

A Novel Strategy to Branched Polyacrylonitrile Via One-Pot RAFT Copolymerization of Acrylonitrile and an Asymmetrical Divinyl Monomer

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ABSTRACT: Branched polyacrylonitriles were prepared via the one-pot radical copolymerization of acrylonitrile and an asymmetric divinyl monomer (allyl methacrylate) that possesses both a higher reactive methacrylate and a lower reactive allyl. RAFT technique was used to keep a low-propagation chain concentration via a fast reversible chain transfer equilibration and thus the cross-linking was prevented until a high level of monomer conversions. This novel strategy was demonstrated to engender a branched architecture with abundant pendant functional vinyl and nitrile groups, and controlled molecular weight as a behavior of controlled/living radical polymerization characteristics. The effect of the various experimental

parameters, including temperature, brancher to monomer molar ratio, and chain transfer agent to initiator molar ratio, on the control of molecular dimension (molecular weight and polydispersity indices) and the degree of branching were investigated in detail. Moreover, ^1H NMR and gel permeation chromatography confirm the branched architecture of the resultant polymer. The intrinsic viscosity of the copolymer is also lower than the linear counterpart. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 663–670, 2009

Key words: reversible addition-fragmentation chain transfer (RAFT); branched polymer; acrylonitrile; allyl methacrylate

INTRODUCTION

Polyacrylonitrile (PAN)¹ is a commercially important polymer with many applications, thanks to its unique and well-known properties, including hardness and rigidity, chemical and mechanical stability, compatibility with certain polar substances, and low gas permeability for oxygen and carbon dioxide. Generally, the preparation of PAN is performed via free radical polymerization.² The resultant polymer is a typical linear structure, which decomposes before the melting point and stops melt processibility. In this regard, it will weaken the potential applications of PAN in many fields, such as melt coatings and thermosetting materials.

In contrast to the linear polymers, branched polymers have three-dimensional globular architecture similar to dendrimers, which endows them with many unique advantages, including low solution and melt viscosity, high functionality and good solubility.³ Therefore, a possible approach to improve

the rheological property of PAN is to introduce this three-dimensional branched architecture into the polymer backbone. No literature or reports have showed the attentions to the preparation of branched PAN to date.

Totally, the most important approaches to generate branched vinyl polymers include the self-condensing vinyl polymerization (SCVP) process^{4–12}, the one-pot copolymerization of a vinyl monomer and a multifunctional vinyl comonomer^{13–18}, and the macromonomer approach^{19–23}. With the appropriate choice of reaction conditions and polymerization techniques, these methods can control over the molecular dimension and the structure of polymer. However, SCVP is difficult to exploit industrially because it always needs tremendous efforts to design expensive, tailored monomers with special functional groups. Thus, the second strategy seems to be an alternate way in preparing branched polymers, as it is facile, versatile, and cost effective. Using chain transfer agents such as mercaptans^{13–15} or controlled/living polymerization techniques such as group transfer polymerization,¹⁶ atom transfer radical polymerization (ATRP),^{16,17} reversible addition-fragmentation chain transfer (RAFT) polymerization,¹⁸ to prevent cross-linking, several groups successively reported the controlled synthesis of soluble branched polymers in one-pot

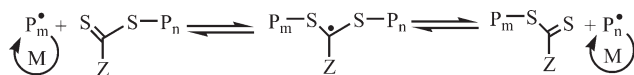
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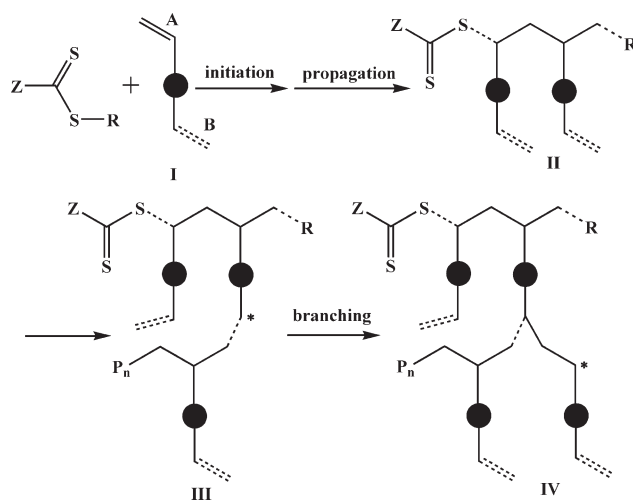
copolymerization of a vinyl monomer and a multifunctional vinyl comonomer. Among these studies, the comonomer is traditionally a symmetrical divinyl monomer, for example, ethylene glycol dimethacrylate and divinyl benzene. In general, the polymerizations were performed at low concentrations for the multivinyl monomers. Therefore, the resultant polymers have a low branched architecture. Furthermore, the branched polymers do not have latent reactive sites used for further chemical functionalization or postpolymerization because most of the double bonds are involved in the polymerization. Moreover, Hutchings's and Frey's groups reported on an innovative macromonomer route for branched polymer structures. This strategy first involves the preparation of macromonomer, and then branched macromonomers are prepared in a "one-pot" single-step, coupling reaction. The resulting branched polymers are polydisperse both in terms of their molecular weight and architecture.^{19–23}

Recently, Wang et al.²⁴ reported the homopolymerizations of divinylbenzene and ethylene glycol dimethacrylate via a deactivation enhanced ATRP to slow down the propagation rate and thus inhibit the rapid cross-linking. This way has successfully synthesized the branched polymers with multiplicity of reactive vinyl and halogen end functional groups. The key restriction to prevent gelation is that the monomer conversion is limited to less than 60%. Independently, we have described a novel methodology to produce such branched polymers by RAFT polymerization (Scheme 1) of an asymmetric divinyl monomer with a general structure AB, which consists of two vinyl groups, where A is more reactive than B toward radical polymerization (Scheme 2).²⁵ It is important that our strategy can engenderate the soluble branched materials with higher (>80%) polymer yields.

In this article, we use RAFT technique to generate branched polymers via the one-pot copolymerization of acrylonitrile (AN) and allyl methacrylate (AMA) containing a high-reactive methacrylic moiety and a lower reactivity alkenyl group. The control of various experimental parameters of molecular dimension and the branched architecture was thoroughly discussed. Finally, the branched architectures of PANs were characterized by ¹H NMR and gel permeation chromatography (GPC) analyses as well as the intrinsic viscosity measurements.



Scheme 1 The RAFT process.



Scheme 2 Mechanism for RAFT polymerization of AMA to branched polymers.

EXPERIMENTAL

Materials

AN and AMA were passed through a column of alumina to remove the inhibitor and distilled before use. Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. Ethylene carbonate (EC) obtained from Aldrich was used as received. 2-Cyanoprop-2-yl dithiobenzoate (CPDB) was synthesized according to literature procedures.²⁶

Polymerization

A Schlenk polymerization tube filled with CPDB, AIBN, EC, AN, and AMA, was deoxygenated by three freeze-pump-thaw cycles, charged with nitrogen and sealed. The polymerization tubes were heated at the appropriate temperature in a thermostated oil bath. After a predetermined time, the polymerization tube was placed in liquid nitrogen to quench the reaction, and the content was diluted with dimethylformamide (DMF). When the mixture becomes a homogenous solution, an excess of methanol was added to precipitate the polymer. The resultant polymer was filtered and dried at 50°C *in vacuo*.

Characterization

The monomer conversions were determined by gravimetry. The ¹H NMR of branched PAN was measured on a Bruker 300 MHz spectrometer with DMSO-*d*₆ as solvent. The number-average molecular weights (\bar{M}_n) and polydispersities indices (PDI) of the polymers were measured on a GPC system, which consists of a Waters 510 HPLC pump, three Waters Ultrastyragal columns (500, 10³, and 10⁵) and

TABLE 1
RAFT Copolymerization of AN and AMA Under Various Conditions

No.	T (°C)	<i>t</i> (h)	[AN]/[CPDB]/ [AIBN]/[AMA]	Conv. %	\bar{M}_n (GPC)	PDI (GPC)	η (dL/g)
1	60	24	600:3:1:0	82.7	56,000	1.26	0.128
2	60	12	600:3:1:18	75.3	72,100	4.68	0.13
3	70	8	600:3:1:18	56.8	65,300	5.96	0.11
4	60	16	600:3:1:6	77.8	72,300	4.40	0.15
5	60	8	600:3:2:18	50.0	137,000	5.37	0.203
6	60	24	600:3:0.5:18	44.4	36,000	2.88	0.09

a Waters 2414 RI detector, with a flow rate of 1.0 mL/min. The intrinsic viscosity $[\eta]$ of branched polymer was measured at 25°C in DMF using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Synthesis of branched PANs via one-pot copolymerization of AN and AMA

As noted previously, the success of the RAFT polymerization of a particular monomer depends on the structures of both Z²⁷ and R²⁸ group of a chain transfer agent (CTA). Qian and coworkers²⁹ and our groups²⁶ successively reported that CPDB is a successful CTA for the synthesis of the controlled PAN via RAFT mechanism. Therefore, CPDB was selected as the CTA to control the copolymerization of AN and AMA. The polymerizations were terminated before the cross-linking, and the results of RAFT copolymerization under various conditions are presented in Table I.

We first chose the optimal experimental parameters for the RAFT homopolymerization of AN to conduct the RAFT copolymerization of AN and AMA, where the ratio of [CPDB]/[AIBN] was fixed at 3, and EC was used as the solvent. Compared with the control experiment (entry 1 in Table I), the monomer conversion of the RAFT copolymerization (entry 2 in Table I) reached a lower value, whereas the \bar{M}_n (GPC) and PDI (GPC) of the copolymer were higher than those of PAN obtained by RAFT homopolymerization. Herein, it must be pointed out that the branched polymers display longer retention times due to less hydrodynamic volumes than those linear counterparts. As a result, the MW values of the branched polymers measured by RI detector are relatively lower than the true ones, which is usually a difficult issue in the \bar{M}_w analyses of branched polymers. Furthermore, such high PDI (GPC) values may be an indication of the formation of branched structure. This result can also be judged from the evolution of GPC curves of the copolymers with an increase in monomer conversion (Fig. 1). At the initial stage of the polymerization, the GPC curves are monomodal and nearly symmetrical and have low

PDI. With the increase of the monomer conversions, the traces almost shift clearly and completely. These observations suggest that the copolymerization of AN and AMA under this condition possess the characteristics of a controlled radical polymerization (CRP).³⁰ However, the most important information is that the curves after the monomer conversion reached 32.1% become broad and multimodal, indicating that the branched reactions occurred during the RAFT copolymerization. Different peaks correspond to the components of the polymers with different branching engenerating during the copolymerization. Similar multimodal observations of GPC curves of branched polymers have also been reported by other groups.^{13–18,24,25}

The most powerful evidence for the formation of the branched architecture can be obtained from the ¹H NMR spectrum of PAN with \bar{M}_n (GPC) = 34,300 and PDI (GPC) = 2.84 (Fig. 2). The clear proof for the incorporation of the CTA fragments as the end group in the polymer chain is acquired from the three peaks of the aromatic protons at 7.4–8.2 ppm.²⁶ In addition, the signals at 4.4–6.2 ppm originated from the pendant unreacted allyl double bonds of

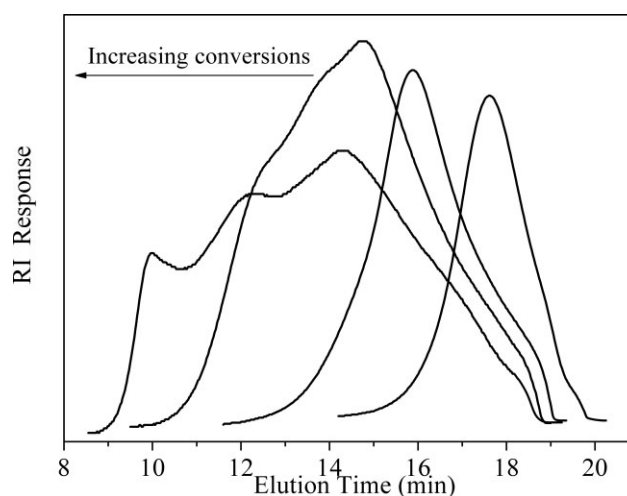


Figure 1 GPC traces of PANs formed via RAFT polymerization mediated by CPDB in EC at 90°C at different conversion: 4.94%, 32.1%, 59.3%, 75.3%. [AN] = 5.09 mol l⁻¹, [AN]/[AMA]/[CPDB]/[AIBN] = 600:18:3:1.

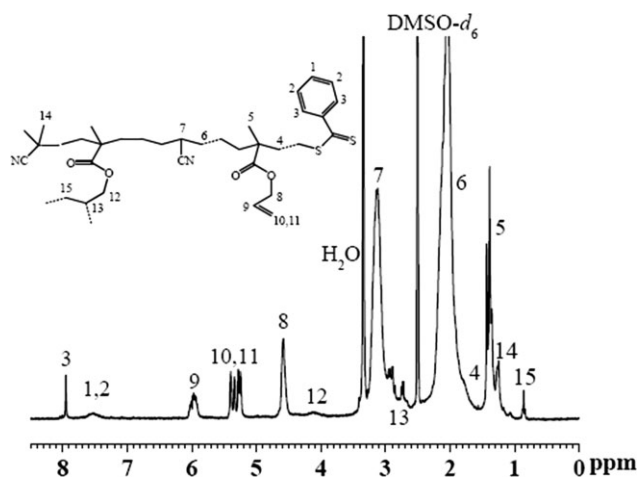


Figure 2 ^1H NMR spectrum of branched PAN mediated by CPDB.

AMA comonomer, whereas no unreacted methacryloyl group exists in the spectrum. Although cyclization reactions to yield five- and six-membered lactone rings have been investigated and discussed, more recent studies involving NMR spectroscopy did not reveal any indication of the formation of in-chain lactone rings.²⁵ However, in our study, a striking observation is that the branching $-\text{OCH}_2-$ group in the AMA residues ($\delta = 3.8\text{--}4.3$ ppm) was observed. The occurrence of the branching unit in NMR spectra of AMA homo- and copolymer has never been reported in the previous studies.^{31–34} The corresponding protons of the reacted allyl double bond can be ascribed to peaks 13 and 15. Moreover, the multisplit of methine proton of AN unit at 2.68–3.23 ppm was an additional evidence for the engeneration of the branched PAN. These results directly confirmed the branched architecture of the copolymers prepared from RAFT process. Finally, the Fréchet and coworkers³⁵ and Frey and coworkers³⁶ definitions for the degree of branching (DB) are not applicable to this system. Herein, we qualitatively compare the DBs by calculating the ratio of the peak 12 integral to the sum integral of peaks 8 and 12. The DB value is ca. 0.1.

Compared with the linear polymer, the branched polymer has unique solution properties, i.e., its intrinsic viscosity is lower than its linear counterpart.³ From the last column of Table I, the intrinsic viscosity of the copolymer with a molecular weight of 65,300 (entry 3 in Table I) prepared in the presence of the brancher is less than that of homopolymer with a molecular weight of 56,000 (entry 1 in Table I) prepared in the controlled polymerization. This result proved the occurrence of the branched reaction, and the resultant polymers possessed the properties of branched polymers.

GPC and ^1H NMR analyses as well as the intrinsic viscosity measurements have confirmed the branched structure of the resultant polymers obtained by RAFT copolymerization of AN and AMA. Thus, we can propose such a mechanism (Scheme 2) to elucidate how a branched vinyl polymer was formed.²⁵ As an unsymmetrical divinyl monomer, AMA has quite high-reactive methacrylic double bonds relative to its allylic bonds (Scheme 2 (I), dash line). Thus, the preferential free radical polymerization occurs in the methacrylic group to form a macromolecular main chain (Scheme 2 (II)). With the progress of the polymerization, the number of the methacryloyl double bonds in the system decreases while the number of the pedant allyl double bonds in the polymer backbone increases accordingly. Despite the low reactivity of allylic group, a few are still able to react with active radical species. As a result, the addition of the growing polymer radical toward the pedant allyl group leads to a branched site (Scheme 2 (III)), which subsequently propagate to generate a branched polymer (Scheme 2 (IV)).

Influence of various parameters on the evolution of molecular dimension and branched structure

Reaction temperature

The aim to investigate reaction temperature is to increase the degree of branching and examine its influence on the control of molecular weight and PDI. Obviously, the rate of polymerization at 60°C is lower than that at 70°C, and there is a retardation effect^{37–43} at the lower temperature (Fig. 3). However, the final monomer conversion at 60°C is relatively higher, which is due to the fact that an

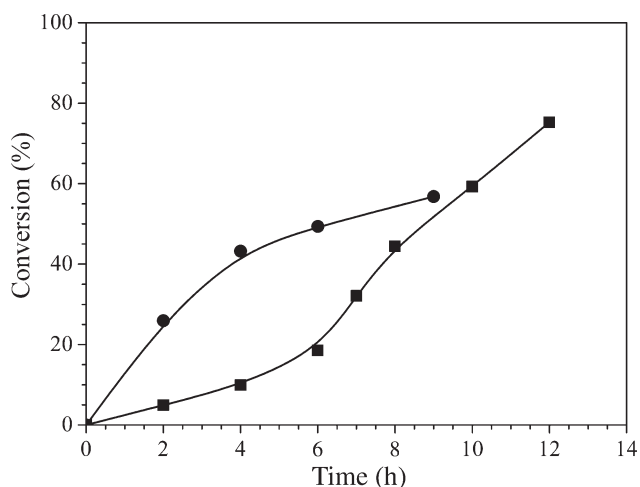


Figure 3 Plots of monomer conversion versus reaction time for the RAFT copolymerization of AN with AMA at different temperature: 60°C (■), 70°C (●). $[\text{AN}] = 5.09 \text{ mol l}^{-1}$, $[\text{AN}]/[\text{AMA}]/[\text{CPDB}]/[\text{AIBN}] = 600:18:3:1$, solvent: EC.

increase in reaction temperature from 60°C to 70°C enhances the reactivity of allyl double bond accordingly, and thus, the branching reaction even gelation easily occurs.

Concerning the control over molecular weights of the resultant branched polymers at two investigated temperatures (Fig. 4), they all increased with monomer conversions, indicating that RAFT copolymerization of AN and AMA possesses the characteristics of a controlled radical polymerization. In addition, \overline{M}_n s (GPC) at 70°C are slightly higher than those at 60°C, which is also true for the evolution of PDIs at two reaction temperatures. This phenomenon can be explained by the increase of the degree of branching with an increase in temperature, which is confirmed by ^1H NMR data.

GPC traces of branched PANs obtained at reaction temperature of 60°C (conv.% = 75.3%) and 70°C (conv.% = 56.8%) are shown in Figure 5. In all instances, the traces are broad and trimodal. However, the two peaks of branched polymer at 70°C is relatively stronger at the high-molecular weight region. This suggests that a higher temperature favors a higher degree of branching, although it is obtained at the expense of monomer conversion.

Molar ratio of [AMA]/[AN]

Generally, the branched structure and the degree of branching are especially influenced by the concentration of the brancher. Thus, the control of [AMA]/[AN] over the evolution of molecular dimension and branched structure was investigated and is shown in Figures 6–8. Obviously, the rates of the polymerization at three molar ratios of [AMA]/[AN] did not depart much from each other except that it slightly enhanced at the later stage for [AMA]/[AN]

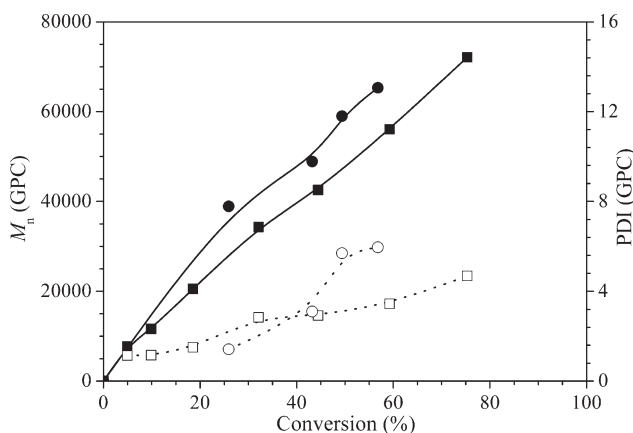


Figure 4 Plots of polymer M_n (●, ■) and PDI (○, □) measured by GPC versus monomer conversion for the RAFT copolymerization of AN with AMA at different temperature: 60°C (■, □), 70°C (●, ○). [AN] = 5.09 mol l⁻¹, [AN]/[AMA]/[CPDB]/[AIBN] = 600:18:3:1, solvent: EC.

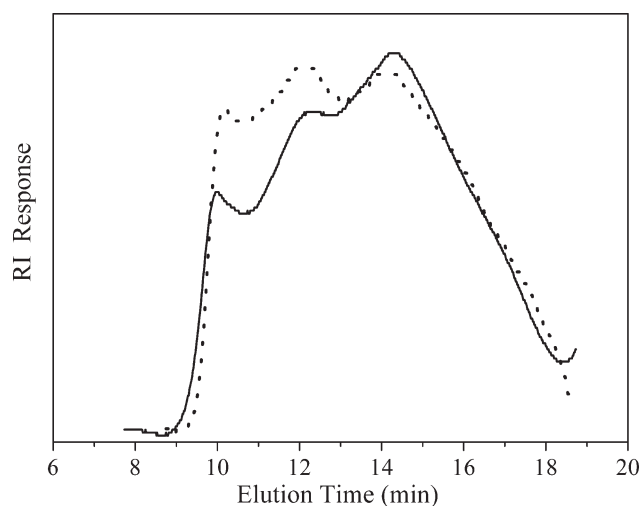


Figure 5 GPC traces of PANs formed via RAFT polymerization at different temperature: 60°C (conv. % = 75.3%, —), 70°C (conv. % = 56.8%,). [AN] = 5.09 mol l⁻¹, [AN]/[AMA]/[CPDB]/[AIBN] = 600:18:3:1, solvent: EC.

of 3 : 100 (Fig. 6). Furthermore, the final monomer conversions with [AMA]/[AN] of 0 : 100, 1 : 100, and 3 : 100 are 82.7, 77.8, and 75.3%, respectively. That is to say, monomer conversion decreased with an increase in the concentration of the brancher AMA. It indicates that the increase of [AMA] leads to an increase in the concentration of allyl ($\text{CH}_2=\text{CHCH}_2-$) vinyl groups, and thus augments the probability of branching or cross-linking.³¹

In the case of molecular weights, they do not have a big difference in the presence of the brancher (Fig. 7). However, they are obviously higher than that of the control experiment. PDIs also increased accordingly. Indeed, when the system was in the absence

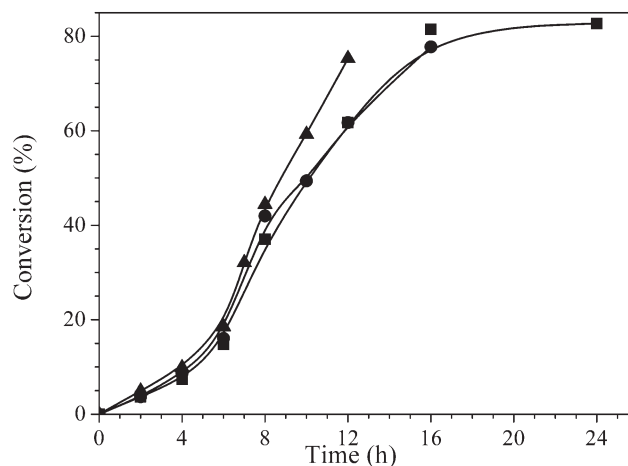


Figure 6 Plots of monomer conversion versus reaction time for the RAFT copolymerization of AN with AMA at different [AMA]/[AN]: 0 : 100 (■), 1 : 100 (●), 3 : 100 (▲). $T = 60^\circ\text{C}$, [AN] = 5.09 mol l⁻¹, [AN]/[CPDB]/[AIBN] = 600:3:1, solvent: EC.

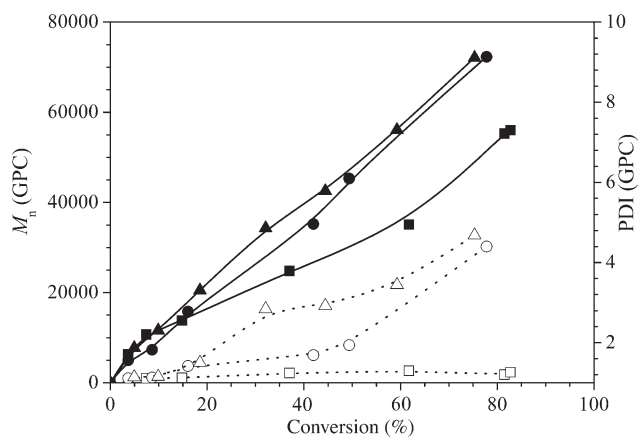


Figure 7 Plots of polymer M_n (■, ●, ▲) and PDI (□, ○, △) measured by GPC versus monomer conversion for the RAFT copolymerization of AN with AMA at different $[AMA]/[AN]$: 0 : 100 (■, □), 1 : 100 (●, ○), 3 : 100 (▲, △). $T = 60^\circ\text{C}$, $[AN] = 5.09 \text{ mol l}^{-1}$, $[AN]/[CPDB]/[AIBN] = 600:3:1$, solvent: EC.

of AMA, the polymerization follows a mechanism of RAFT process and produces the well-defined PANs with predictable molecular weights, low PDIs, and precisely controlled macromolecular architectures. Contrarily, when the brancher was introduced, the branching even gelling occurred with the progress of the polymerization, which accordingly induce the loss of the control as evidenced by the increase of \bar{M}_n (GPC) along with the broadness of the molecular weight distributions.

GPC molar mass distribution curves of branched PANs prepared via RAFT polymerization at three ratios of $[AMA]/[AN]$ were measured and are shown in Figure 8. In the control reaction, the curve

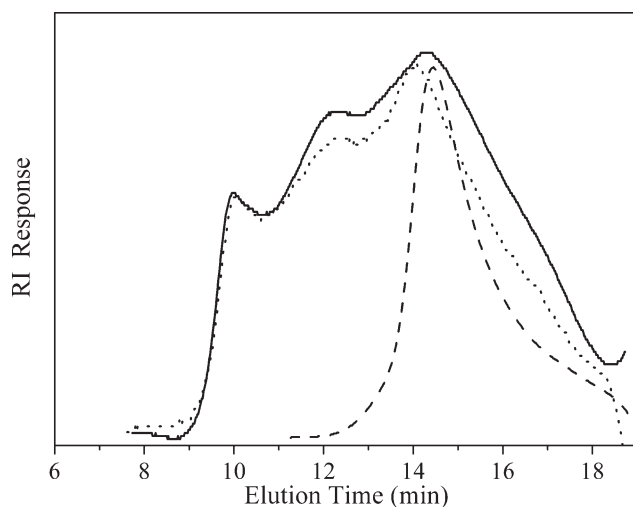


Figure 8 GPC traces of PANs formed via RAFT polymerization at different $[AMA]/[AN]$: 0 : 100 (conv. % = 82.7%, —), 1 : 100 (conv. % = 77.8%,), 3 : 100 (conv. % = 75.3%, - - -). $T = 60^\circ\text{C}$, $[AN] = 5.09 \text{ mol l}^{-1}$, $[AN]/[CPDB]/[AIBN] = 600:3:1$, solvent: EC.

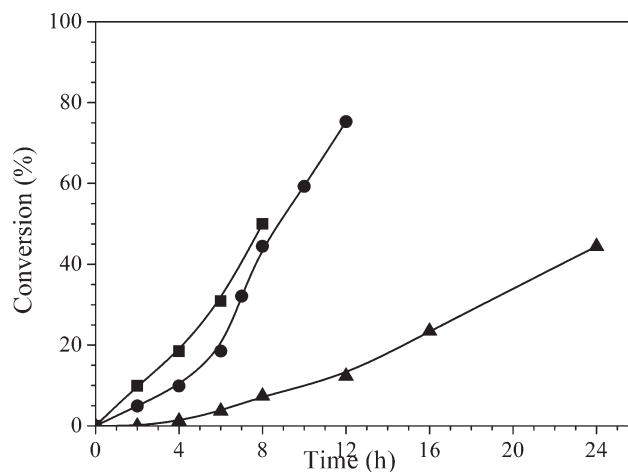


Figure 9 Plots of monomer conversion versus reaction time for the RAFT copolymerization of AN with AMA at different $[CPDB]/[AIBN]$: 1.5 (■), 3 (●), 6 (▲). $T = 60^\circ\text{C}$, $[AN] = 5.09 \text{ mol l}^{-1}$, $[AN]/[CPDB]/[AMA] = 200:1:6$, solvent: EC.

is nearly symmetrical and has low PDI, suggesting that the polymerization of AN under this condition possess the characteristics of CRP. However, in the cases of $[AMA]/[AN] = 1 : 100$ and $3 : 100$, the traces turned to be broad and trimodal. These results show that the introduction of AMA induced the branching reaction, and thus the branched structure engendered at moderate-to-high monomer conversions.

Molar ratio of $[CPDB]/[AIBN]$

To achieve the highest degree of branching and monomer conversions, it is clearly desirable to keep a moderate molar ratio of chain transfer agent to initiator. Figure 9 reveals the relationship between

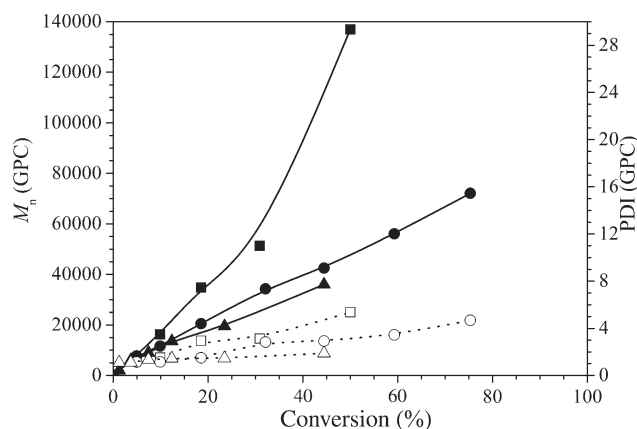


Figure 10 Plots of polymer M_n (■, ●, ▲) and PDI (□, ○, △) measured by GPC versus monomer conversion for the RAFT copolymerization of AN with AMA at different $[CPDB]/[AIBN]$: 1.5 (■, □), 3 (●, ○), 6 (▲, △). $T = 60^\circ\text{C}$, $[AN] = 5.09 \text{ mol l}^{-1}$, $[AN]/[CPDB]/[AMA] = 200:1:6$, solvent: EC.

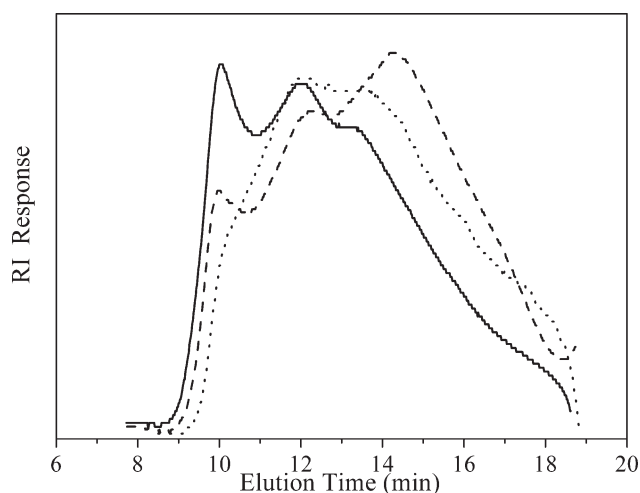


Figure 11 GPC traces of PANs formed via RAFT polymerization at different [CPDB]/[AIBN]: 1.5 (conv. % = 50.0%, —), 3 (conv. % = 75.3%, - -), 6 (conv. % = 44.4%, ·····). $T = 60^{\circ}\text{C}$, $T = 60^{\circ}\text{C}$, $[\text{AN}] = 5.09 \text{ mol l}^{-1}$, $[\text{AN}]/[\text{CPDB}]/[\text{AMA}] = 200:1:6$, solvent: EC.

monomer conversion and reaction time for the RAFT copolymerization of AN with AMA at different [CPDB]/[AIBN] ratios. It is a clear indication that the rate of polymerization decreased in the order $[\text{CPDB}]/[\text{AIBN}] = 1.5 > 3 > 6$, namely, the rate of polymerization decreased with the increase of [CPDB]/[AIBN] ratio, which is ascribable to the influence of chain length-dependent termination rate coefficients on the rate of polymerization.^{44–49} The monomer conversion reaches 75.3% in 12 h when the [CPDB]/[AIBN] ratio is 3. However, when the [CPDB]/[AIBN] ratio is decreased to 1.5, it only reaches 50.0%. That is because that the concentration of the radical reactive species increased accordingly, which leads to the increase of the reaction possibilities in the allyl double bonds. Furthermore, it was noteworthy that there existed an inhibition period of about 2 h when the [CPDB]/[AIBN] ratio is 6. The rate of the polymerization decreased greatly, and the monomer conversion only reaches 44.4% even in a longer duration of 24 h.

In accord with the evolution of monomer conversion, \overline{M}_n s (GPC) prepared at three [CPDB]/[AIBN] molar ratios follow the same rule (Fig. 10), namely \overline{M}_n s (GPC) decreased with the increase of [CPDB]/[AIBN] molar ratios. This implies a decrease of control of the copolymerization of AN and AMA together with increase of the initiator concentration, which is in line with the general RAFT polymerization.⁵⁰ Thus, the branching can easily take place along with the increases of \overline{M}_n s and PDIs.

Figure 11 shows GPC traces of branched PANs obtained at different [CPDB]/[AIBN] ratio. In all stances, the traces are broad. However, concerning a ratio of [CPDB]/[AIBN] = 6, the curve exhibits a

monomodal profile. In the case of a low value of RAFT agent to initiator (1.5 and 3), the curves are all trimodal. It indicates that the branched architectures increased with the decrease of the [CPDB]/[AIBN] ratio.

CONCLUSIONS

The RAFT polymerization of AN has been performed in the presence of a small amount of an asymmetrical divinyl monomer brancher (AMA), with the purpose to synthesize branched PANs. The key to success is to use RAFT technique to keep a low-propagation chain concentration for inhibiting gelation via a fast reversible chain transfer equilibrium. GPC and ^1H NMR analyses confirmed that the resultant polymers have branched structure as evidenced by broad PDIs and low intrinsic viscosities compared with the linear counterpart. Furthermore, RAFT copolymerization possesses the characteristics of a controlled radical polymerization, i.e., the molecular weights of branched polymers increased with monomer conversions. The experimental parameters, reaction temperature, $[\text{AMA}]/[\text{AN}]$ molar ratio, and [CPDB]/[AIBN] molar ratio considerably affected radical copolymerization of AN and AMA. An increase in temperature from 60°C to 70°C leads to an increase in the molecular weight and PDI. Similarly, the increase of the molecular weights and PDI was observed when $[\text{AMA}]/[\text{AN}]$ improves whilst the [CPDB]/[AIBN] ratio decreases. Finally, GPC proves that the branched structure was gradually formed with the progress of the polymerization. ^1H NMR analysis also confirms that the resultant polymer possess abundant vinyl and nitrile functional groups, which are potential reactive sites for further postpolymerization or subsequent chemical modifications. In summary, we have demonstrated a facile and cost-effective way to prepare branched materials with abundant vinyl groups via one-pot RAFT copolymerization in the presence of an asymmetrical divinyl monomer. This strategy can also be extended to other controlled or living polymerization mechanisms, including radical, cationic, anionic, group transfer, and coordination.

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