300 mm^2), and the solvent used was distilled water. Polymer standards of Dextran were used from NICPBP (National Institute for the Control of Pharmaceutical and Biological Products). The samples were dissolved in 0.1 M NaCl solution and analyzed at a flow rate of 0.8 mL min^{-1}.

The light scattering instrument employed with a BI-200SM multi-angle laser light scattering detector was purchased from Brookheaven Instrument Corp., operating at 532 nm. The BI-200SM detector was calibrated with toluene and Rayleigh ratio 2.803×10^{-5} cm^{-1}. The dn/dc value for PAM in water at 25°C is 0.1700 mL/g. Data were collected and processed by Zimm Plot Software Ver. 3.41 (Brookheaven Instrument Corp.). The weight average molecular weight (M_w) and radius of gyration (R_g) reported in this paper were based on the double extrapolation method of Zimm (Kc/R_θ vs $\sin^2(\theta/2) + kc$.

Intrinsic viscosities of polymers were measured with the "five-spot" dilution method using an Ubbelohde viscometer at 30°C, where the solvent was distilled water.

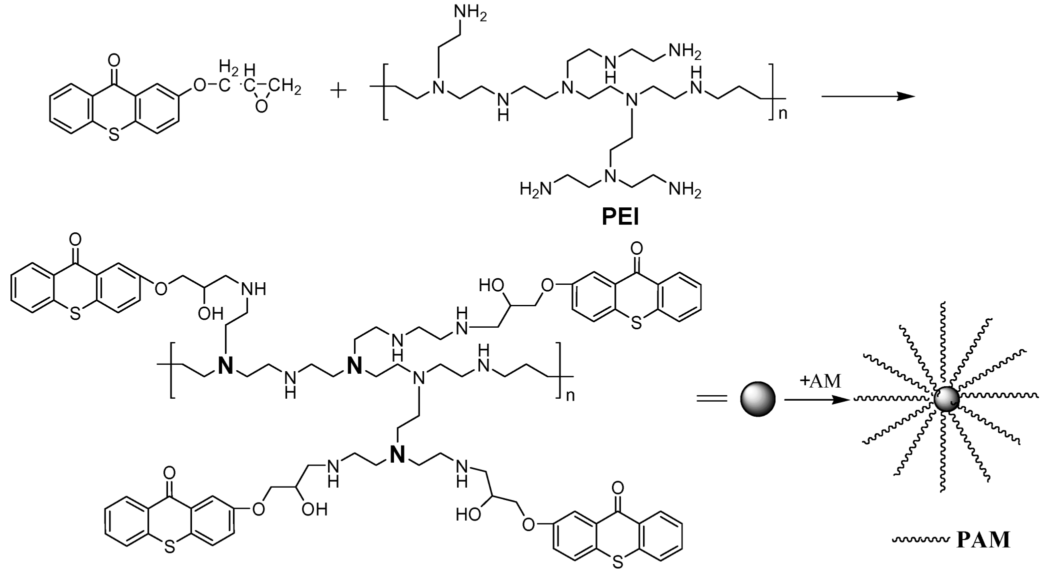
3 Results and Discussions

Macrophotoinitiatiors, shown in Scheme 1, were synthesized and confirmed by ^{1}H-NMR, FT-IR, and elemental analysis. In these experiments, $x : y$ratios are all about 1: 0.7 calculated according to the elemental analysis (nitrogen/sulfur contents), which suggest that there are more TX moieties in macro-photoinitiatiors with higher molecule weights.

3.1 Determination of the Concentration of TX in Water

Because of the polydisperse nature of the TX-PEI, a quantitative tool is desired to assess the concentration of TX when TX-PEIs are dissolved in water.

UV-Vis spectra of the four macro-photoinitiators in aqueous and $CHCl_3$ solutions are shown in Figure 1. They exhibit the usual characteristic absorption of TX, and the maximum absorption peaks λ_{max}) are all at 406 nm, which suggests that the molecular structure of PEIs has



Sch. 1. Synthetic routes of the water-soluble thioxanthone-terminated PEI macro-photoinitiator.

Table 1. Concentration of TX of the four macrophotoinitiators in their saturated aqueous solutions at 10°C

Macrophotoinitiator	*TX-PEI600*	*TX-PEI1800*	*TX-PEI3000*	*TX-PEI10000*
$C_{TX}(10^{-3}$mol $L^{-1})$	4.20	3.21	2.92	0.05

no significant influence on the UV-Vis absorption from the TX moieties. In addition, it was found that the macrophotoinitiators and 2-acetoxy thioxanthone have the same λ_{max} in $CHCl_3$ (Fig. 1). The above results are useful in determining the concentration of TX in water by an ultraviolet spectrophotometric method. Plotting the UV absorption intensity of 2-acetoxy thioxanthone at $\lambda = 406$ ($[A]_{\lambda max}$) gainst its concentration in $CHCl_3$ ([C]) gave a straight line as shown in Figure 2. The linear relationship between the concentration of TX in $CHCl_3$ and its UV absorption intensity enables us to establish an equation: $[C]_{TX} = 0.1679 \times [A]_{\lambda max}$. Since all four macrophotoinitiators have the same λ_{max} (= 406 nm) in both water and $CHCl_3$, the equation can also be used for their aqueous solutions. With the use of the equation, the concentrations of TX of the four macrophotoinitiators in their saturated aqueous solutions were determined at 10°C, and the results are shown in Table 1. As suggested in these concentration results, solubility of these macro-photoinitiators in water decreases with the increasing numbers of TX in their molecules, which is probably the reason that Jiang (18, 19) used a macro-photoinitiator to photoinitiate the polymerization of AM in a water plus DMSO solution.

3.2 Synthesis of StarPAMs in Water

In the presence of co-initiators, such as tertiary amine groups, photolysis of TX leads to the formation of a ketyl-type radical produced from a carbonyl compound and another radical derived from the co-initiator amine through reactions between the excited triplet state of TX and the co-initiator amine. The photopolymerization of vinyl monomers is usually initiated by the amine radicals, while the ketyl radicals are normally not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electrons (21). The overall mechanism of the photoinitiation is proposed in Scheme 2. Because there are many TXs and tertiary amine groups in each TX-PEI molecule, the resulting polymer could exist as a star polymer.

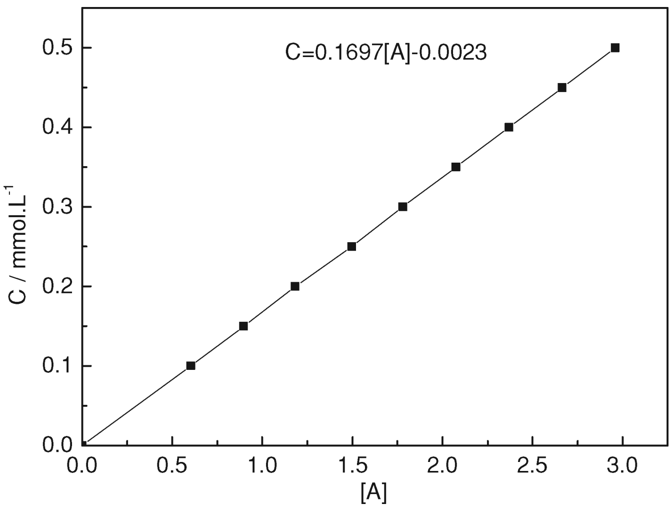


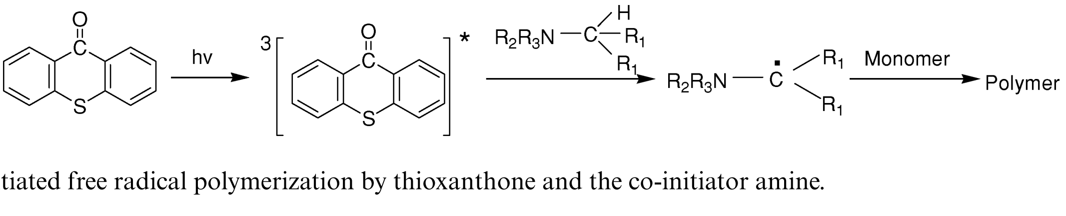
Fig. 2. Concentration of TX vs. its UV absorption intensity.

Figure 3 reveals the conversion-time correlation for the photopolymerization of AM initiated by various TX-PEIs, i.e., TX-PEI 600, TXPEI 18000, TX-PEI 3000 and TX-PEI 10000. All the TX-PEIs were employed with the same TX end-group concentration (5×10^{-3} mol L^{-1}). The figure clearly indicates that the choice of the TX-PEI has no influence on the rate of polymerization. Such observation is not surprising because the TX functionality is identical in all cases, and only the architectural embedding of the group is different. After approximately 50% of the monomer-to-polymer conversion, the rate of polymerization for all the studied photopolymerization systems decreases slowly because of the depletion of the monomers.

Figure 4 shows the relationship between the number average molecule weight M_n of the resulting PAM initiated by TX-PEI 10000 and the conversion. When the conversion is below 80%, the M_n increases with the proceeding of the monomer conversion, at the same time the polydispersity index (PDI) decreases. The M_n of the resulting polymer, however, decreases as the conversion increases above 80%, probably due to the main chain scission by prolonged irradiation (22, 23), which can be confirmed by the increase of the PDI after the conversion exceeding 80%.

3.3 Sta PAM Confirmation with Three Characteristic Plots

According to the reaction mechanism shown in Scheme 2, the resulting PAMs are star polymers. In this paper, three characteristic properties with the star or branched



Sch. 2. Photoinitiated free radical polymerization by thioxanthone and the co-initiator amine.

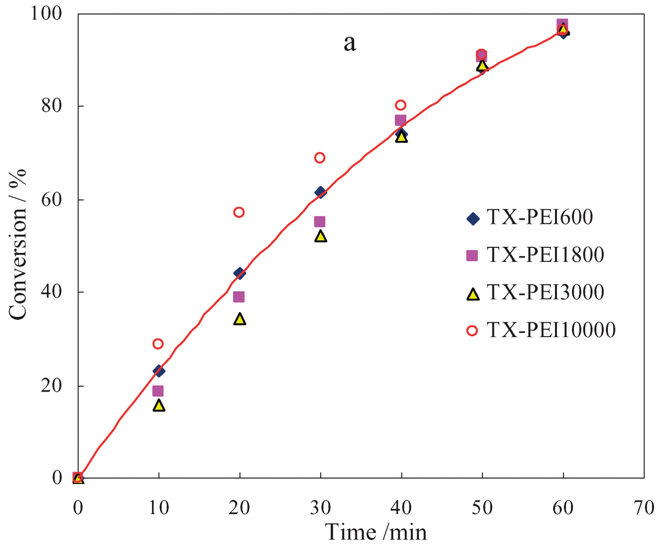


Fig. 3. Evolution of the overall monomer-to-polymer conversion with the reaction time for AM polymerizations photoinitiated by TX-PEI 600, TX-PEI1 800, TX-PEI 3000 and TX-PEI 10000 in water at 40°C (concentration = 5×10^{-3} mol L^{-1} measured in TX).

polymers were studied to confirm the existence of arms in the resulting star PAMs imitated by TX-PEI 10000. The experimental data are collated in Table 2.

The plot of R_g vs. M_w is shown in Figure 5, and the slope of the linear progression line is 0.38, which is much smaller than that for a linear polymer in the range 0.5–0.6 (24, 25). A low value in the slope is indicative of the existence of branches.

The molecular weight dependence of A_2, as shown in Figure 6, deviates from the scaling concept prediction, i.e., $A_2 \sim N^{-\alpha}$ and $\alpha = 0.57$, where N is the degree of

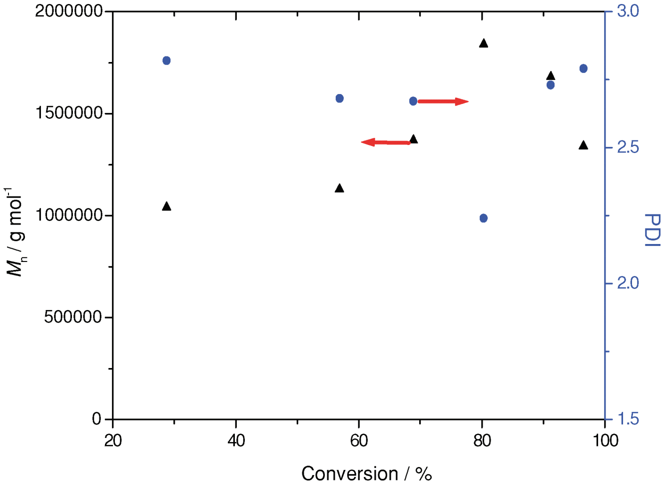


Fig. 4. Relationships between the conversion and number average molecule weight of PAMs initiated by TX-PEI 10000 in water at 40°C (concentration = 5×10^{-3} mol L^{-1} measured in TX).

Table 2. Complete reaction data for the PAMs photoinitiated by TX-PEI 10000 at 40°C in water with a TX concentration of 5×10^{-3}mol L^{-1}

Reaction time(min)	*10*	*20*	*30*	*40*	*50*	*60*
Conversion	28.8	56.9	68.9	80.3	91.2	96.5
$[\eta]$ (dL/g)	7.45	7.90	8.40	9.23	8.95	8.31
$M_{n,\ SEC} \times 10^6$(g/mol)	1.04	1.13	1.37	1.84	1.68	1.34
M_w / M_n (PDI)	2.82	2.68	2.67	2.24	2.73	2.79
$M_{w,\ MALLS} \times 10^6$(g/mol)	4.90	5.27	6.47	7.00	6.73	6.22
R_g(nm)	168.3	174.4	186.9	191.9	189.4	182.6
$A_2 \times 10^{-4}$ (mol g^{-2} cm^3)	2.68	2.45	2.27	2.12	2.20	2.31

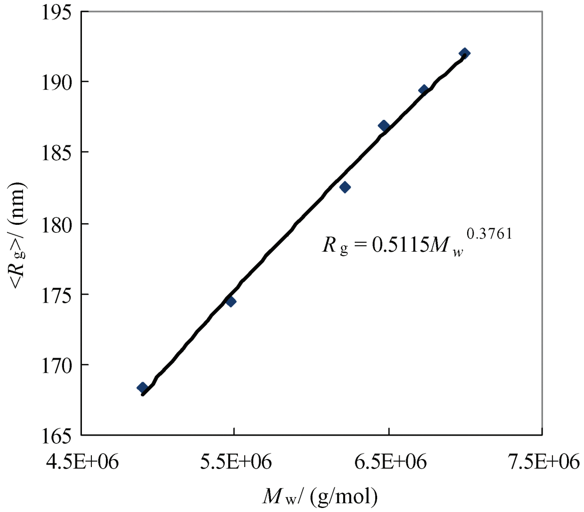


Fig. 5. R_g vs. M_w plot of the resulting PAMs photoinitiated by TX-PEI10000 in water at 40°C (concentration = 5×10^{-3} mol L^{-1} in terms of TX).

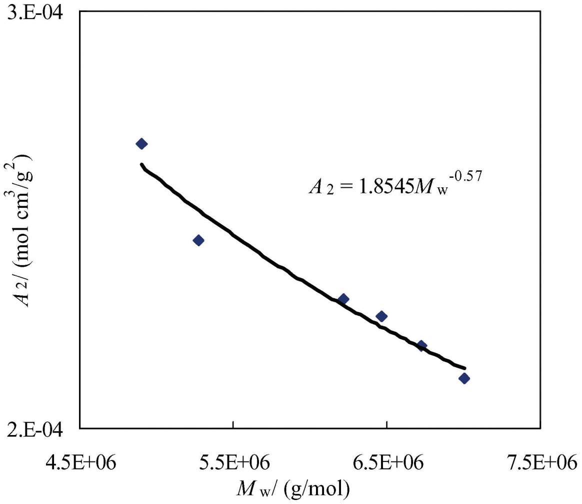


Fig. 6. A_2 vs. M_w plot of the resulting PAMs photoinitiated by TX-PEI 10000 in water at 40°C (concentration = 5×10^{-3} mol L^{-1} measured in TX).

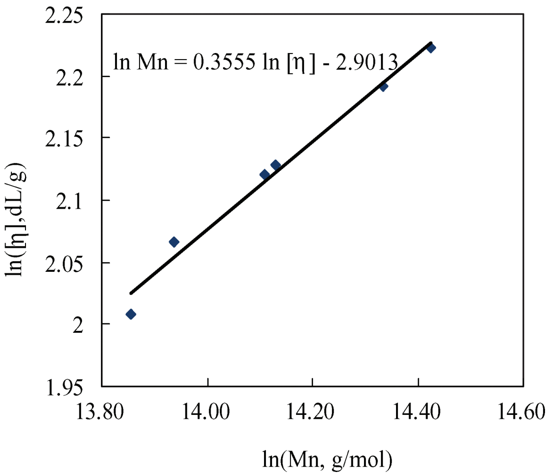


Fig. 7. [η] vs. M_n plot of the resulting PAMs photoinitiated by TX-PEI 10000 in water at 40°C (concentration = 5×10^{-3} mol L^{-1} measured in TX).

polymerization of a polymer chain (26). It is well-known that the value of the exponent α could be greater than 0.2 for star or highly branched chain polymers (27, 28).

As shown in Figure 7, a straight line was obtained after plotting ln[η] against ln$M$n according to the Mark-Houwink Equation, and the slope is the constant α. Compared to a linear PAM, the constant α of a branched polymer is usually smaller (29, 30). The constant α of a linear PAM in water was reported at 0.66 at 30°C (31), while in this experiment, the constant α of the resulting PAM is about 0.36, which is much smaller than 0.66. The result confirms that the resulting PAMs are branched.

4 Conclusions

This article reports the preparation of water-soluble thioxanthone-terminated poly(ethylene imine) macrophotoinitiators. An ultraviolet spectrophotometric method was successfully employed to determine the concentration of TX in the macrophotoinitiator aqueous solution. Star PAMs were synthesized via photopolymerization using the macro-photoinitiators as a core in water, and their star structures were successfully confirmed by three plots of the characteristic properties of the star polymers.

Acknowledgements

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