Polymer Side-Chain Conjugates를 위한 전구체인 Polydiacetone Acrylamide

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Polydiacetone Acrylamide as Precursors to Polymer Side-Chain Conjugates

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Abstract: Polydiacetone acrylamide (PDAAM), a reactive polymer containing pendant ketone groups was synthesized *via* reversible addition-fragmentation chain transfer (RAFT) polymerization. Kinetic studies indicated a well-controlled behavior of this RAFT polymerization. The characteristics of this RAFT polymerization was also confirmed by a well-controlled chain-extending RAFT polymerization using the above-synthesized PDAAM as a macromolecular chain transfer agent. Acid-catalyzed ketalization of PDAAM with trimethylol propane (TMP) was carried out to obtain the polymer containing pendant cyclic ketal groups and hydroxyl groups, PDAAM-TMP. PCL was grafted from PDAAM-TMP by ring-opening polymerization (ROP) in the presence of tin 2-ethylhexanoate as a catalyst to obtain graft copolymer. Base-catalyzed aldol condensation of PDAAM with benzaldehyde was also used to obtain poly[*N*-(1,1-dimethyl-3-oxo-5-phenyl-pent-4-enyl)-acrylamide] (PDMOPPEAM) having cinnamoyl groups, and the photoreactivity of polymer with cinnamoyl group was studied by UV-visible and IR absorption spectroscopy. Both of these two polymers prepared from PDAAM were characterized by FTIR and ^{1}H NMR spectroscopy. PDAAM can be a multifunctional platform that can undergo further polymerization by ketalization and aldol condensation.

Keywords: reversible addition fragmentation chain transfer (RAFT), functionalization of polymers, ring-opening polymerization (ROP), photochemistry.

Introduction

Construction of polymers with highly reactive functionalities that allow for further diverse functional group transformation has become an attractive research area in modern polymer chemistry.[1-5] Polymers bearing ketone groups that can be modified easily and in high yield have been not only used as materials for films and coating, but also found use as a platform for post-polymerization modification.[6-11] For example, Bertozzi prepared ketone-functionalized polymers derived from methyl vinyl ketone and isopropenyl methyl ketone *via* free-radical

polymerization and reversible addition-fragmentation chain transfer (RAFT) polymerization, and the resulting polymers could be quantitatively modified with aminoxy-functionalized sugars.[10] Poly(norbornene)-based random copolymers containing ketone functionalities were synthesized using ring-opening metathesis polymerization, and the polymers can be quantitatively functionalized with a library of hydrazines.[6,8] A class of polyketoesters containing ketone functionalities was prepared through condensation polymerization, and the modification of the ketone functionalities with oximes proceeded quantitatively.[12] Taylor prepared polydiacetone acrylamide (PDAAM) of any molecular weight range *via* free-radical polymerization, and then quantitatively oximated the polymer to obtain polyoximes.[13] However, other functional group transformations of ketone functional polymers, such as ketalization

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and aldol condensation, have not been reported.

Diacetone acrylamide (DAAM), an important fine chemical product, possesses the reactivity of an activated double bond and a methyl ketone. The polymerization of DAAM could be achieved using conventional free-radical polymerization.[13-17] In general, the application of polydiacetone acrylamide (PDAAM) synthesized by conventional radical polymerization is limited where well-defined polymer architectures are required. Normally living radical polymerization (LRP) is one of the most powerful tools for the preparation of well-defined polymers.[18-20] Rizzardo and coworkers first reported the RAFT synthesis homo- and block copolymer of DAAM.[21] Recently, Cai *et al*. reported the RAFT polymerization of DAAM on irradiation with visible light.[22]

In this paper, PDAAM with well-controlled number-average molecular weights (M_n) and relatively narrow PDI and PDAAM-*b*-P*t*BA block copolymers were prepared *via* RAFT, and the post-polymerization modification were carried out using acid-catalyzed ketalization reaction[23,24] and base-catalyzed aldol condensation reaction.[25-27] The modified polymer containing pendant cyclic ketal groups and hydroxyl groups, PDAAM-TMP, was prepared using the acid-catalyzed ketalization reaction of PDAAM with trimethylol propane, and the obtained polymer was used as a macroinitiator for graft-polymerization of ε-CL to give graft copolymer. The photosensitive polymer containing pendant cinnamoyl groups was obtained by using the base-catalyzed aldol condensation reaction of PDAAM with benzaldehyde.

Experimental

Materials. Diacetone acrylamide (DAAM; Shanghai Bang-cheng Chemical Co., Ltd., China) was recrystallized twice using a mixture of toluene/petroleum ether (1:3). *tert*-Butyl acrylate (*t*BA; Aladdin; 99%) was purified according to literature.[28] The initiator α,α'-azobisisobutyronitrile (AIBN) was recrystallized in anhydrous ethanol twice before use. S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (DDMAT) was synthesized according to literature.[29] ε-Caprolactone (ε-CL; Aladdin; 99%) and Tin 2-ethylhexanoate ((Sn(Oct)$_2$; Aladdin; 95%) were purified according to literature.[30] N,N-dimethyl-formamide (DMF) was dried over CaH$_2$ and distilled before use. Benzaldehyde (Sinopharm Chemical Reagent Co., Ltd, AR) was vacuum distilled before use. All other reagents were commercially available chemicals and used as received.

Measurement. Gel permeation chromatography (GPC) was performed on an Alltech 626 HPLC pump equipped with an evaporative light scattering detector, and Jordi Gel DVB column (10000 Å, 300 mm×7.8 mm) using THF as eluent at a flow rate of 1.0 mL/min at 30 ℃. Polystyrene standards were used for calibrations. ^{1}H NMR spectra was recorded using a Varian INOVA-300FT-NMR spectrometer (Pola Alto, America) operating at 500 MHz using CDCl$_3$ or DMSO-d$_6$ with tetramethylsilane (TMS) as standard at room temperature. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet310 FTIR spectrometer. UV-visible absorption spectra were recorded on a UV 2300 spectrophotometer (Techcomp Limited Company, China) with a 1.0 cm path length quartz cell.

RAFT Homopolymerization of DAAM. DAAM (6 g, 35.4 mmol), DDMAT (129.4 mg, 0.354 mmol), AIBN (6 mg, 0.036 mmol) and DMF (9 mL) were added to a 25 mL Schlenk flask, and the reaction mixture was purged with N$_2$ for 30 min to remove the dissolved oxygen. Then, the flask was sealed and placed in an oil bath at 65 ℃ with stirring to initiate the polymerization. After a predetermined time, the polymerization was stopped by quenching the flask in cold water and exposing to air. The reaction mixture was poured into water. The precipitates were dried under vacuum to a constant mass at 40 ℃. For kinetic studies, aliquots of the solution were withdrawn at timed intervals and monomer conversion was obtained by gravimetry. ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.20-6.90 (-NH-), 3.30-2.5 (-CH$_2$-CO), 2.13 (CH$_3$CO), 2.00-1.44 (polymer backbone protons) 1.36 (-NC $\underline{(CH_3)_2}$), 1.25 (($\underline{(CH_2)_{10}}$CH$_3$) 0.88 ((CH$_2$)$_{11}$$\underline{CH_3}$). IR (KBr, cm^{-1}): 3381 (N-H), 1709 (ketone C=O), 1669 (amide C=O).

Preparation of PDAAM-*b*-P*t*BA. PDAAM (0.5 g, 0.1 mmol, M_n^{GPC}=5000 g/mol, PDI^{GPC}=1.25), *t*BA (1.28 g, 10 mmol), AIBN (1.6 mg, 0.01 mmol) and ethyl acetate (5 mL) were added to a 25 mL Schlenk flask, and the reaction mixture was purged with N$_2$ for 30 min to remove the dissolved oxygen. Then, the flask was sealed and placed in an oil bath at 70 ℃ with stirring to initiate the polymerization. After 12 h, the polymerization was stopped by quenching the flask in cold water and exposing to air. The polymer was purified by precipitation from water/methanol solution. The final product was then dried under vacuum to a constant mass at 40 ℃. ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.20-6.90 (-NH-), 3.30-2.5 (-CH$_2$-CO), 2.13-2.24 (polymer backbone protons), 2.13 (CH$_3$CO-), 2.00-1.44 (polymer backbone protons), 1.43 (-C(CH$_3$)$_3$), 1.36 (-NC (CH$_3$)$_2$). M_n^{GPC}=18400 g/mol, PDI^{GPC}=1.27.

Conjugation of Trimethylolpropane (TMP) to PDAAM. PDAAM (2.00 g, 11.8 mmol of ketone), trimethylolpropane (TMP 4.76 g, 35.5 mmol), *p*-toluenesulfonic acid (*p*-TSA, 0.20 g, 1.16 mmol) and 30 mL of toluene were charged in a 100-mL round-bottom flask equipped with a water separator. The solution was refluxed for 12 h, and the generated water was removed by azeotropic distillation. The mixture was cooled down to room temperature. Then sodium carbonate (0.2 g, 1.89 mmol) was added to the reaction solution. After filtration, the solvent was removed by rotary evaporation. Then the reactant was dissolved in ethanol and the polymer was isolated by precipitation into water to give PDAAM-TMP. The final product was then dried under vacuum to a constant mass at 40 °C. M_n^{GPC}=10700 g/mol, PDI^{GPC}=1.30. ^{1}H NMR (500 MHz, DMSO-d$_6$): 0.748 (CH$_2$C$\underline{H}_3$), 0.85 ((CH$_2$)$_{11}$-C$\underline{H}_3$), 1.37 (CH(C$\underline{H}_3$)$_2$), 3.33 (C-O-CH$_2$), 7.16 (CO-NH-C). IR (KBr, cm^{-1}): 3365 (N-H and O-H), 1669 (amide C=O).

Synthesis of PDAAM-*g*-PCL Copolymer. In a dried polymerization tube, PDAAM-TMP (0.5 g, M_n^{GPC}=10700 g/mol, PDI^{GPC}=1.30, 1.75 mmol OH groups), *ε*-CL (5 g, 43.8 mmol), Sn(Oct)$_2$ (60 mg, 0.15 mmol), and 5 mL of freshly distilled anhydrous DMF were added, and the air in the mixture was exchanged with nitrogen three times. The tube was immersed in an oil bath at 110 °C with vigorous stirring for 12 h. The resulting product was diluted with THF, and precipitated into methanol. The final product was dried under vacuum to a constant mass at 40 °C. M_n^{GPC}=86400 g/mol, PDI^{GPC}=1.24.

Synthesis of Poly{*N*-(1,1-dimethyl-3-oxo-5-phenyl-pent-4-enyl)-acrylamide}, PDMOPPEAM. PDAAM (2 g, 11.8 mmol of ketone group, M_n^{GPC}=5000 g/mol, PDI^{GPC}=1.25) were dissolved in ethanol (20 mL) and water (5 mL) mixed solvent in a glass vial at room temperature. NaOH (1 mL, 2.5 mol/L) and benzaldehyde (1.87 g, 17.7 mmol) were added to the solution. The resulting solution was stirred for 12 h at 25 °C. Then,
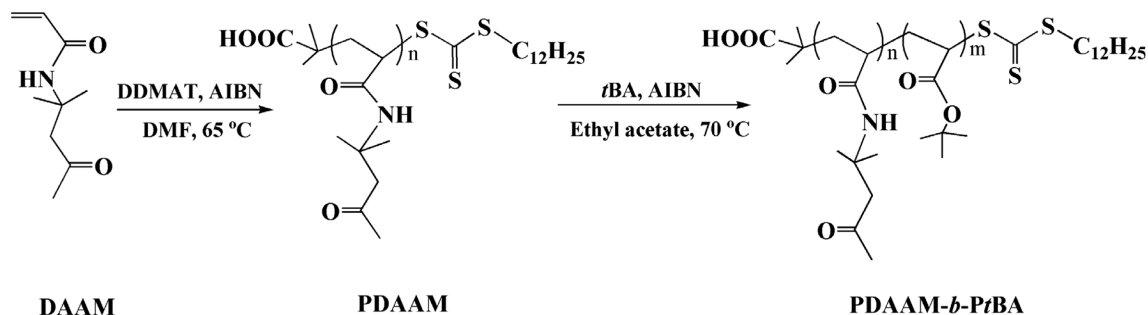
the pH of reaction system was adjusted to 6-7 and the reactant was evaporated to dryness in rotary vacuum evaporator. Then the reactant was dissolved in THF and the polymer was isolated by precipitation into methanol and dried under vacuum. ^{1}H NMR (500 MHz, CDCl$_3$): 0.86 ((CH$_2$)$_{11}$-C$\underline{H}_3$), 1.37 (CH(C$\underline{H}_3$)$_2$), 6.64 (Ar-CH=C$\underline{H}$) 7.13-7.60 (A$\underline{r}$-C$\underline{H}$=CH). IR (KBr, cm^{-1}): 3370 (N-H), 1661 (amide C=O and cinnamoyl C=O), 1605 (olefinic >C=C<), 1449 (Ar, >C=C<), 750 and 691 (Ar, C-H out-of-plane bending).[31,32]

Photoreactivity Measurements. The photoreactivity of the prepared polymers was evaluated by dissolving the sample in acetonitrile or THF and irradiated (quartz tube) with UV light at 365 nm using super high pressure mercury lamp (150 W) at a distance of 10 cm from the surface of the light source for different intervals of time. The change in absorption spectra of polymer during photoirradiation was monitored by UV-visible absorption spectra.[32]
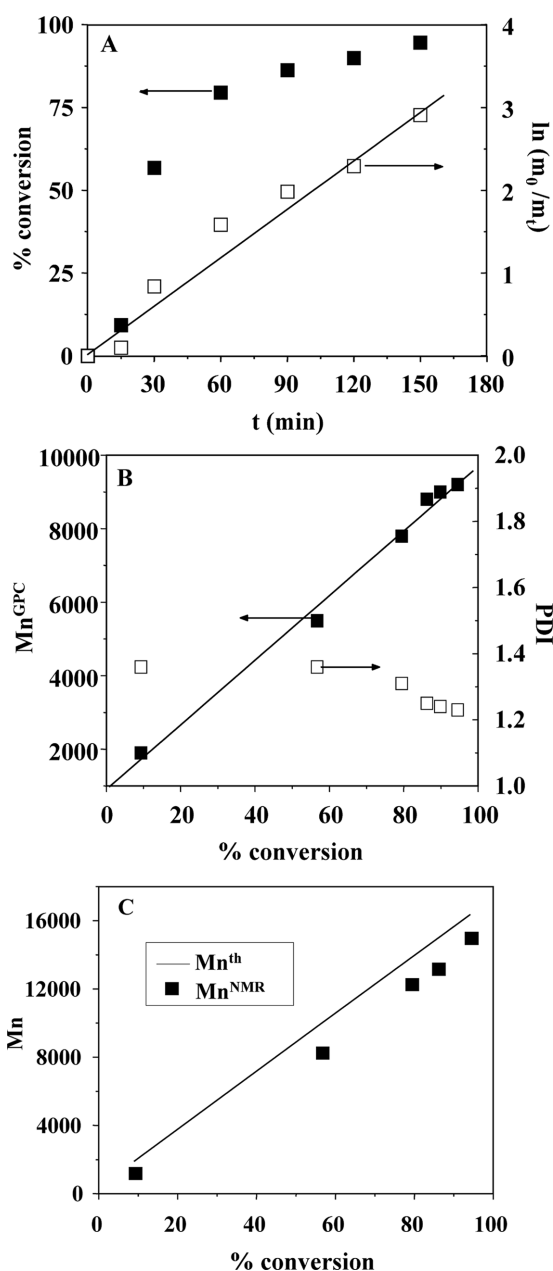
Results and Discussion

The polymerization of DAAM *via* copper-mediated ATRP has been tried and failed to obtain polymer, which could be attributed to the presence of the unfavorable coordination between copper catalyst and the monomer.[33] RAFT synthetic strategy has been proved to be a facile method for the preparation of vinyl ketone-based homopolymers and block copolymers with well-controlled structures.[34]

RAFT homopolymerization of DAAM was conducted at 65 °C in DMF. AIBN was used as the initiator, and DDMAT was selected as the RAFT agent due to its easy synthesis and less unfavorable odor relative to most other RAFT agents (Scheme 1). A linear relationship was observed between the semilogarithmic plot and time (Figure 1(A)) indicating a constant number of propagating species throughout the reaction. Polymerization process of DAAM was monitored by gel per-
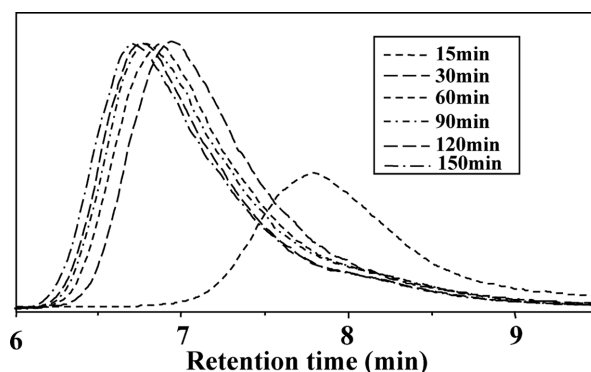

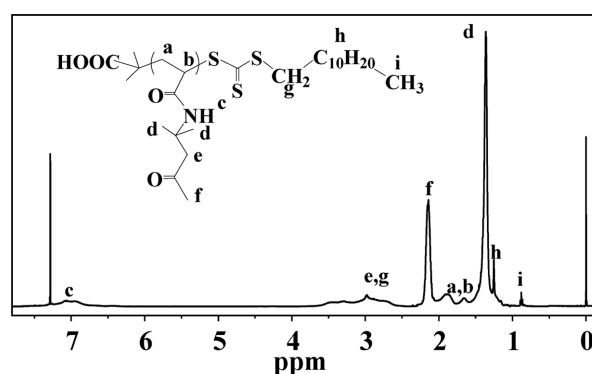**Scheme 1.** Synthetic reactions for PDAAM and PDAAM-*b*-P*t*BA.

Figure 1. RAFT polymerization of DAAM: A-Semilogarithmic kinetic plot; B-M_n^{GPC} and PDI^{GPC} *vs.* monomer conversion; C-M_n^{NMR} and M_n^{th} *vs* monomer conversion.

Figure 2. GPC traces of the evolution of molecular weight obtained from samples at different time intervals for the polymerization of DAAM.

Figure 3. ^{1}H NMR spectrum (CDCl$_3$) obtained from PDAAM.

meation chromatography (GPC). The molecular weight distributions with increasing conversions are shown in Figure 2, and only mono-modal peak was observed throughout the reaction. The molecular weights increased linearly with conversion, and the molecular weight distributions decreased with conversion and at the end of the reaction were relatively narrow (PDI=1.25, Figure 1(B)), which was consistent with a living polymerization. Both the kinetic plots and low PDI suggest

that this system is a controlled radical polymerization.

The polymer was obtained by precipitation of the reaction mixture in water, and the ^{1}H NMR spectrum of the homopolymer was obtained (Figure 3). The ^{1}H NMR spectrum reveals that polymer has been synthesized successfully, and the degrees of polymerization (DP) can be calculated from the eq. (1).

$$M_n^{NMR} = \frac{169.2 \times I_f}{I_i} + 365 \tag{1}$$

I_f: The peak area of functional group *f* in NMR

I_i: The peak area of functional group *i* in NMR

As shown in Figure 1(C), the molecular weight calculated from ^{1}H NMR spectroscopy, M_n^{NMR}, agrees well with M_n^{th}. In each case, M_n^{NMR}, M_n^{th}, and M_n^{GPC} increase linearly with monomer conversion.

To further demonstrate the living characteristics of the RAFT polymerization, the PDAAM obtained was used as macro-RAFT agents for chain extension reactions as showed
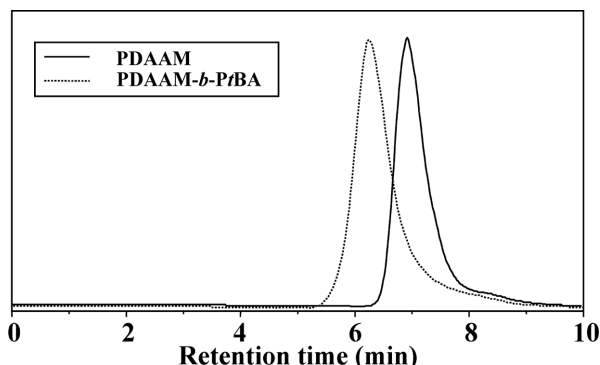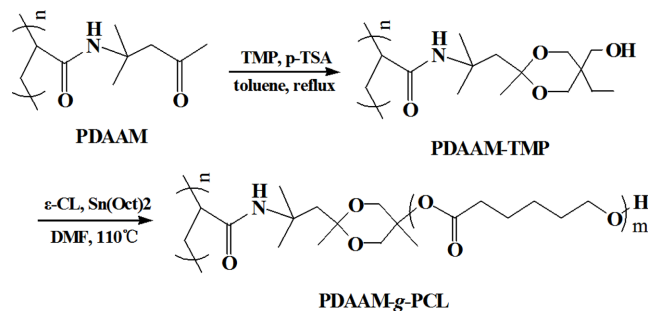
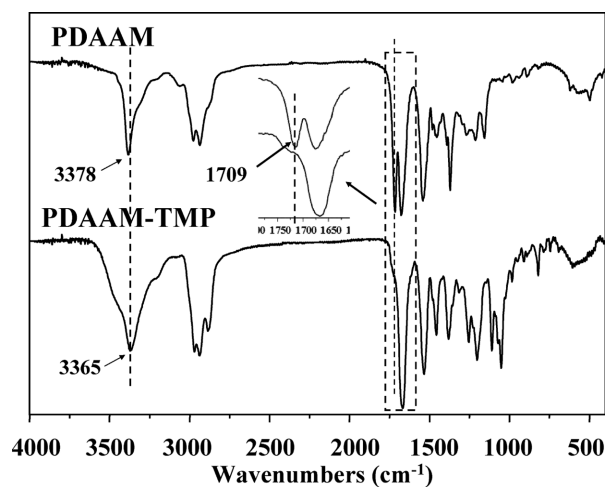**Figure 4.** GPC traces obtained from PDAAM and PDAAM-*b*-P*t*BA.
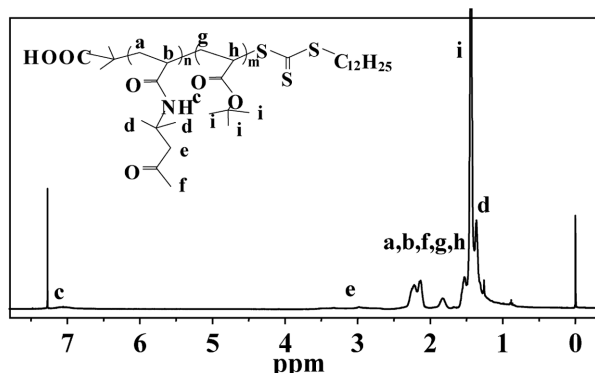
Figure 5. ^{1}H NMR spectrum (CDCl$_3$) obtained from PDAAM-*b*-P*t*BA.

in Scheme 1. Using PDAAM (M_n^{GPC}=5000 g/mol, PDI^{GPC}=1.25) as the macro-RAFT agents and AIBN as the initiator, RAFT polymerizations of *t*BA were conducted at 70 °C in ethyl acetate for 12 h. As shown in Figure 4, the formation of diblock copolymers PDAAM-*b*-P*t*BA (M_n^{GPC}=18400 g/mol, PDI^{GPC}=1.27) from the chain extension experiment was verified by GPC analyses. The increase of the molecular weight and the narrow molecular weight distributions illustrate the quantitative chain transfer efficiency of the PDAAM-based macro-RAFT agents.[29] Figure 5 presents the ^{1}H NMR spectrum of PDAAM-*b*-P*t*BA. Besides the characteristic chemical shifts of PDAAM segment, there is a characteristic strong peak at 1.43 ppm (peak i) which correspond to methyl protons in *t*-butyl group (-C(CH$_3$)$_3$),[18] revealing that the diblock copolymer has been synthesized successfully.

The reactivity of the ketone moiety was investigated. Acid-catalyzed ketalization of PDAAM with trimethylol propane (TMP) was carried out with the feed molar ratio of [ketone]:[TMP]:[*p*-TSA]=1:3:0.1 using the toluene azeotropic removal of water (Scheme 2). The coupling was confirmed by FTIR as

Scheme 2. Synthetic reactions for PDAAM-*g*-PCL.
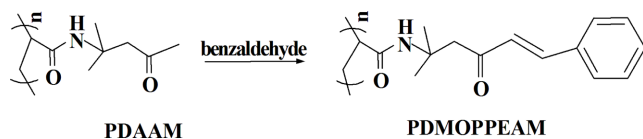

Figure 6. FTIR spectra obtained from PDAAM and PDAAM-TMP.
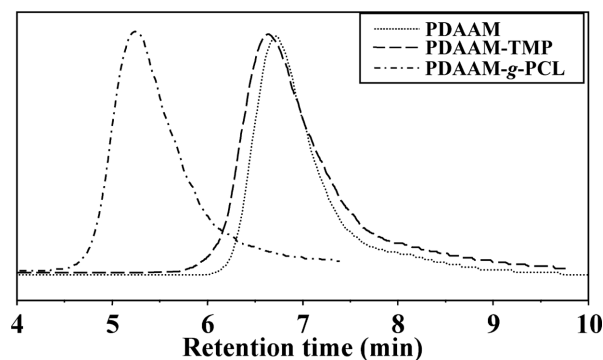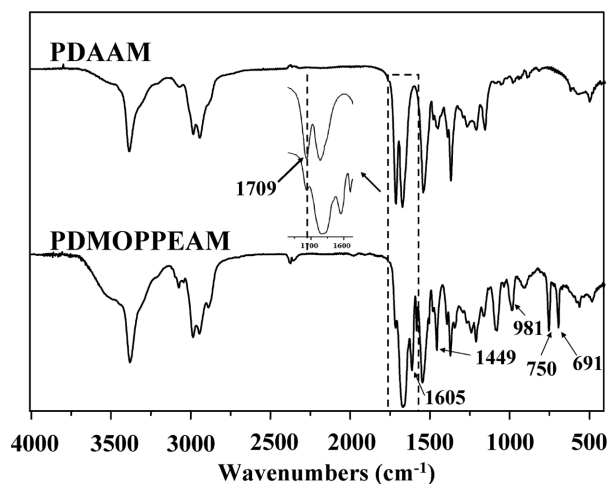

Figure 7. GPC traces obtained from PDAAM, PDAAM-TMP and PDAAM-*g*-PCL.

shown in Figure 6. After the coupling reaction, the characteristic stretching vibration absorption at 1709 cm^{-1} due to the carbonyl group in PDAAM disappeared, indicating the nearly complete ketalization of ketone group.[13] Meanwhile, the characteristic band for amide at 1669 cm^{-1} remained, indicating the amide was not hydrolyzed during the reaction.[27] Furthermore, the obtained polymer was used as a macroinitiator for graft-
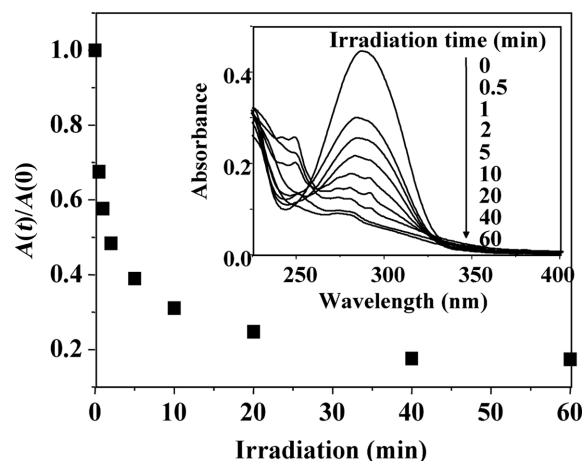
Scheme 3. Coupling of benzaldehyde to PDAAM.

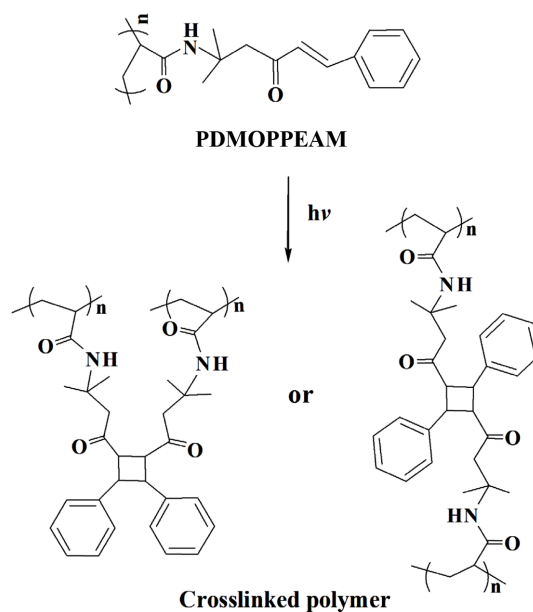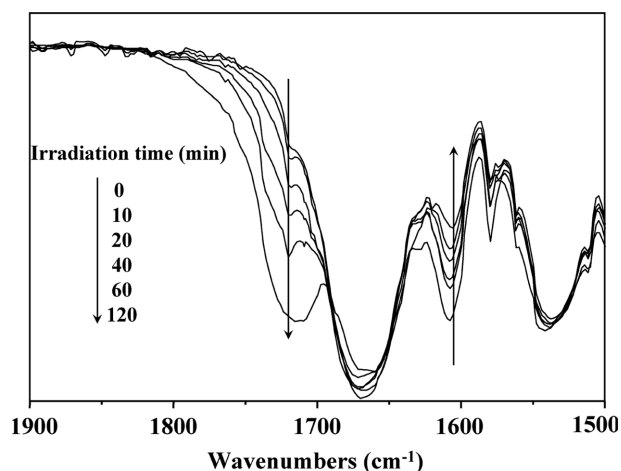
Figure 8. FTIR spectra of PDAAM and PDMOPPEAM.

Figure 9. Decrease in $A(t)/A(0)$ for the cinnamoyl residues determined from the absorption spectra of PDMOPPEAM as a function of irradiation time (t). Here, $A(t)$ and $A(0)$ are the absorbances at 285 nm at irradiation time t and 0 min, respectively. Inset: changes in absorption spectra for the cinnamoyl residues in 20 mg/L acetonitrile solution caused by UV-irradiation, and the irradiation time is indicated in the figure.

polymerization of ε-CL in the presence of tin 2-ethylhexanoate catalyst at 110 °C to give graft copolymer. The conversion of ε-CL was 70% after 12 h. The formation of polymer brush PDAAM-*g*-PCL (M_n^{GPC}=86400 g/mol, PDI^{GPC}=1.24) from the graft polymerization was verified by GPC analyses as shown in Figure 7.

Base-catalyzed aldol condensation of PDAAM with benzaldehyde was carried out with the feed molar ratio of [ketone]:[benzaldehyde]=1:1.5 using NaOH as catalyst at 25 °C in water/ethanol mixed solvent (Scheme 3). The final product was characterized by FTIR as shown in Figure 8. The characteristic absorption due to the carbonyl group in PDAAM shifts from 1709 to 1661 cm⁻¹ and overlap with amide carbonyl. The olefinic bonds in the cinnamoyl at 1605 cm⁻¹, the characteristic absorption band of >C=C< of benzene at 1449 cm⁻¹, and C-H (out-of-plane bending) of benzene at 750 and 691 cm⁻¹ indicate that PDMOPPEAM has been synthesized successfully.[32,35]

The photoreactivity of PDMOPPEAM has been examined in acetonitrile with concentration of 20 mg/L. Polymer solutions were irradiated with a mercury lamp (UV source) at room temperature in the presence of air. The samples in acetonitrile solution show UV absorption bands at 285 nm attributed to the π-π* transitions of >C=C< of the pendant cinnamoyl groups. The

Scheme 4. Photocycloaddition scheme of PDMOPPEAM upon irradiation.

effect of irradiation on the photosensitive polymers was studied by measuring the changes in the UV absorption intensity at various time intervals, as shown in Figure 9. It is obvious that the absorbance at 285 nm decreased with an increase in the irradiation time and disappeared almost completely after 60 min of irradiation. This is clearly due to the formation of the cyclobutane ring by the 2π+2π addition of pendant cinnamoyl

Figure 10. FTIR spectra of PDMOPPEAM after irradiation.

units of polymers, which destroys conjugation in the entire *p*-electron system and thus leads to a decrease in UV absorption intensity as shown in Scheme 4. Thus, PDMOPPEAM react photochemically according to a mechanism similar to that found for cinnamic acid and its derivatives.[32,36] To verify this conclusion, the product from the UV-irradiated PDMOP-PEAM has also been examined by FTIR. To obtain the samples, THF solutions of the polymers at higher concentrations (20 g/L) were irradiated for 2 h. After that, the solvent was evaporated, the obtained polymers were a solid and measured by FTIR. Figure 10 shows the changes in the IR spectra of the obtained polymers with various irradiation times. With an increase in the irradiation time, the carbonyl band at 1709 cm^{-1} increased due to the loss of conjugation in the photocyclo-addition reactions, and the absorption band at 1605 cm^{-1} attributed to the olefinic bonds in the cinnamoyl decreased because of the photocycloaddition reactions. The results were in good agreement with the measurement results of UV absorption.

Conclusions

In conclusion, well-defined PDAAM with controlled molecular weight and narrow polydispersity has been prepared by RAFT. Kinetic studies indicated living characteristics of the RAFT polymerizations. Chain extension experiment was carried out and well-defined diblock copolymer could be obtained, confirming the living character of the polymerization. Chemical modifications of PDAAM with pendant ketone groups were carried out using acid-catalyzed ketalization reaction and base-catalyzed aldol condensation reaction. Acid-cat-

alyzed ketalization of PDAAM with trimethylol propane (TMP) was carried out to obtain the modified polymer containing pendant cyclic ketal groups and hydroxyl groups, PDAAM-TMP. PCL was grafted from PDAAM-TMP by ROP to obtain graft copolymer. The photosensitive polymer containing pendant cinnamoyl groups was obtained after the base-catalyzed aldol condensation of PDAAM with benzaldehyde, and irradiation under UV light resulted in the formation of the cyclobutane ring by the 2π+2π addition of the pendant cinnamoyl units of the polymers.

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