

Facile synthesis of functional copolymers with pendant vinyl groups by using asymmetrical divinyl monomers

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ABSTRACT: Polymers bearing pendant vinyl groups have attracted significant attraction because they can be further modified for required applications, but their syntheses are still a big challenge. Herein, allyl methacrylate was catalyzed using a phosphazene base to homopolymerize or copolymerize with 2-(N, N-dimethylamino) ethyl methacrylate, affording vinyl functional polymers, which were further successfully tailored by the thiol–ene coupling reaction. The result showed that both the homopolymerizations and copolymerizations could proceed at room temperature with very high monomer conversions. The contents of pendant double bonds in the copolymers were approximately equal to the monomer feeds, but the LCST of the statistical copolymers linearly decreased with increasing AMA content. This strategy offered a new scalable and facile strategy for vinyl functional polymers, would have a wide practical application in many fields. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42758.

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INTRODUCTION

Polymers bearing pendant vinyl groups on the backbone have attracted much attraction, because they provide reactive sites for further modification for required applications such as cross-linked,^{1,2} hyperbranched,^{3–5} and functionalized polymers.^{6–9} However, their syntheses are still a great challenge for chemists, due to the difficulty of avoiding the reaction of the pendant vinyl group. Selective polymerization of asymmetrical divinyl monomers is one of the most feasible approaches for the synthesis of functional polymers with pendant vinyl groups.^{1,8,10–13} With respect to the reactivity discrepancy of the two vinyl groups, functional polymers bearing pendant vinyl groups on each repeat unit can be obtained.

Allyl methacrylate (AMA) containing a conjugated methacrylate group and an unconjugated allylic group is one of the most studied commercial asymmetrical divinyl monomers.¹⁴ This monomer is commonly used as a crosslinking agent in the preparation of coatings, resin foams, and high water absorption materials. Unfortunately, its free radical polymerization is inevitable to gel even at the early stages of the reaction, yielding a polymer with a crosslinking polymeric network.^{15,16} Controlled/living radical polymerization such as atom transfer radical polymerization, and reversible addition–fragmentation chain transfer techniques were also applied for the polymerization of AMA.^{7,10,17–20} Their main

disadvantages include the low monomer conversion before gelation and/or large quantities of transition-metal catalysts. Selective polymerization has also been performed by anionic polymerization. However, this polymerization generally occurs at $< -45^{\circ}\text{C}$. High temperature deactivates the propagating species, resulting in uncontrollable molecular weight, broad distribution, and low monomer conversion.⁸ Apparently, the exploration of the controlled polymerization of divinyl monomer using commercial monomers under mild conditions is still largely required.

As one of the extremely strong and neutral Brønsted bases, (1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris-(dimethylamino)-phosphoranylideneamino]-2 Λ^5 ,4 Λ^5 -catenadi(phosphazene) (*t*-BuP₄) has been used as a counterion for the anionic polymerization of epoxides, cyclosiloxanes, cyclic esters, lactams, and cyclopropane-1,1-dicarboxylates.^{21–25} In particular, *t*-BuP₄ with small amounts of ethyl acetate was found to initiate the anionic polymerization of methyl methacrylate (MMA) to afford a polymer with narrow polydispersity.^{26,27} Different from the conventional anionic polymerization of MMA proceeding at low temperatures, this polymerization was performed at 60°C. Recently, *t*-BuP₄ was employed for the group transfer polymerization of AMA to synthesize well-defined star-shaped polymers.²⁸

This study reported a facile synthesis of functional polymers bearing pendant vinyl groups, which could further be tailored

via the thiol–ene click reaction. This method benefits from commercial availability of divinyl monomer, mild reaction conditions, and high monomer conversions, and would have wide potential applications in the polymer synthesis.

EXPERIMENTAL

Materials

AMA purchased from Sinopharm was distilled over calcium hydride, and stored under nitrogen atmosphere at 0°C. 2-(*N,N*-dimethylamino)ethyl methacrylate (DMAEMA) purchased from Sigma-Aldrich was passed through a basic alumina column, then vacuum distilled over calcium hydride, and stored at –20°C. Benzyl alcohol (BA) from Sigma-Aldrich was dried over sodium under a nitrogen atmosphere and distilled under vacuum after refluxing for hours. *t*-BuP₄ (1.0 mol L^{–1} in *n*-hexane) was purchased from Sigma-Aldrich and used as received. Tetrahydrofuran (THF) from Sinopharm was freshly distilled over sodium/benzophenone and stored under argon atmosphere. Other reagents from Sinopharm were used as received.

Characterization

The molecular weight and polydispersity were obtained by size exclusion chromatography equipped with on-line light scattering (LS) and viscosity detectors (VD) at 35°C. The instrumentation consists of a Waters 1515 isocratic HPLC pump with 5 mm Waters styragel columns (guard, HR3, HR4, HR5, and HR6; the molecular weight ranges of the four HR columns are 500–30,000, 5,000–600,000, 50,000–4,000,000, and 200,000–10,000,000 g mol^{–1}, respectively), Waters 717 PLUS autosampler, Waters 2414 differential refractive index (DRI) detector at a wavelength of 880 nm, multiangle laser LS detector (Wyatt mini-DAWN HELEOS-II) with an 18-angle LS detector at a wavelength of 690 nm and 220 W power, Wyatt Visco Star viscometer detector, and Waters Breeze data manager. HPLC grade THF was used as the eluent and delivered at a rate of 1.0 mL/min. NMR spectra were recorded using a Bruker ARX400 NMR spectrometer in deuterated chloroform (CDCl₃) as the solvent and tetramethylsilane as the internal standard. Differential scanning calorimetry was performed using a TA Instruments Q2000 under a nitrogen flow of 50 mL/min. Samples were quickly heated to 120°C and held for 10 min to remove the thermal history, and cooled to –40°C at a rate of 10°C/min, and finally reheated at 120°C at the same rate.

Homopolymerization of AMA in the Presence of *t*-BuP₄

A typical polymerization procedure is as follows. BA (3.90 μL, 0.04 mmol, 1.0 equiv), AMA (0.051 g, 0.4 mmol, 10 equiv), and THF (0.5 mL) were placed in a flame-dried and nitrogen purged round-bottom flask equipped with a magnetic stirrer. *t*-BuP₄ (40 μL, 0.04 mmol, 1.0 equiv in hexane) was added through a rubber septum with a syringe to start the polymerization at 25°C. After the polymerization, the reaction was terminated with hydrochloric acid/methanol (1/20 v/v). The resulting reaction mixture was dissolved in THF and precipitated into a large excess of petroleum ether. The precipitated polymer was filtered and dried under vacuum.

Copolymerization of AMA and DMAEMA in the Presence of *t*-BuP₄

A typical polymerization procedure was performed as follows: AMA (1.26 g, 10 mmol), DMAEMA (1.57 g, 10 mmol), BA (8 μL, 0.1 mmol), and THF (5 mL) were placed in a flame-dried and nitrogen-purged round-bottom flask equipped with a magnetic stirrer. The flask was placed in ice water. *t*-BuP₄ (100 μL, 0.1 mmol) was added through a rubber septum with a syringe, and the polymerization was performed at 25°C. After the completion of the reaction in 12 h, the reaction mixture was poured in *n*-hexane. The precipitate obtained was filtered, washed with *n*-hexane, and dried under vacuum at room temperature.

Thiol–ene Click Reaction

A typical procedure was performed as follows: the copolymer was dissolved in 10 mL dry methanol, followed by the addition of 8 equiv of cysteamine hydrochloride and 8 equiv of AIBN per double bonds, and the resulting reaction mixture was refluxed for 36 h. After the completion of the reaction, the solvent was removed by rotary evaporation. The crude product was dissolved in THF, reprecipitated several times, and dried under vacuum.

RESULTS AND DISCUSSION

Homopolymerization of AMA

AMA is a multifunctional monomer with a methacrylate group and an allyl group. The addition polymerization can be performed on both types of double bonds and cyclization reactions, yielding a crosslinked polymer even at an early stage of the reaction.⁹ For obtaining a linear soluble polymer, low temperature (generally below –45°C) is necessary. Herein, phosphazene base *t*-BuP₄ was found to catalyze the homopolymerization of AMA at room temperature. BA was employed as initiator due to the phenyl protons can be easily observed by NMR. All the resulting poly(allyl methacrylates) (PAMAs) could be dissolved in common organic solvents (e.g., CH₂Cl₂, CHCl₃, THF, DMAc), indicating that the allyl group of AMA did not participate in the polymerization, because if the allyl groups react, they would form a crosslinked, thus insoluble polymer. The conversions of AMA were close to 100% (Table I) suggesting a high efficiency of *t*-BuP₄.

Based on the report by Seebach *et al.* on the *t*-BuP₄ catalyzed polymerization of MMA,²⁶ we speculated that the active species for this system were anions as well, which could only initiate the methacrylate groups, but were not strong enough for the polymerization of the allyl groups. Scheme 1 shows the proposed mechanism. First, *t*-BuP₄ deprotonated the hydroxyl group of BA, generating anions, which further reacted with the methacrylate groups of AMAs. Finally, the active species were quenched by an acid, yielding a linear polymer with allyl groups. This mechanism was supported by the fact that the molecular weights of the resulting polymers increased with increasing [AMA]/[BA] ratios, indicating some of the living polymerization characteristics (Table I). The polymerization could be performed at room temperature, and this might be attributed to the presence of bulk *t*-BuP₄ counterion.²⁶ Moreover, the PDIs increased with the increasing [AMA]/[BA] ratios as listed in Table I, probably because of the side reactions such as transesterification.

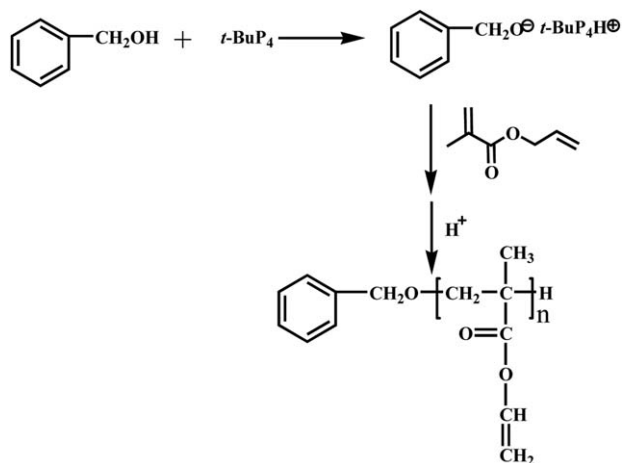
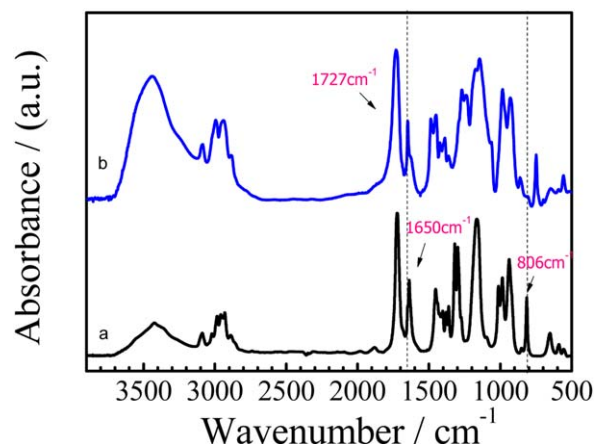
Table I. Characterization Data of the PAMAs

Sample	[AMA]/[BA] ^a (mol/mol)	Conv _{AMA} ^b (%)	$M_{n,NMR}$ ^c (10 ⁴ g/mol)	$M_{n,SEC}$ ^d (10 ⁴ g/mol)	PDI
H1	60	96.3	0.55	0.80	1.21
H2	80	96.4	0.78	0.77	1.14
H3	100	96.1	1.03	1.13	1.37
H4	120	96.5	1.38	1.67	1.40
H5	150	95.9	1.57	1.97	1.49

^aMolar ratio for AMA to BA.^bConversion of AMA determined by GC.^cExperimental number-average molecular weight measured by ¹H-NMR.^dEstimated by SEC (THF as an eluent and polystyrene standards).

The structures of the polymers were first studied by FTIR spectroscopy as shown in Figure 1. Compared to the spectrum of AMA, the peak at 806 cm⁻¹ corresponding to the methacrylate group in AMA disappeared after the polymerization. However, the peak at 1650 cm⁻¹ assigned to the C=C group in the allyl groups persisted, indicating that the polymerization of AMA catalyzed by *t*-BuP₄ proceeded by the reaction of the methacrylate double bonds. Furthermore, no peak for lactone was observed between 1750 and 1850 cm⁻¹ in the FTIR spectrum of PAMA, indicating that either the lactone groups were not present in the polymer or were in very small quantities.¹⁵

¹H-NMR spectrum of the synthesized polymer is shown in Figure 2. The characteristic signals in the range 0.74–1.23 ppm were assigned to the methylene protons of the AMA units. The signals at 1.30–2.77 ppm were ascribed to other alkyl protons of the AMA units. The chemical shifts in the range of 5.04–5.39 and 5.72–5.98 ppm were attributed to -CH=CH₂ and -CH=CH₂ groups of the allyl groups, respectively. The chemical shifts at 4.25–4.45 ppm were attributed to the protons in -CH₂-O- group. Besides, the signals assigned to phenyl protons of the initiator were observed in the range 7.25–7.33 ppm, indicating the existence of the BA moieties in the end of the polymer chain. The NMR results agree with the results of the FTIR spectra, further confirming that only methacrylate double bonds participated in the polymerization, whereas the allyl groups remained as pendant

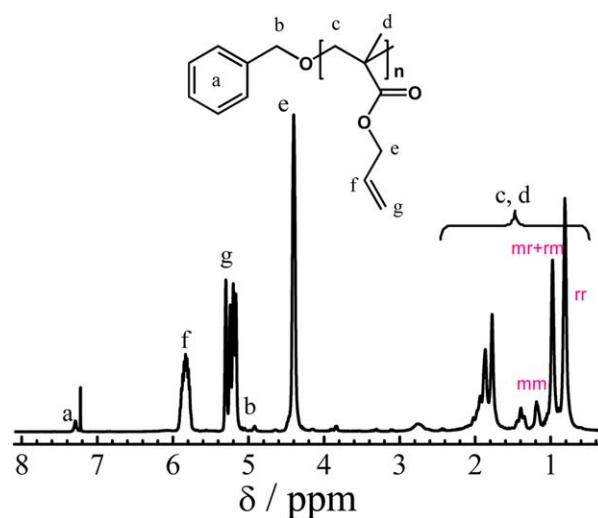
**Scheme 1.** Synthesis of PAMA with *t*-BuP₄ as the catalyst.**Figure 1.** FTIR spectra of (a) AMA and (b) PAMA synthesized in THF solution (50% m/m) at room temperature ([AMA] : [BA] : [*t*-BuP₄] = 100 : 1 : 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in the polymer chain. Moreover, the resonance signals of α-CH₃ splitted into three peaks at 0.88, 1.04, and 1.23 ppm were assigned to syndiotactic (*rr*), heterotactic (*mr* and *rm*), and isotactic (*mm*) triads, respectively.^{29,30} Hence, it is possible to calculate the stereochemical configuration (*rr* %) of AMA units along the polymer backbone. Herein, the syndiotacticity of the PAMA calculated from the average integral values of these signals was 62.8%.

The molecular weights of the PAMAs ($M_{n,NMR}$) were estimated according to the integrals calculated by ¹H NMR spectra as expressed by the following equation:

$$M_{n,NMR} = \frac{(I_{4.25-4.45} + I_{5.04-5.35} + I_{5.72-5.98})/5}{I_{7.25-7.33}/4} \times M_{AMA} + M_{BA}$$

where $I_{4.25-4.45}$, $I_{5.04-5.35}$, $I_{5.72-5.98}$, and $I_{7.25-7.33}$ are the integrals of the signals at 4.25–4.45, 5.04–5.35, 5.72–5.98, and 7.25–7.33 ppm as shown in Figure 2. As shown in Table I, the $M_{n,NMR}$

**Figure 2.** ¹H-NMR spectrum in CDCl₃ of the PAMA synthesized in THF solution (50% m/m) at room temperature ([AMA] : [BA] : [*t*-BuP₄] = 100 : 1 : 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

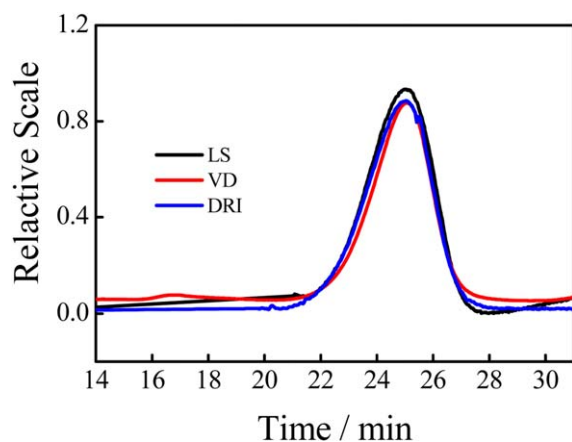


Figure 3. The tri-SEC signals of the PAMA synthesized in THF solution (50% m/m) at room temperature ([AMA] : [BA] : [*t*-BuP₄] = 100 : 1 : 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

values are smaller than the values determined from SEC ($M_{n,SEC}$), probably because the SEC data just provides relative molecular weights using monodisperse polystyrenes as the standard. Both the $M_{n,NMR}$ and $M_{n,SEC}$ values increased with increasing [AMA]/[BA] ratio, indicating the homopolymerization of AMA have good control over the degree of polymerization. Furthermore, all the resulting polymers have a narrow molecular weight distribution ($PDI < 1.50$), further indicating that *t*-BuP₄ is an efficient catalyst for the polymerization of AMA.

The SEC traces of PAMA detected by DRI, LS, and VD are shown in Figure 3, respectively. Clearly, the chromatograms from all the detectors retained the monomodal nature. The LS and VD detectors showed quite similar weight-average molecular weights traces to RI detector, a typical SEC characterization for linear polymers. Because the LS detector is highly sensitive to the high molecular weight part, a slight amount of branching and/or crosslinking structure coexisting in the polymer would result in a sharp difference between LS and DRI signals. Therefore, the SEC result indicates the absence of the crosslinking structures in the polymer, further confirming that allyl groups did not participate in this polymerization.

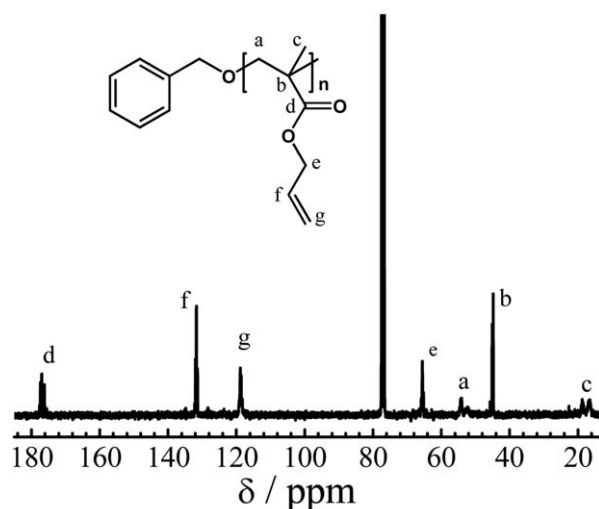


Figure 4. ¹³C-NMR spectrum of PAMA in CDCl₃. ([AMA] : [BA] : [*t*-BuP₄] = 100 : 1 : 1, room temperature)

Figure 4 shows the ¹³C-NMR spectrum of PAMA. The peaks for the vinyl bonds completely disappeared, and new peaks from the carbons in the polymer backbone were observed at 42.5 and 52.9 ppm. However, the peaks corresponding to the allyl group appeared at 132.5 and 117.1 ppm in the spectrum of PAMA, further confirming that allyl groups did not participate in the polymerization. No peaks corresponding to five- or six-member lactones were observed distinctly, indicating that the cyclization reaction did not occur in the polymerization. This result was also confirmed by the ¹H-NMR and FTIR spectra.

Copolymerization of AMA and DMAEMA

Polymers with pendant vinyl groups on the backbone have diverse application, because the double bonds can be easily modified to the desired functional groups.³¹ Poly(2-(dimethylamino)ethyl methacrylate) is a water soluble polymer sensitive to both temperature and pH changes,^{32,33} exhibiting a lower critical solution temperature (LCST)-type phase separation upon heating at neutral or basic conditions. Hence, DMAEMA was used as a model compound to copolymerize with AMA to afford a functional polymer with pendant vinyl groups.

Table II. Characterization Data of the Synthesized Copolymers^a

Sample	f_{AMA}^b (mol/mol)	F_{AMA}^c (mol %)	$M_{n,NMR}^d$ (10 ⁴ g/mol)	$M_{n,SEC}^e$ (10 ⁴ g/mol)	PDI	T_g	Conv _{DMAEMA} (%)
C1	0	0	1.99	2.01	1.35	10.9	92.1
C2	4.17	5.38	1.51	1.78	1.38	13.6	90.7
C3	8.33	8.90	1.56	1.61	1.42	14.2	86.9
C4	12.5	11.6	1.80	1.93	1.47	15.8	91.3
C5	100	100	1.03	1.13	1.37	44.2	96.1

^a Monomer to BA were 100 : 1, react temperature is room temperature.

^b AMA molar fraction in the comonomer feed.

^c AMA unit molar fraction in the copolymer measured by ¹H-NMR.

^d Experimental number-average molecular weight measured by ¹H-NMR.

^e Estimated by SEC (THF as an eluent, polystyrene standards).

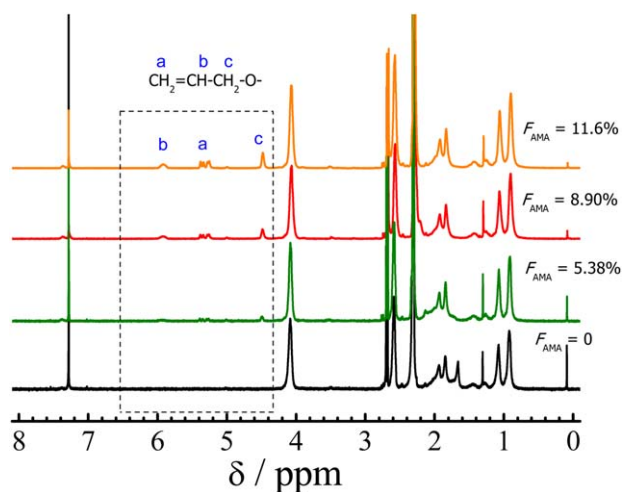


Figure 5. The $^1\text{H-NMR}$ spectra of P(AMA-*co*-DMAEMA)s in CDCl_3 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The copolymers of DMAEMA and AMA were prepared using $t\text{-BuP}_4$ as the catalyst at room temperature. Similar to the homopolymerization, high monomer conversions were

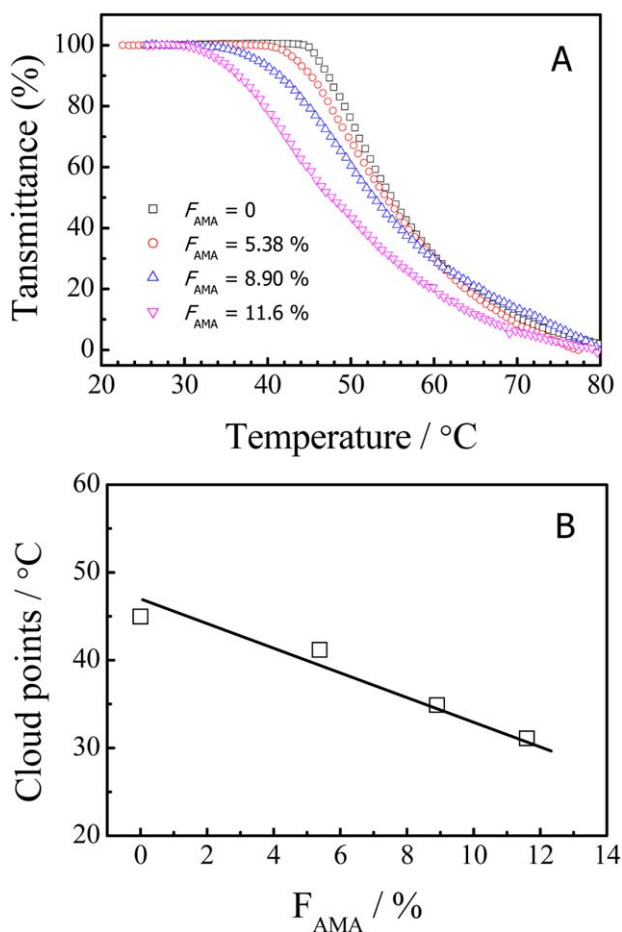


Figure 6. A: Transmittance at 560 nm for the copolymers aqueous solutions (5 mg/mL) with different AMA contents at a heating rate of $0.1^\circ\text{C}/\text{min}$. B: Cloud points for the copolymers with different AMA contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

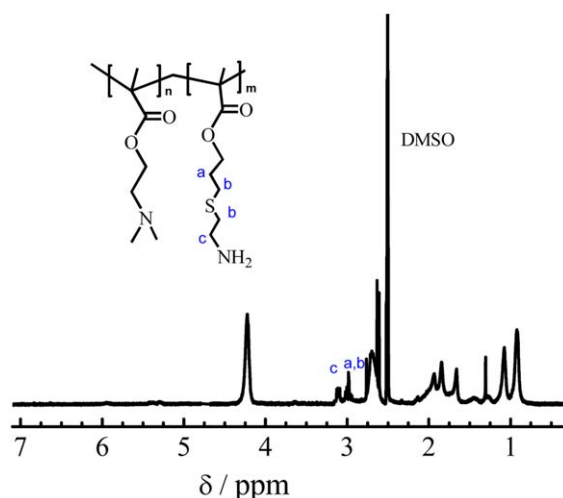


Figure 7. ^1H NMR spectrum of P(AMA-*co*-DMAEMA) (Sample C4) after the thiol-ene coupling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

obtained. No gelation was observed in the copolymerization. All the resulting copolymers completely dissolved in water, but longer time was needed for the copolymers with high AMA contents. The molecular weights and their compositions are listed in Table II. As shown, the synthesized copolymers showed narrow molecular-weight distributions ($\text{PDI} < 1.50$), indicating that $t\text{-BuP}_4$ efficiently catalyzed the copolymerization of AMA and DMAEMA. Moreover, all the copolymers featured only one single glass transition temperature, indicating the presence of a random structure.

Figure 5 shows the $^1\text{H-NMR}$ spectra of copolymers with different AMA contents. The signals because of the protons of DMAEMA units were observed in the ranges $0.71\text{--}2.79$ and $3.93\text{--}4.16$ ppm. The signals of the protons in $\text{CH}_2=\text{CH}-$ and $\text{CH}_2=\text{CH}-$ were observed in the ranges $5.18\text{--}5.40$ ppm (a) and $5.82\text{--}5.98$ ppm (b), respectively. The signals because of the protons in $-\text{CH}_2-\text{O}-$ were observed in the range $4.42\text{--}4.52$ ppm (c). Moreover, the signals attributed to the phenyl protons of the initiator appeared in the range $7.32\text{--}7.36$ ppm, indicating that both DMAEMA and AMA were successfully incorporated in the polymer. The experimental molar ratios of AMA (F_{AMA}) in the copolymer were calculated from the ratio between the intensity of the signal corresponding to the protons of the AMA units and the intensity of the DMAEMA segment signals (See Table II). As shown, the F_{AMA} values in the copolymer are close to the feed ratios (f_{AMA}), allowing adjusting the amount of pendant double bonds by changing the monomer feeds.

The effect of the AMA contents on the LCST of the copolymers was further studied. The results in Figure 6 show that the composition played an important role on the LCST of copolymers. The LCST of the statistical copolymers linearly decreased with increasing AMA content. This is reasonable because the AMA units incorporated into the copolymer are hydrophobic.

In this study, we successfully developed a facile synthesis of functional polymers with pendant vinyl groups by the copolymerization of a commercially available divinyl monomer. Moreover, the pendant vinyl groups in the copolymers can be easily

tailored as required. Hence, the thiol-ene coupling reaction between the ene polymers with cysteamine hydrochloride was performed.³⁴⁻³⁷ ¹H NMR spectrum of the modified copolymer (Figure 7) shows the proton signals at chemical shifts in the ranges 5.04–5.39 and 5.72–5.98 ppm corresponding to the complete disappearance of the allyl double bond of the copolymer. Instead, new signals in the ranges 2.94–3.04 and 3.09–3.17 ppm for $-CH_2-$ were observed, indicating the successful modification of the ene-functionalized polymers.

CONCLUSIONS

In summary, a scalable and facile strategy was developed for the synthesis of functional polymers with pendant vinyl groups by the copolymerization of a commercially available divinyl monomer, AMA. A detailed investigation of the homo- and copolymerization of AMA was investigated. The homopolymerization was performed at room temperature without consideration of gelation or cyclization reaction even at a very high monomer conversion. The copolymerization shows the same results. Moreover, the amount of pendant vinyl bonds in the copolymer was readily adjusted by varying the monomer feeds, and the functional pendant vinyl groups can be easily modified by the click reaction.

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