Polymer Chemistry

Facile Synthesis of Highly Branched Poly(acrylonitrile-co-vinyl acetate) with Low Viscosity and High Thermal Stability via Radical Aqueous Solution Polymerization

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Scheme 1.cdx

Facile Synthesis of Highly Branched Poly(acrylonitrile-*co*-vinyl acetate) with Low Viscosity and High Thermal Stability via Radical Aqueous Solution Polymerization

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Abstract

Branched poly(acrylonitrile-*co*-vinyl acetate) [P(AN-*co*-VAc)] was prepared through radical polymerization using new 2-(3-mercaptopropionyloxy) ethyl methacrylate (MPOEM) as chain transfer monomer (CTM) in sodium thiocyanate (NaSCN) aqueous solution. The development of branching and the changes of molecular weight were analyzed using triple detection size exclusion chromatography (TD-SEC). Below 50% monomer conversion in the presence of MPOEM, weight average molecular weight ($M_{w.MALLS}$) of copolymer increased with conversion and the molecular weights of the primary chains were much higher. The Zimm branching factor (g') was lower than one and decreased with increasing conversion, and this result illustrated that the branched chains were formed and the highly branched structures were obtained very fast even at lower monomer conversion. While above 50% monomer conversion in conjunction with complete MPOEM consumption, $M_{w.MALLS}$ slightly decreased with increasing monomer conversion and almost reached a constant at the end while PDI increased quickly. The g' slightly increased and then remained constant with increasing conversion, which indicated that the branching degree was invariable in the absence of MPOEM. The zero-shear viscosity and glass transition temperature of branched P(AN-*co*-VAc)s were lower than those for their linear analogues, which further confirmed the formation of branched P(AN-*co*-VAc)s. Furthermore, these branched P(AN-*co*-VAc)s were found to have higher thermal stability than their linear counterparts. These highly branched P(AN-*co*-VAc)s with lower viscosity and higher thermal stability are amenable for environmentally benign

processing with less solvent.

Introduction

Polyacrylonitrile (PAN) is a commercially important polymer, mainly due to its excellent properties of rigidity, resistance against oil and low gas permeability.[1, 2] Because the flow temperature of PAN is higher than its decomposition temperature, acrylonitrile (AN) is generally copolymerized with one or two comonomers, such as acrylates, styrene, vinyl acetate (VAc) and so on.[3-8] AN-based polymers have many applications in fibers.[9, 10] The copolymerization of AN/VAc was commonly accomplished via aqueous polymerization and proposed as the precursor of Acrylon.[9] The concentration of P(AN-*co*-VAc) solution is usually restricted to a low level with excess solvent to avoid too high a viscosity in Acrylon processing. The use of excess solvent creates the obvious problems of waste solvent disposal and associated costs. Branching in polymers can result in low solution and melt viscosity compared with their linear analogues. Therefore, it is necessary to prepare branched P(AN-*co*-VAc) in order to decrease its intrinsic viscosity and solution viscosity. This can lead to higher solids content and lower solvent amount in preparing the solution[11, 12] for environmentally benign processing of this polymer.

Previous attempts to prepare branched PANs and AN-based branched copolymers involved some strategies, such as self-condensing vinyl polymerization (SCVP) ,[13] nitroxide mediated radical polymerization (NMP) ,[14] atom transfer radical polymerization (ATRP)[1, 8, 15-18] and reversible addition- fragmentation chain transfer (RAFT) polymerization.[5] Apparently, these approaches had the ability to generate well-defined branched architectures while controlling the molecular weight.[19, 20]

Despite their advantages, these living radical polymerization methods still have some drawbacks for commercialization. The issues involved are tedious preparation of multifunctional-initiator, complexity of steps, and high cost,[17, 19, 21-24] which limit the mass scale production and application of branched polymers.

To enlarge the range of applications for branched PANs and AN-based branched copolymers, a facile and practical method needs to be developed. Recently our group made a new advance in developing an approach to branched vinyl polymers via radical polymerization using 3-mercapto-hexyl methacrylate (MHM) as CTM,[25] and branched polymers with high molecular weight and relatively narrow polydispersity were obtained via emulsion polymerization.[26] Unfortunately, MHM is too expensive to meet large scale applications. Consequently, a new CTM of MPOEM, was prepared via classical esterification using cheaper raw materials in contrast to MHM.[25] We firstly reported the preparation and properties of AN-based branched copolymer via conventional free radical copolymerization in the presence of MPOEM. This newer method for making advanced branched PANs and AN-based branched copolymers is believed to provide good prospects for scaling-up and wide industrial applications at a lower cost.

In the present work, the important factors involved in preparing branched PANs and AN-based branched copolymers were investigated and their rheological and thermal properties were studied in detail. The key novelty of this research is synthesizing branched P(AN-*co*-VAc)s via radical polymerization using a new CTM of MPOEM. We also found that the selection of NaSCN as the solvent for the P(AN-*co*-VAc)

solution can be beneficial as it can be directly used as precursor without generating waste solvent in Acrylon spinning process.[27]

Results and discussion

Preparation of highly branched P(AN-co-VAc)s

The first significant result of our experiments was the successful synthesis of MPOEM, which is cost-effective and has good storage stability. The highly branched copolymer of AN and VAc was expected to be prepared using MPOEM as the CTM. Scheme 1 shows the ideal formation process of branched P(AN-*co*-VAc). Owing to the special structure of MPOEM with a polymerizable vinyl group and a chain transferring/initiating thiol group, both macromolecular chain transfer agent (A in Scheme 1) and macromonomer (B in Scheme 1) can be formed in the polymerization. Further reaction of the formed macromolecular chain transfer agent and / or the macromonomer will generate branched molecules.

Scheme 1 Formation of branched P(AN-*co*-VAc) via radical polymerization in the presence of a CTM.

Fig. 1 illustrates the kinetics data of the copolymerization of AN with VAc in the presence of MPOEM in 45 % NaSCN solution. The consumption rate of AN was always higher than that of VAc, owing to higher activity of AN, the monomer reactivity ratios for AN and VAc were 4.2 and 0.05, respectively.[28] The consumption rate of MPOEM was higher than those of monomers. Notably, when AN and VAc

were consumed about half and only about 30%, respectively, i.e. approximately 50%

monomer conversion, MPOEM was fully consumed. This is because MPOEM has

two reactive groups and can enter the primary chain through either the polymerization

of the vinyl group or the chain transferring/initiating reaction via the -SH group.

Fig.1 Kinetics of the copolymerization of AN with VAc using MPOEM in NaSCN aqueous

solution at 60 °C in the following ratio: [AN]/[VAc]/[MPOEM]/[AIBN]=88:11:1:1.

Fig. 2 ^{1}H-NMR spectra of MPOEM and P(AN-*co*-VAc)s.

BP(AN-*co*-VAc) is branched P(AN-*co*-VAc); LP(AN-*co*-VAc) is linear P(AN-*co*-VAc); *Conv.*$_m$ is

the conversion of monomer

Fig. 2 shows the ^{1}H-NMR spectra of MPOEM, branched P(AN-*co*-VAc)s and their

linear analogue prepared without MPOEM. The signals at δ_H 3.1 ppm are

crossponding to protons in the methylene next to nitrile group from AN, while those

at δ_H 5.2 ppm belong to the methylene linked with ester group from VAc. These

typical signals were observed in spectra B, C and D (see Fig. 2), indicating the

formation of copolymer of AN and VAc. The related signals from MPOEM were

assigned in spectrum A. The signals around δ_H 4.4 ppm in spectra B and C are due to

MPOEM, indicating MPOEM entered the polymer chain and the branched structure

may have formed. Integration of the signals around δ_H 4.4 ppm in spectra B and C

was performed to determine the areas of the signals. The area of the signal in the

spectrum B at *Conv.*$_m$=4.7% was larger than that in the spectrum C at *Conv.*$_m$=97%,

indicating MPOEM was consumed faster than AN and VAc and the above results are

consistent with those presented in Fig. 1. Surprisingly, there is no signal relating to the vinyl group of MPOEM even at $Conv._m$=4.7% as shown in spectrum B, implying no evidence for the presence of the macromolecular monomer as shown in Scheme 1. It is an unusual branching formation mechanism compared to the previos results which were quite different from those that were observed in our previously studies.[25, 26]

In this paper, the copolymer of AN and VAc with an 8:1 molar ratio was studied because the influence of VAc on the dn/dc value of PAN can't be ignored. For the precise measurement of the absolute weight average molecular weight ($M_{w.MALLS}$) from laser light scattering detector, the instantaneous dn/dc value of the copolymer during polymerization was calculated by calculation using equation 1 given below.[29] The dn/dc value of PAN in DMF solution containing 0.07mol L^{-1} NaNO$_3$ at 25 °C was measured to be 0.0791 mL g^{-1}. This value is similar with those of linear PAN (0.078 mL g^{-1}) and branched PAN, (0.0807 mL g^{-1}) found in the literature.[13, 30] The dn/dc value of PVAc in DMF solution containing 0.07mol L^{-1} NaNO$_3$ at 25 °C was measured to be 0.0206 mL g^{-1}.

$$(dn/dc)_{copolymer} = x_{AN}(dn/dc)_{PAN} + (1 - x_{AN})(dn/dc)_{PVAc} \qquad (1)$$

Here, the dn/dc value is refractive index increments with concentration c in units of mass/solution volume and x_{AN} stands for the weight fraction of component AN in the copolymer.

Fig. 3 shows the changes of $M_{w.MALLS}$ and PDI with conversion of monomers (AN and VAc) in the presence of MPOEM. Even at low monomer conversion, $M_{w.MALLS}$

was larger than 10^5 g mol^{-1}, markedly differing from those observed in the literature,[25, 26, 31-33] where the primary chain formed during the early stages exhibited low molecular weight, usually lower than 10^4 g mol^{-1}. This result indicates unusual branching formation mechanism. Below $Conv._m$=50%, $M_{w.MALLS}$ increased and PDI exhibited slight increase with the conversion of monomers. Above $Conv._m$=50% and complete MPOEM consumption, $M_{w.MALLS}$ slightly decreased with the monomer conversion and almost reached a constant at the end, while PDI increased quickly. From this we can infer that there was no more high molecular weight branched copolymer formed due to the consumption of MPOEM, the low molecular weight molecules were formed in the later stage owing to more chain transfer reaction and lower concentration of the monomers. In order to clarify the accuracy of the influencing factor, linear polymerization processing was studied (shown in Fig. S1). In the linear polymerization, $M_{w.MALLS}$ also exhibited slight decreases and PDI increased gradually in the later stage, owing to lower concentration of monomers resulted in the formation of low molecular weight molecules.[34]

Fig. 3 Relationships of the weight average molecular weight and PDI with the monomer conversion for the copolymerization of AN and VAc using MPOEM in NaSCN aqueous solution at 60 °C using the following ratio:[AN]/[VAc]/[MPOEM]/[AIBN]=88:11:1:1

Fig. 4 shows the evolution of the differential molecular weight distribution with conversion during the copolymerization. The curves of all the traces are asymmetric and appear to consist of two peaks, illustrating the existence of two components with markedly different molecular weights and suggesting the formation of branching.[31]

When $Conv._m$ was lower than 50% (before MPOEM was consumed as shown in Fig.1), there are apparently two peaks related to two components: one component is branched chains with high molecular weight (shown as peak 2 in Fig.4 A) and the other is primary chains (shown as peak 1 in Fig.4 A). It is surprising that the branched chains were formed much faster even at lower monomer conversion and the molecular weights of these primary chains were much higher than those reported by us previously.[25, 26] From this we can infer that the branching formation mechanism is quite different from those observed in our previous studies. The rapid formation of branched chains was due to the high reactivity ratio (r) of MPOEM in the copolymerization reaction system. Here, we find that the r of MPOEM is similar to that of methyl methacrylate (MMA), because they have the same vinyl double bond. In order to explain the accuracy of the influencing factor, we listed the detailed r of comonomers in Table S1[28]. These data suggested that the vinyl radicals of AN, VAc, MPOEM in the reaction system all tended to initiate vinyl double bond of MPOEM. Therefore, the macromolecular monomer was consumed so fast that there was almost none in the reaction system. The results are consistent with the absence of double bond signal at $Conv._m$=4.7% shown in Fig.2 B. The relatively higher molecular weights of the primary chains were because of the lower reaction temperature used, which resulted in less chain transfer reaction. With the monomer conversion increasing, the evolution of the curve was toward the high molecular weight and the amount of the chains with low molecular weight decreased. The primary chains and the branched macromolecular chain transfer agents were polymerized further, and the

highly branched structures were formed.

When $Conv._m$ was above 50% (the MPOEM was consumed completely), there was just macromolecular chain transfer agent left in the reaction system. The evolution of the curve was toward the lower molecular weight as shown in Figure 4 B, which is due to further chain transferring/initiating reaction and polymerization of the formed macromolecular chain transfer agent generating inactive linear chains with no additional higher molecular weight polymer formed. With the decrease of the monomer's concentration, the low molecular weight molecules were formed, which directly resulted in a decrease of the average molecular weight with a broad molecular weight distribution. The results were consistent with those described in Fig. 3.

Fig. 4 The differential molecular weight distribution changing with molecular weight at different conversions for the copolymerization of AN and VAc using MPOEM in NaSCN aqueous solution at 60 °C using the following ratio: [AN]/[VAc]/[MPOEM]/[AIBN]=88:11:1:1

For further proof to support the unusual branching formation mechanism described in Fig.4, we measured the g' with monomer conversion (Figure 5) as g' is a qualitative indicator of the degree of branching. The value of g' is lower than one, suggesting that a branched structure was formed. The lower value of g' indicates higher branching degree of polymer.[35] Fig. 5, the average g' is around 0.65 at $Conv._m$=4.7%, indicating that the branched structure was formed rapidly even at low conversion due to all the radicals of the system tending to initiate the vinyl double bond of MPOEM. When $Conv._m$ was below 50%, the value of g' decreased with the monomer conversion in the presence of MPOEM, illustrating the development of branched structure and the

degree of branching PAN-*co*-VAc increased owing to further polymerization of the macromolecular chain transfer agent. While *Conv.*$_m$ was above 50% (when the MPOEM was consumed completely), the value of *g′* increased slightly, then did not vary significantly with the evolution of the polymerization process and leveled off to one constant with conversion, owing to less branched chains and more low molecular weight of linear polymer formation. To some extent, the average branching degree decreased with the polymerization proceeding due to those linear polymers. While the *g′* decreased and the degree of branching increased gradually with monomer conversion owing to the coupling reaction, which mainly takes place between the primary chains in living radical polymerization. So the character of branching formation mechanism of branched P(AN-*co*-VAc) prepared through radical polymerization using MPOEM is different from that of branched polymers reported previously.[16, 25, 31]

Fig. 5 Relationships of the average Zimm branching factor with conversion during the copolymerization of AN and VAc using MPOEM in NaSCN aqueous solution at 60 °C using the following ratio: [AN]/[VAc]/[MPOEM]/[AIBN]=88:11:1:1.

Insert Table 1

A series of branched P(AN-*co*-VAc) copolymers with different molecular weight

and degrees of branching and the linear counterpart were synthesized in the presence

and absence of MPOEM and relevant data are listed in Table 1. As described in

Scheme 1, MPOEM entered in the polymer chain with the competition between the

chain transferring/initiating reaction and the vinyl polymerization. The higher the

initial concentration of MPOEM, presumably the more chain transferring/initiating

reaction occurred followed by more vinyl polymerization, ultimately resulting in more

formation of branching and more chain transfer reaction occurring in the reaction

system. Thus the branched P(AN-*co*-VAc)s with lower molecular weight and higher

branching degree were obtained (see BPAN-1, BPAN-2 and BPAN-3 in Table 1) as

the content of MPOEM increased. In addition, the chain transferring/initiating

reaction was stimulated much more at elevated temperature, resulting in the formation

of the lower molecular weight branched P(AN-*co*-VAc) (see BPAN-4, BPAN-5 and

BPAN-6 in Table 1). Fig. 6 further illustrates that the relatively low average molecular

weight was indeed caused by many low molecular weight molecules formed during

the polymerization.

Fig. 6 The differential molecular weight distribution for the P(AN-*co*-VAc) in various MPOEM
concentrations and at different temperatures

Rheological properties of branched P(AN-*co*-VAc)s

Fig. 7 illustrates the variation of the viscosity with shear rate for the branched

P(AN-*co*-VAc)s solutions and their linear analogues at the same solid content (16%

by weight). The viscosity of branched P(AN-*co*-VAc) solution was lower than that of

linear P(AN-*co*-VAc) with similar average molecular weight in any range of shear rate

from $0.01s^{-1}$ to $1000s^{-1}$ as shown in Fig. 7. Moreover, the zero-shear viscosity of

branched P(AN-*co*-VAc) ($M_w = 100800$ g mol^{-1}) solution was much lower than that of

linear counterpart ($M_w = 100600$ g mol^{-1}), namely, the former was just 17% of the

latter (see curves A and D in Fig. 7). In addition, the higher the branching degree of

the P(AN-*co*-VAc), the lower was the viscosity exhibited. When the average g' for the

two P(AN-*co*-VAc)s with similar molecular weight was slightly changed from 0.84 to

0.71 (i.e., the change was 16%), the zero shear viscosity of these two branched

P(AN-*co*-VAc)s solutions drastically changed from 22 Pa s to 7.6 Pa s (i. e., the

decrease in viscosity was 65%) (see curves B and C in Fig. 7). While the average

molecular weight for another two branched P(AN-*co*-VAc)s solutions with the similar

g' was changed from 120100 g mol^{-1} to 100800 g mol^{-1} (i.e., the decrease in molecular

weight was also 16%), but the zero shear viscosity of these two P(AN-*co*-VAc)s

solutions only changed from 7.6 Pa s to 3.5 Pa s (i.e., the rate of decrease was just

54%) (see curves C and D in Fig. 7). On the other hand, the zero shear viscosity of

linear P(AN-*co*-VAc) solution ($M_w = 100600$ g mol^{-1}) was higher than that of the

branched copolymer ($M_w=120300$ g mol^{-1}, $g'=0.84$) with higher average molecular

weight, due to the branched structure in the latter. It is well known that the magnitude

of the shear viscosity is related with molecular weight and degree of branching.[36, 37]

Generally, both the lower M_w and higher degree of branching of P(AN-*co*-VAc)s

contributed towards a decrease of the viscosity of polymer. In fact, as shown in Fig. 7,

it was believed that the lower solution viscosity of branched P(AN-*co*-VAc)s was caused by the compact conformation and their lower entanglements. Apparently, the branching structure played a more important role than the lower M_w in decreasing the viscosity of the polymers.

Fig. 7 Variation of the viscosity with shear rate for the 16 % by weight of linear and branched P(AN-*co*-VAc)s in the 58 % NaSCN solution at 25 ºC.

Thermal properties of branched P(AN-co-VAc)s

Fig. 8 shows differential scanning calorimetry (DSC) curves for linear and branched P(AN-*co*-VAc) with similar average molecular weight at a heating rate of 10 ºC min^{-1}. Compared to the linear analogue, it was not surprising that both the onset of endothermic temperature and maximum exothermic temperature for the branched P(AN-*co*-VAc) were lower because of the branched structure. Accordingly, glass transition temperature (T_g) of the branched P(AN-*co*-VAc) derived from the DSC curves was about 13 °C lower than that of the linear counterpart (Fig 8). Generally, T_g of the polymer is associated with the flexibility of the polymer chain and the concentration of the end groups. For the branched polymer, the branching point had an effect on the flexibility of the polymer chain, which can hinder the rotations of backbone and decrease its motility. The above factor resulted in increasing the T_g of the branched polymer. On the other hand, the presence of higher quantities of end groups in branched polymer brought about more free volume of the chains along with

increasing mobility of the chains, which led to a decrease in the T_g. In addition, there

was the effect of the bond between carbon and sulfur (C-S) owing to the MPOEM in

the branched P(AN-*co*-VAc). The rotation of C-S was easier than that of the bond

between two carbons (C-C), which also resulted in lowering of the T_g. Comprehensive

consideration of the above factors led us to believe that they had an advantageous

effect on the mobility of the branched polymer chains, which ultimately caused lower

T_g of branched P(AN-*co*-VAc) than that of the linear counterpart.

Fig. 8 DSC curves for linear and branched P(AN-*co*-VAc) with similar average molecular weight determined at a heating rate of 10 ºC min^{-1}.

Fig. 9 TGA and DTG curves for linear and branched P(AN-*co*-VAc) with similar average molecular weight at a heating rate of 10 ºC min^{-1}.

Fig. 9 shows thermogravimetric analysis (TGA) for linear and branched

P(AN-*co*-VAc) with similar average molecular weight at a heating rate of 10 ºC min^{-1}

in nitrogen atmosphere. The decomposition mechanism for the linear and branched

P(AN-*co*-VAc) was found to be similar (Fig. 9). In both cases, there were losses of

mass in two stages during the heating process. For the first stage, decomposition

occurred in the temperature range from 250 ºC to 360 ºC while decomposition

occurred from 360 ºC to 564 ºC for the second stage. Indeed, the temperature of the

maximum weight loss rate during first stage for both the branched and linear

P(AN-*co*-VAc) polymers was similar (Fig. 9B) even though the initial decomposition

temperature for the branched P(AN-*co*-VAc) was slightly lower than that of the linear

analogue. However, the temperature of the maximum weight loss rate for the

branched P(AN-*co*-VAc) in the second stage was 12 ℃ higher than that of the linear

analogue (Fig. 9B). In addition, the weight loss in first stage for the branched

P(AN-*co*-VAc) was about 20 % but lower than that of the linear P(AN-*co*-VAc) with

approximately 30 % weight loss. While in the second stage the weight losses for

branched and linear P(AN-*co*-VAc) were about 25 % and 21 %, respectively, as

shown in TGA curves (Fig. 9A). In order to get quantitative information to understand

the development of thermolysis, we determined the weight loss of every stage by

splitting the DTG curves using Gaussion function (Fig. 9 B).[31, 38]

Insert Table 2

The ratios of weight losses in two stages were 60:40 and 45:55 for the branched

P(AN-*co*-VAc) and linear analogue, respectively (Table 2). These results coincided

with the above results derived from TGA curves (Fig. 9A). The lower weight loss of

the first stage for the branched P(AN-*co*-VAc) as indicated by lower peak area (Table

2) directly resulted in the lower total weight loss and the higher char residue in the

whole degradation process. The char residue was 55 % for the branched

P(AN-*co*-VAc), which was higher than that of the linear counterpart with 49 % (Fig.

9A). In fact, the char residue of 55 % for the branched P(AN-*co*-VAc) is also higher

than that reported for P(AN-*co*-VAc) in the literature.[10, 39] There were several types of

competitive thermal reactions for the nitrile and carbonyl groups on the side chain of

polymer during the pyrolysis process, such as cyclization reactions, chain scissions,

dehydrogenation reactions and/or oxidation reaction as described in the literature.[39, 40]

Generally, cyclization reactions occurred in the temperature range of 282 ºC to 350 ºC,

and the cyclized structure formed previously through the conversion of an open chain

structure into a closed chain aromatic structure, which led to the formation of a ladder

polymer with many accompanying side reactions but little or no byproducts formed.[39]

While the dehydrogenation reaction along with a few chain scissions would give out

some byproducts. There were cyclization and dehydrogenation reactions during the

first stage, some weight loss probably caused the dehydrogenation reaction. We

inferred from the above that the lower the weight loss, the greater were the cyclization

reactions. In the second stage of subsequent pyrolysis, some weight loss was caused

likely by the release of some byproducts from the stabilization, dehydrogenation and

carbonization reactions.[39, 40] Accordingly, the total weight loss of branched

P(AN-*co*-VAc) was less than that of the linear analogue. We, therefore, postulate that

the cyclization reaction in the first stage of the pyrolysis process for branched

P(AN-*co*-VAc) proceeded more preferentially than that of the linear P(AN-*co*-VAc).

In the second stage, the temperature of the maximum weight loss rate for the branched

P(AN-*co*-VAc) was 12 ºC higher than that of the linear analogue, which further

demonstrated that more cyclization reactions were involved in the first stage (Fig. 9B).

The more cyclization reactions in the degradation of polymer would bring about the

higher thermal resistance. In conclusion, the TGA and DTG results presented here

indicated that the thermostability of the branched P(AN-*co*-VAc) was higher than that

of the linear analogue.

Conclusions

In summary, the branched P(AN-*co*-VAc)s were successfully prepared via radical polymerization using a new CTM of MPOEM in NaSCN aqueous solution. A cost-effective MPOEM with good storage stability was synthesized and used as a CTM. The relatively high molecular weight and high branching degree of branched P(AN-*co*-VAc)s were formed in the presence of MPOEM even at low monomer conversion. The copolymers employing relatively high initial MPOEM concentration possessed high degree of branching. Higher MPOEM concentration and higher reaction temperature resulted in the lower molecular weight of branched P(AN-*co*-VAc)s.

Due to the compact conformation and little chain entanglement in the solution, the zero-shear viscosity of branched P(AN-*co*-VAc)s was just 17% of linear counterpart with similar average molecular weight at 25 ºC. It is significant to note that the decrease of zero-shear viscosity was associated with the increased degree of branching prior to a decrease in the molecular weight.

The glass transition temperature of branched P(AN-*co*-VAc)s was 13 ºC lower than its linear analogues with similar molecular weight due to the increased mobility of the chains caused by the larger quantities of end groups and the weaker bonds of carbon and sulfur introduced by MPOEM. In the thermal degradation process, the char residue of branched P(AN-*co*-VAc) was higher than that of its linear analogue, because the cyclization reaction proceeded more facilely in the former than that in the latter. Thus the extent of cyclization reactions indicated that the thermal stability of

the branched P(AN-*co*-VAc) was higher than that of the linear analogue.

The new approach developed here for synthesizing the branched P(AN-*co*-VAc)s using the NaSCN aqueous solution via radical polymerization along with CTM is facile and cost-effective. Therefore, the applications of branched P(AN-*co*-VAc)s could be expanded in the future.

Experimental Section

Materials

Acrylonitrile (industrial grade, China Petroleum & Chemical Co. Anqing Branch), vinyl acetate (analytical grade, Shanghai Chemical Co.) were distilled under reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN, analytical grade, Shanghai Chemical Co.) was recrystallized in ethanol. 2-Hydroxyethyl methacrylate (HEMA) of analytical grade from Shanghai Chemical Co. and 3-Mercapto-propionate (MPA) of analytical grade from Wujiang Rongtai dye Co. Jiangsu, China were used as received. Other reagents and solvents of analytical grade were procured from Shanghai Chemical Co. and were used as received.

Preparation of MPOEM

HEMA (26.00 g, 200 mmol), MPA (15.44 g, 240 mmol), toluene-4-sulfonic acid (3 % of HEMA by weight) and hydroquinone (0.3 % of HEMA by weight) with benzene (25 mL) and diethyl ether (25 mL) were added to a three-necked round-bottomed flask (250 mL). A Dean-Stark trap was introduced between the flask and the reflux condenser. The mixture was stirred and refluxed for 10 hours and then

cooled to room temperature followed by the removal of the solvent (benzene and
diethyl ether) under reduced pressure. Afterwards the contents were washed with
distilled water three times to remove the residual reactants and then they were
immersed in ethyl acetate. The obtained oil phase was dried with Na_2SO_4 for 24 hours
and the product was isolated by removing the ethyl acetate under reduced pressure.
The crude product was found to be of about 50% purity as determined by high
performance liquid chromatography, HPLC. The above product was further purified
via column chromatography (silica gel, ethyl acetate/petroleum ether = 1/3 in volume)
to yield a colorless liquid of about 95% purity (HPLC). ^{1}H NMR: δ_H ppm(400 MHz;
$CDCl_3$; Me_4Si) 6.2ppm(1H, d, CH=CCH$_3$), 5.6ppm(1H, d, CH=CCH$_3$), 4.4ppm(4H, t,
OCH_2CH_2O), 2.8ppm(2H, m, CH$_2$CH_2SH), 2.6ppm(2H, m, OOCCH_2CH$_2$), 2.0ppm
(3H, s, CH$_2$=CCH_3) and 1.6ppm(1H, t, CH$_2$SH). The structure of MPOEM is as
follows:
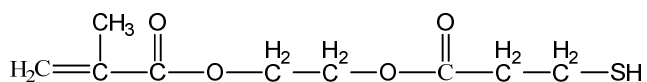
Preparation of branched poly(AN-*co*-VAc) in 45%NaSCN solution

In a typical polymerization, AN (5 mL, 76.0 mmol), VAc (0. 8174 g, 9.50 mmol),
MPOEM (0.3767 g, 0.86 mmol) and AIBN (0.1419 g 0.86 mmol) were added to a 100
mL round-bottomed flask equipped with a stirrer. Then 45% NaSCN solution
(12.6035 g, $m_{45\%NaSCN}/m_{monomer}$=7/1) was added as the solvent. The flask was
cycled between vacuum and argon (6 times) and then it was immersed in a
preheated oil bath, which was maintained at 60 °C for 24 h. In this reaction the

conversion of the reactants was measured by gas chromatography (GC) using the following procedure: the reactant samples (1.0 g) were extracted with cyclohexane (approximately 3 g) followed by the addition of anisole (10 % of the reactant sample by weight) in the solvent phase as external standard. The mixture was dried with Na_2SO_4 for GC analysis. The rest of the sample (water phase) was diluted into 45% NaSCN solution and precipitated in distilled water. Then the product was obtained by suction filtration and vacuum drying. ^{1}H NMR: δ_H ppm (400 MHz; DMSO-D6; Me4Si) 5.2ppm(1H, m, CH_2CHOOCCH$_3$), 4.3ppm(4H, t, OCH_2CH_2O), 3.1ppm(1H, m, CH$_2$CHCN) and 2.0ppm(3H, m, CH_3).

Preparation of linear poly(AN-*co*-VAc) in 45%NaSCN solution

In a typical polymerization, AN (5 mL, 76.0 mmol), VAc (0. 8145 g, 9.50 mmol) and AIBN (0.1407 g 0.86 mmol) were added to a 100 mL round-bottomed flask equipped with a stirrer followed by the addition of 45% NaSCN solution (12.6101 g, $m_{45\%NaSCN}/m_{monomer}$=7/1) as the solvent. The flask was cycled between vacuum and argon (6 times), and the flask was immersed in a preheated oil bath, which was maintained at 60 °C for 24 h. In this reaction the conversion of the reactants was measured by GC as has been described above for branched poly(**AN-*co*-VAc**). The rest of the sample (water phase) was diluted into 45% NaSCN solution and precipitated in distilled water. Then the product was obtained by suction filtration and vacuum drying. ^{1}H NMR: δ_H ppm (400 MHz; DMSO-D6; Me4Si) 5.2ppm(1H, m, CH$_2$CHOOCCH$_3$), 3.1ppm(1H, m, CH$_2$CHCN) and 2.0ppm(3H, m, CH_3).

Preparation of poly(AN-*co*-VAc) solution

A certain quantity of P(AN-*co*-VAc) was dissolved by adding to 58 % NaSCN aqueous solution using mass ratio of $m_{\text{P(AN-}co\text{-VAc)}}/m_{\text{solution}}$=16/100 at 60 °C for 10 h. The above solution was stirred to disperse the P(AN-*co*-VAc) uniformly in the solution and then the solution was placed in an oven at 40 °C for 6 hours to remove air bubbles.

Proton nuclear magnetic resonance spectroscopy

^{1}H-NMR (500 MHz) spectra were recorded on a Bruker ARX-500 type NMR spectrometer at 25 °C with DMSO-D6 as the solvent and tetramethylsilane as the internal standard.

Measurement of monomer conversion

The conversion of the monomers was determined using a HP-689 gas chromatograph equipped with a HP-5 column (30 m×0.54 mm×0.5μm). Anisole was used as the internal as well as external standard. The carrier gas was hydrogen at 1 mL min^{-1}, and the column temperature was increased from a starting value of 70 °C to a maximum of 280 °C at the rate of 15 °C min^{-1}.

Triple detection size exclusion chromatography (TD-SEC)

The molecular weight, polydispersity (PDI) and intrinsic viscosity were obtained by TD-SEC detection at 25 °C. The instrumentation consisted of the following: a Waters 1515 isotratic HPLC pump with 5 μm Waters styragel columns (Waters Styragel HR 3 DMF, HR 4 DMF, HR 5 DMF); a Waters 717 PLUS autosampler; a Waters 2414 differential refractive index (DRI) detector with a wavelength of 880 nm; a multi angle laser light scattering (MALLS)

detector (Wyatt mini Dawn TRISTRA light scattering, the three detection angles are 45°, 90° and 135° and the wavelength and power are 690 nm and 220 w, respectively); a Wyatt Visco Star viscometer detector; and a Waters Empower data manager. Polymethylmethacrylate standards with the narrow molecular weight distributions and molecular weights in the range of analyzed molecular weights were used to calibrate the columns and obtain calibration curve. The eluent was HPLC-grade DMF delivered at 1.0 mL min^{-1}.

The dn/dc value of PAN and PVAc in DMF solution containing 0.07mol L^{-1} NaNO$_3$ at 25 °C was measured by a differential refractometer at a wavelength of 680 nm.

Rheological properties of P(AN-co-VAc) solution

The viscosity was determined using Anton Paar Physica MCR-301 Rheometer instrument equipped with a DG-26.7 measuring system. The shear rate was in the range of 0.01 to 1000 s^{-1} at 25 °C. The angular frequency was from 0.1 to 500 rad s^{-1} in the frequency sweep curve under the condition of the fixed 5% strain.

Differential scanning calorimetry (DSC) analysis

The glass transition temperature was measured using a Perkin Elmer Pyris 1 DSC. The appropriate method used was as follows: The sample (ca. 8-20 mg) was weighed in a crimped aluminum pan, and testing was performed under a flow of nitrogen (20 mL min^{-1}); heated from room temperature to 250 °C at a heating rate of 10 °C min^{-1} and equilibrated at 250 °C for 5 min followed by rapid cooling to room temperature to remove the heat history; heated from room temperature to 40 °C at a heating rate of 10 °C min^{-1}, equilibrated at 40 °C for 1 min, then heated from 40 °C to 250 °C at the

same rate to determine the T_g of sample.

Thermal gravimetric analysis (TGA)

The **TGA** was performed using a TA SDTQ-600. The appropriate method used was as follows: the sample (approximately 3.0 mg) was weighed in a crucible, and heating was performed under a flow of nitrogen (40 mL min^{-1}) at a heating rate of 10 °C min^{-1}.

Supporting information Relationships of the weight average molecular weight and PDI with conversion during the copolymerization of AN and VAc in NaSCN aqueous solution at 60 °C (Fig. S1). The reactivity ratio of comonomers (Table S1).

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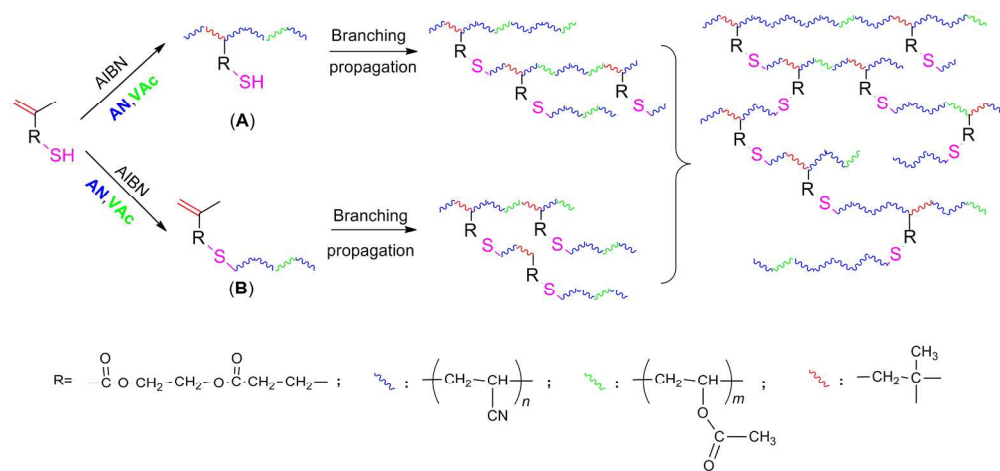
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Tables

Table 1 TD-SEC analysis results of linear and branched P(AN-*co*-VAc)

Sample	[AN]:[VAc]:[AIBN] :[MPOEM] :[MPA]	T (°C)	Conversion / %		$M_{n.GPC}$ / g mol^{-1}	$M_{w.MALLS}$ / g mol^{-1}	PDI	g'
			AN	VAc				
LPAN[a]	88:11:1:0:0.3	60	100	95.6	93700	100600	2.3	-
BPAN-1[b]	88:11:1:0.6:0	60	99.1	93.7	91500	120300	2.5	0.83
BPAN-2	88:11:1:1:0	60	98.3	95.0	71600	100800	2.9	0.70
BPAN-3	88:11:1:2:0	60	96.8	91.9	56100	96800	2.9	0.66
BPAN-4	88:11:1:1:0	50	98.4	80.9	89452	167300	2.5	0.69
BPAN-5	88:11:1:1:0	60	97.8	90.0	71600	120100	2.1	0.71
BPAN-6	88:11:1:1:0	70	98.5	93.4	51609	96300	3.0	0.65

a: LPAN denotes linear P(AN-*co*-VAc); b: BPAN denotes branched P(AN-*co*-VAc).

Table 2 Peak areas and weight losses calculated by splitting the DTG curves using Gaussion function for linear and branched P(AN-*co*-VAc) (Fig. 9 B)

Sample	S_f	S_s	S_f: S_s	WL_f:WL_s
LPAN	27.52	18.20	3:2	60:40
BPAN	18.64	22.43	9:11	45:55

S_f denotes the peak area of the first stage of thermolysis; S_s denotes the peak area of the second stage of thermolysis; WL_f denotes weight loss of the first stage of thermolysis; WL_s denotes weight loss of the second stage of thermolysis.

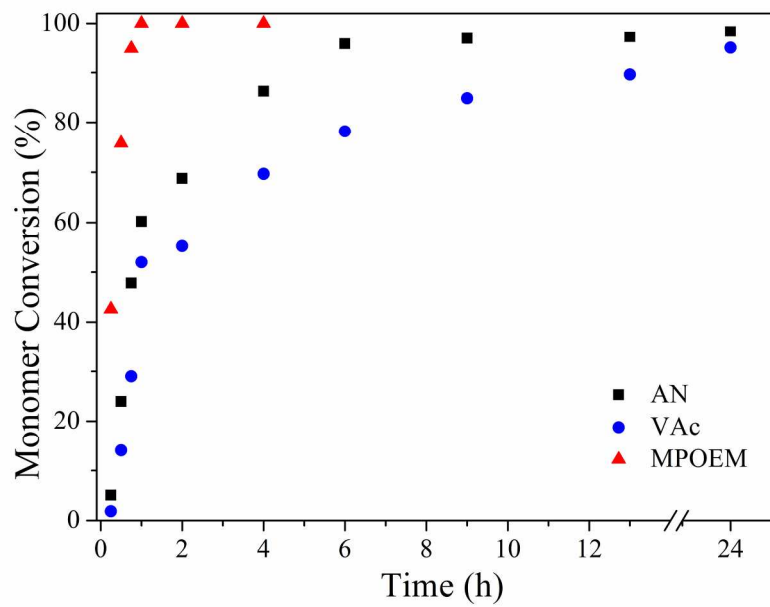Fig.1 Kinetics of the copolymerization of AN with VAc using MPOEM in NaSCN aqueous solution at 60 °C in the following ratio: [AN]/[VAc]/[MPOEM]/[AIBN]=88:11:1:1.
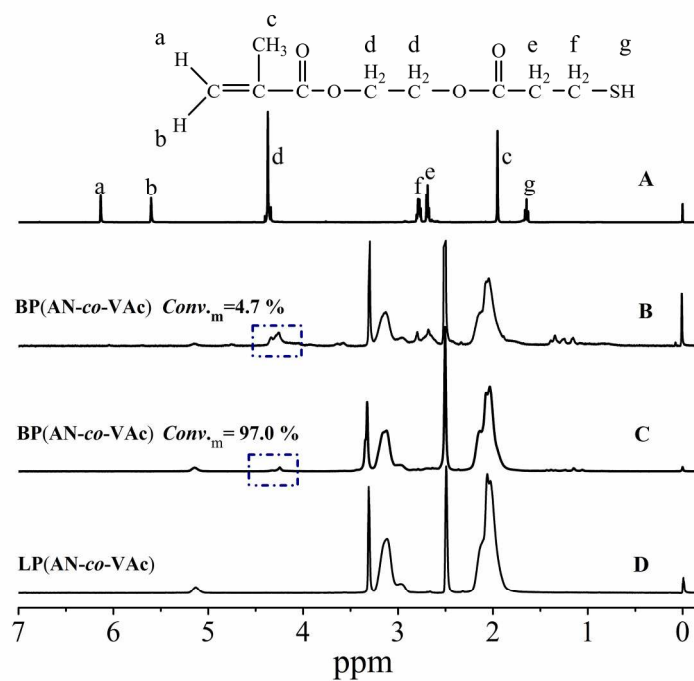209x148mm (300 x 300 DPI)

Fig.2 1H-NMR spectra of MPOEM and P(AN-co-VAc)s.
BP(AN-co-VAc) is branched P(AN-co-VAc); LP(AN-co-VAc) is linear P(AN-co-VAc); Conv.m is the conversion
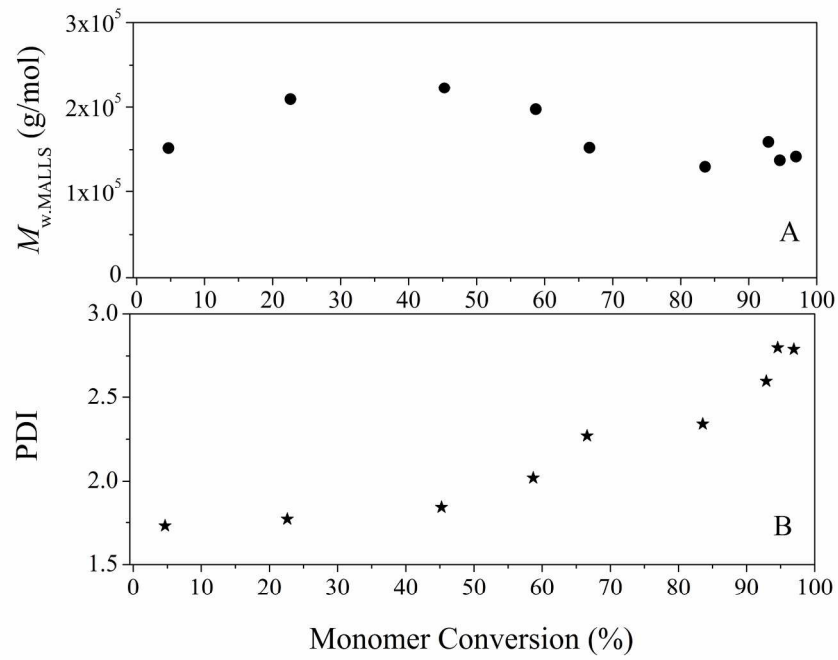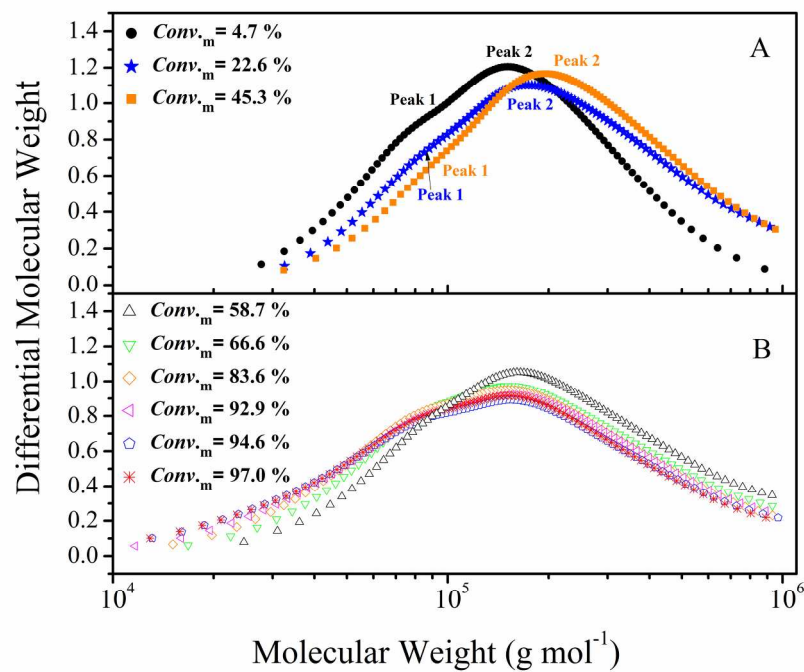of monomer
200x139mm (300 x 300 DPI)

Fig.3 Relationships of the weight average molecular weight and PDI with the monomer conversion for the copolymerization of AN and VAc using MPOEM in NaSCN aqueous solution at 60 °C using the following ratio:[AN]/[VAc]/[MPOEM]/[AIBN]=88:11:1:1.
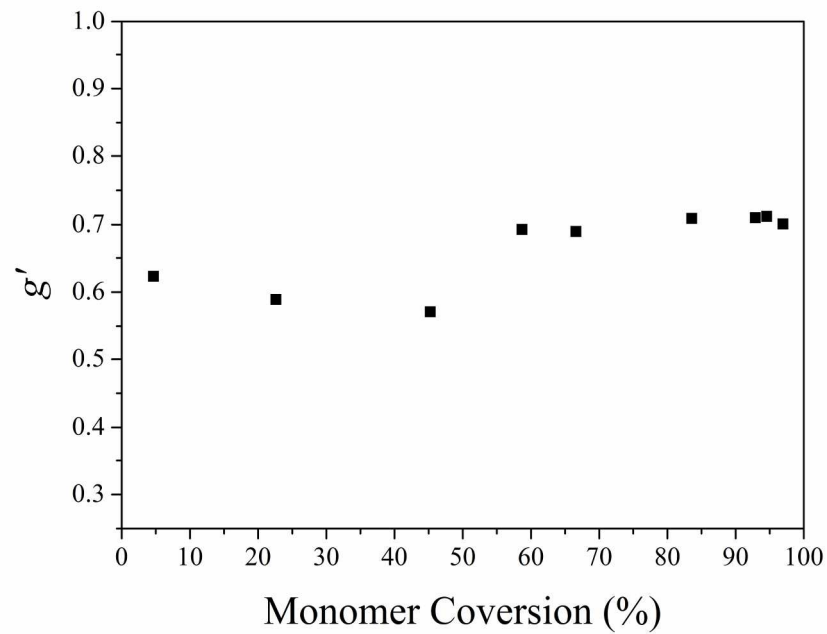209x148mm (300 x 300 DPI)

Fig.4 The differential molecular weight distribution changing with molecular weight at different conversions for the copolymerization of AN and VAc using MPOEM in NaSCN aqueous solution at 60 °C using the following ratio: [AN]/[VAc]/[MPOEM]/[AIBN]=88:11:1:1.
209x148mm (300 x 300 DPI)

Fig.5 Relationships of the average Zimm branching factor with conversion during the copolymerization of AN and VAc using MPOEM in NaSCN aqueous solution at 60 °C using the following ratio: [AN]/[VAc]/[MPOEM]/[AIBN]=88:11:1:1.
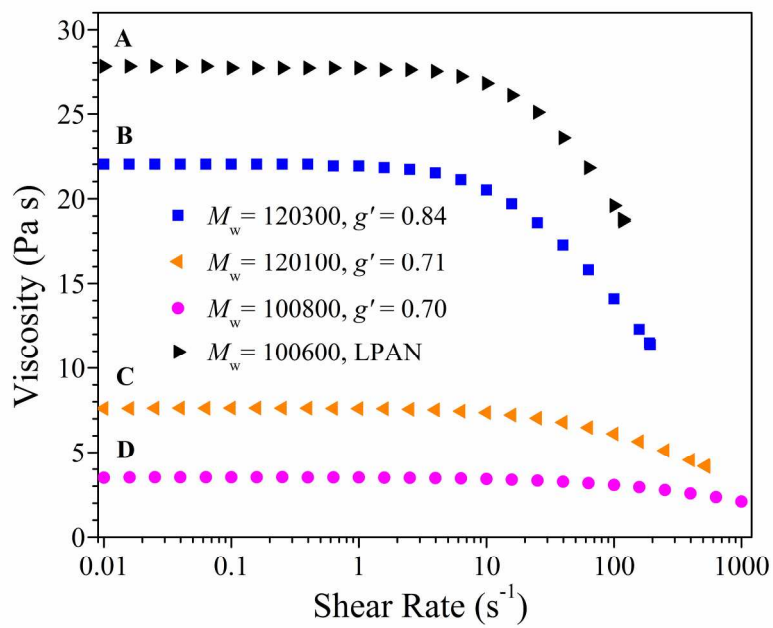209x148mm (300 x 300 DPI)

Fig.7 Variation of the viscosity with shear rate for the 16 % by weight of linear and branched P(AN-co-VAc)s in the 58 % NaSCN solution at 25 ºC.
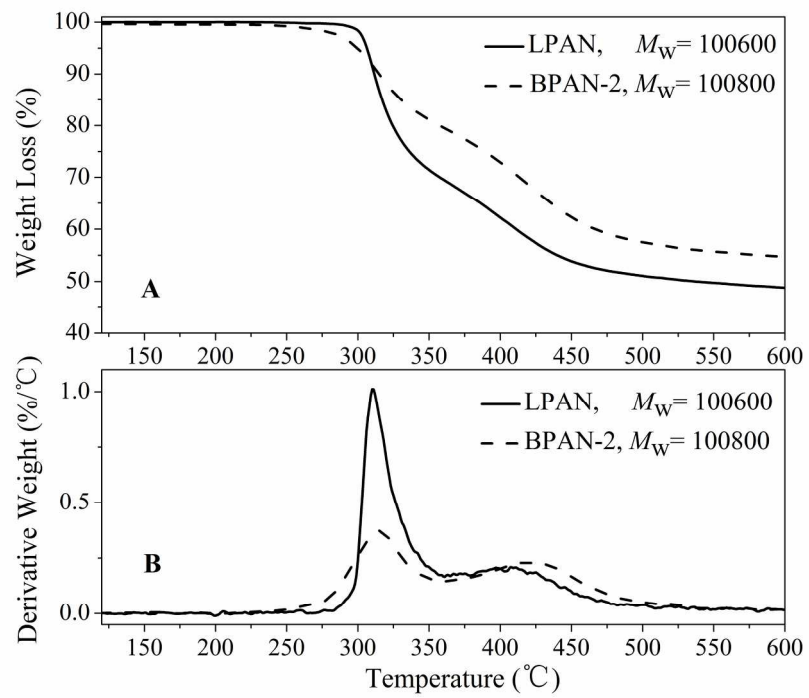209x148mm (300 x 300 DPI)

Fig.9 TGA and DTG curves for linear and branched P(AN-co-VAc) with similar average molecular weight at a heating rate of 10 ºC min-1.
209x148mm (300 x 300 DPI)

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Facile Synthesis of Highly Branched Poly(acrylonitrile-*co*-vinyl acetate) with Low Viscosity and High Thermal Stability via Radical Aqueous Solution Polymerization

Wenyan Huang[a], Chang Liu[a], Hongjun Yang[a], Xiaoqiang Xue[a], Bibiao Jiang[a*], Dongliang Zhang[a],

Lizhi Kong[a], Yan Zhang[a], and Sridhar Komarneni[;b*]
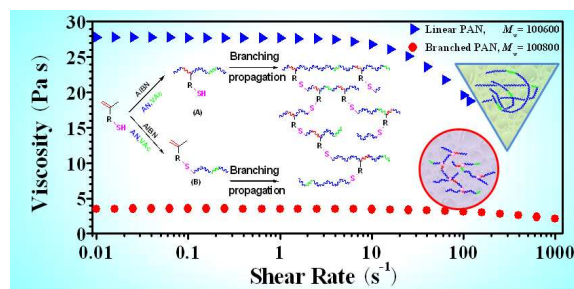
Branched P(AN-*co*-VAc)s were obtained via radical polymerization using a new chain transfer monomer of 2-(3-mercaptopropionyloxy) ethyl methacrylate.