Preparation of Branched Polyacrylonitrile through Self-Condensing Vinyl Copolymerization

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ABSTRACT: Branched polyacrylonitrile (PAN) was prepared through a self-condensing vinyl copolymerization of acrylonitrile and 2-(2-bromopropionyloxy)ethyl acrylate (BPEA). The branched architecture of the product was confirmed by NMR spectra and the average degree of branching ($\overline{DB}$) was estimated. Through a comparison of the intrinsic viscosity of the product with that of its linear analogue, the contraction factor g' was calculated. It was found that the viscosity of the branched PAN was obviously lower that that of linear PAN. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 494–500, 2008

Key words: self-condensing vinyl copolymerization; atom transfer radical polymerization; branched polymer; polyacrylonitrile

INTRODUCTION

Polyacrylonitrile (PAN) is a very important polymer, mainly due to its excellent properties of rigidity and resistance against oil. It can be spun into Acrylon, which is one of the most wildely used synthetic fibers. PAN is also the precursor of carbon fiber. Despite these virtues, PAN cannot be processed under melted state because of its thermal decomposition. It can be spun only after dissolved in polar solvents such as DMF and DMSO. When PAN is spun, the concentration of PAN is usually restricted low to avoid too high viscosity. As has been widely known, branched polymer often has lower solution viscosity when compared with its linear analogue.[1] Therefore, PAN that may be spun at high concentration and even processed at melt is very important in terms of the requirement of environmental friendly technique. So it is meaningful to prepare branched PAN to decrease the solution viscosity. Though polymerization of acrylonitrile (AN) to prepare linear PANs has been well-established,[2–5] very few papers related to the preparation of the branched PANs have been found. Barboiu et al.[6] have synthesized three-arm star PAN by atom transfer radical polymerization (ATRP) of AN using 1,1,1-tris(4-chlorosulfonylphenyl)ethane as an initiator in the presence of Cu$_2$O/2,2′-bipyridine catalyst. Pitto et al.[7] have prepared well-defined star PANs with 3, 4, and 6 arms and star-shaped polymers with a hyperbranched poly (ester amide) as core. These two examples applied multifunctional chemicals to initiate controlled polymerization of AN. Though these star PANs were well-defined, their preparations were tedious.

The branched polymers include star polymers, grafted polymers, dendrimers, and hyperbranched polymers. Star polymers are usually synthesized through multifunctional-initiator or living-chain-coupling approach. And grafted polymers are usually synthesized through "graft from," "graft onto," or "graft through" approach. Dendrimers can be prepared through convergent or divergent approach. These methods for the synthesis of branched polymers usually involve several steps and, therefore, are inconvenient. Besides these methods, self-condensing vinyl polymerization (SCVP)[8] used to prepare hyperbranched polymer seems to be one of the most promising methods to synthesize branched polymer because it is very convenient and does not generate gel even at high monomer conversion. In such a polymerization process, the inimer $AB*$ is essential and it contains a polymerizable vinyl group A and an initiator $B*$ which can initiate the polymerization of vinyl group A. Many polymerization techniques such as nitroxide mediated radical polymerization,[9,10] ATRP,[11,12] iniferter,[13,14] group transfer polymerization,[15] cationic polymerization,[16] and anionic polymerization,[17] have been realized through SCVP to generate the polymers with hyperbranched architecture. Recently, self-condensing vinyl copolymerization (SCVCP) has attracted lots of attention because it enlarges the range of applied monomer
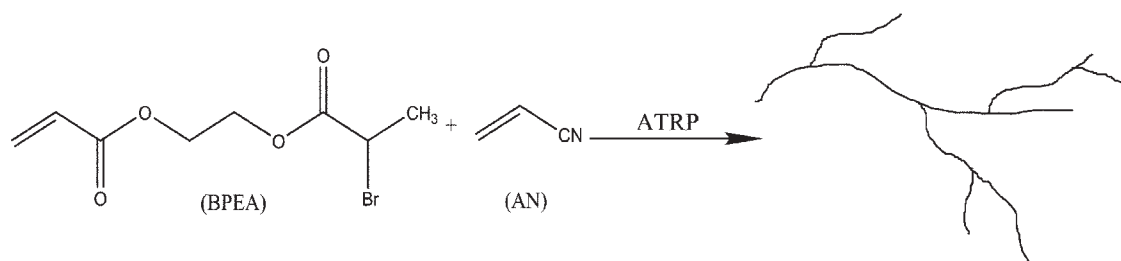
Scheme 1 Synthesis of branched polyacrylonitrile with randomly dispersed branch points.

like styrene and (meth)acrylates just through the copolymerization of these monomers and the inimers.[18–21] In such cases, the branch points are "diluted" by the copolymerization and some linear segments are incorporated into the branched polymers. Therefore, the degree of branching is lower than that of the homopolymerization of the inimers. Depending upon the feed ratio of the comonomers, the branch density can be changed in a large region. Though the branched architecture generated by this approach is not well-defined as good as that by stepwise approach to synthesis other types of the branched polymer, the preparation is easy to carry into execution and, therefore, is more facile in terms of practical production.

What is concerned in this article is the branched PAN with low degree of branching and the branch points are dispersed randomly in the polymer architectures as shown in Scheme 1. We present the preparation of branched PAN through SCVCP of AN and an inimer 2-(2-bromopropionyloxy) ethyl acrylate (BPEA) by ATRP. The results indicated that the branched PAN thus prepared has lower viscosity comparing to the linear PAN of the same molecular weight, which may benefit the spinning of PAN solution.

EXPERIMENTAL

Materials

AN was passed through a short basic alumina column to remove inhibitor before use. CuBr was prepared from $CuBr_2$ and Na_2SO_3 and purified by washing with acetic acid, ethanol, and diethyl ether. 2,2′-Bipyridine (Bpy, Beijing Shiying Chemical Factory), 2-hydroxyethyl acrylate (TCI), 2-bromopropionyl bromide (Aldrich), and ethylene carbonate (EC, Acros) were used as received. BPEA was prepared by reaction of 2-bromopropionyl bromide and 2-hydroxyethyl acrylate according to literature.[12]

Typical polymerization procedure

A typical process of the SCVCP of AN and BPEA was described as follows: CuBr (15 mg, 0.11 mmol) and Bpy (49 mg, 0.32 mmol) were put into a Schlenk

flask sealed with a rubber plug. Three cycles of vacuum-nitrogen were performed to remove the oxygen in the flask. AN (5.52 g, 0.105 mol) and BPEA (0.131 g, 0.53 mmol) were mixed with EC (13.2 g) and the solution was bubbled by nitrogen for 30 min, and then transported to the Schlenk flask via a syringe. Then the flask was immersed in a 40°C oil bath with stirring. After 6 h, the flask was withdrawn from the oil bath and the seal was removed to expose the solution to the air. The polymer solution was poured into methanol. After stirred over night, the precipitate was filtered and dried under vacuum, and then redissolved in DMF and reprecipitated into methanol. The product was filtered and dried at 50°C under vacuum. Finally 2.68 g of off-white powder was obtained.

Characterization

The ^1H NMR measurements were performed with a Bruker 300MHz spectrometer with DMSO-d_6 as solvent and TMS as an internal standard. The d_n/d_c value of PAN solution in DMF was measured by a differential refractometer (Dawn DSP, Wyatt Technology Corp.). Static light scattering spectrometer (SLS, ALV5000) with He-Ne laser ($\lambda_0 = 632.8$ nm) was used to measure the absolute molecular weight of PAN. Gel permeation chromatography (GPC) measurement was performed by a set of a Waters 1515 HPLC pump, a Waters 717 autosampler, three Waters Styragel columns (HT3, HT4, and HT5), and a Waters 2414 refractive index detector using DMF with $0.05M$ LiBr as eluent at a flow rate of 1.0 mL/min at 50°C. Linear PAN broad standards were used for the calibration as mentioned in the literature.[22] The weight-average molecular weights of the standards with broad polydispersity for the calibration were measured by SLS. This method neglects column peak spreading. Intrinsic viscosity of the products was measured with an Ubbelohde type viscometer in DMF or DMSO at 25°C. The difference of the choice of solvent in the intrinsic viscosity measurement was for the convenience of citation and comparison with the Mark-Houwink exponent in different literatures. Measurement of polymer shear
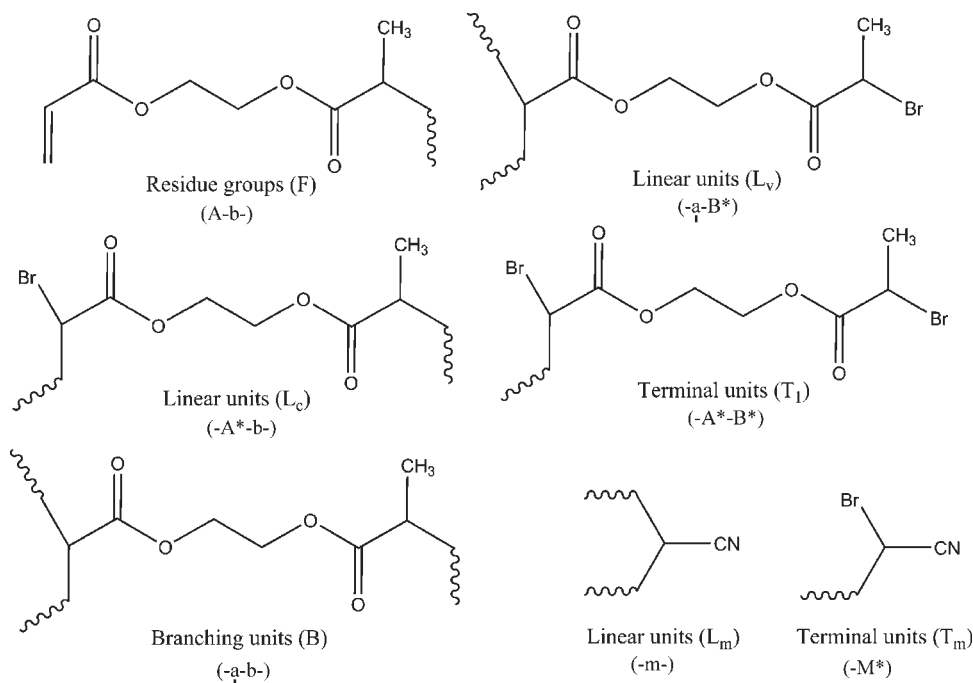
Scheme 2 The structure units in the copolymer of AN and BPEA after SCVCP.

viscosity was performed on an ARES rheometer (TA) equipped with a concentric cylinder.

RESULTS AND DISCUSSION

As described by Müller,[23] the SCVCP of inimer BPEA and monovinyl monomer AN would produce hyperbranched with kinds of structural units such as residue groups (F), linear units (L_v, L_c, L_m), terminal units (T_I, T_m), and branching units (B) as illustrated in Scheme 2. In the scheme, group A stood for unreacted vinyl group, A* and B* as well as M*

for active centers, a, b, and m for reacted ones. Table I showed some samples of the copolymerization of AN and BPEA. Samples from 1 to 6 were synthesized under the same polymerization conditions except polymerization time. Their GPC traces were shown in Figure 1. According to Müller's theory analysis, the conversion of the inimer is governed by the feed ratio of monomer to inimer, and for high ratio, the conversion of inimer reaches 100% promptly after the start of the reaction.[23] In our experiment, the ratio of monomer to inimer was kept in the range of 30–200, so the conversion of

TABLE I
The Copolymerization of AN and BPEA Through SCVCP

Sample	Feed molar ratio[a] AN/BPEA/ CuBr/Bpy	Reaction time (min)	Conversion of AN[b] (%)	M_n (apparent, GPC)	M_w (apparent, GPC)	M_w/M_n (GPC)	M_n (NMR)	$\overline{DB}$ (NMR)	[η] (mL/g)
1	50 : 1 : 0.2 : 0.6	25	18.0	1,800	2,500	1.4	3,320	0.023	11
2	50 : 1 : 0.2 : 0.6	60	34.9	2,600	4,200	1.6	4,760	0.024	14
3	50 : 1 : 0.2 : 0.6	90	44.1	3,200	5,800	1.8	7,150	0.024	19
4	50 : 1 : 0.2 : 0.6	150	60.1	4,300	9,500	2.2	11,560	0.025	26
5	50 : 1 : 0.2 : 0.6	210	75.8	5,900	17,100	2.9	21,780	0.027	33
6	50 : 1 : 0.2 : 0.6	390	87.8	8,100	33,200	4.1	25,770	0.024	42
7	30 : 1 : 0.2 : 0.6	140	58.6	5,100	11,200	2.2	8,100	0.038	47[c]
8	200 : 1 : 0.2 : 0.6	360	46.2	13,100	26,100	2.0	–	–	–

[a] The initial concentration of AN, $[AN]_0$, was kept to be 6.2 M.
[b] Conversions of AN were measured by gravimetric method, assuming BPEA was consumed completely in the beginning of polymerization.
[c] All other intrinsic viscosity values were measured in DMSO at 25°C except that of sample 7, which was measured in DMF at 25°C. The difference of the choice of solvent was for the convenience of citation and comparison with the Mark-Houwink exponent in different literatures.
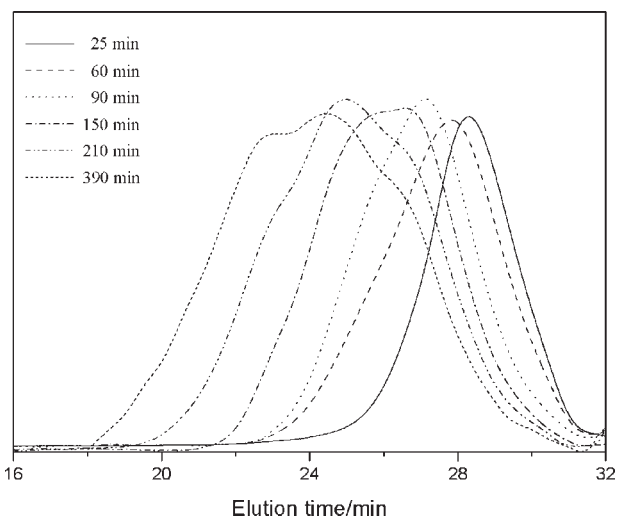
Figure 1 The GPC traces of branched PAN prepared through self-condensing vinyl copolymerization of AN and BPEA.

Figure 2 The relationship between $\ln([AN]_0/[AN])$ and polymerization time.

BPEA was considered to be 100% after the beginning of the copolymerization. Thus the conversion of AN could be calculated conveniently through gravimetric method. When the conversion of AN kept low, the GPC traces were an uniodal. However, they would turn to multimodal when the conversion of AN became high, which might be caused by radical coupling termination at high conversion. The apparent molecular weight of the samples synthesized under the same polymerization conditions increased gradually and the polydispersity of samples became large with prolonged polymerization time. It was consistent with the conclusion in literatures[23,24] that the polymer distribution of SCVP and SCVCP became broader with the increase of monomer conversion. In the SCVCP of BPEA and AN, all active centers were secondary bromides and they might have close activity due to the structural similarity. For the convenience of analysis, we assumed equal reactivity of all active centers. Figure 2 showed the relationship between $\ln([AN]_0/[AN])$ and polymerization time ($[AN]_0$ stands for the initial AN concentration and $[AN]$ stands for the AN concentration at determined time). The linear relationship of the semilogarithmic plot below 75% of AN conversion was the typical characterization of controlling/living polymerization. When the conversion of AN exceeded 75%, the plot deflected from linear relation, which could be attributed to the less controlled polymerization resulted from the radical coupling termination at high conversion.

Scheme 2 illustrated the structure units in the copolymer of AN and BPEA generated through the SCVCP respectively. In principle there was only one residue vinyl group on a macromolecular chain,[23,24] providing intrapolymer cyclization and interpolymer
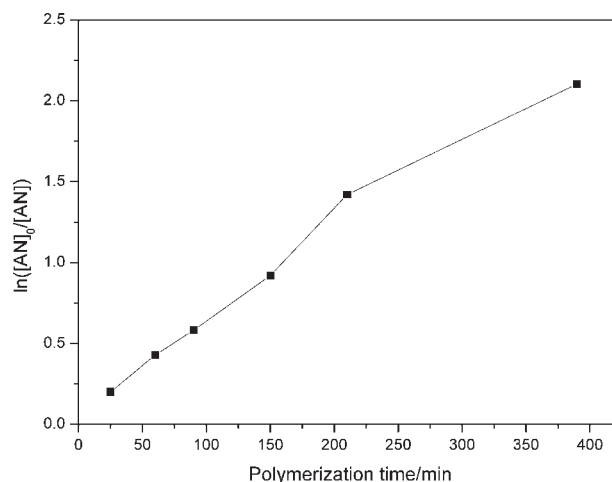
radical coupling termination were not taken into account, which made it possible to estimate the number-average molecular weight of the product through the ratio of the peak areas in ^{1}H NMR spectra. Indeed, the probability of intrapolymer cyclization could be ignored because of low feed ratio of BPEA to AN and thus low concentration of residue vinyl group on branched polymer in the solution. The interpolymer radical coupling termination was also slight, otherwise one polymer chain would carry more than one vinyl group and the gelation would take place easily.

To obtain detail information of the polymer architecture, Sample 7 was prepared by low feed ratio of AN to BPEA and the signals of two components in ^{1}H NMR spectrum were large enough as shown in Figure 3. All signals were assigned in Table II. Peak H was the proton signals of —CH$_3$ on the residue group (F) and branching points (B) as well as linear units (L$_c$), whose area was four times of that of peak A, the signal of residue vinyl double bond on
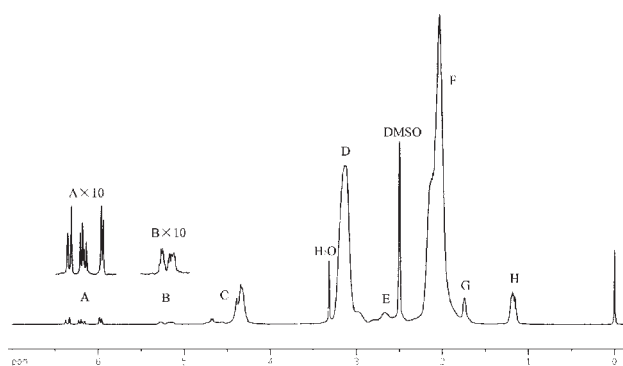

Figure 3 The typical ^{1}H NMR spectrum of branched PAN (Sample 7) prepared through SCVCP of AN and BPEA.

TABLE II
The Assignments of Signals of ^{1}H NMR Spectrum of Branched PAN Shown in Figure 3

Signal	Chemical shift region (ppm)	Assignments of signals[a]
A	5.9–6.4	H atom of CH_2=CH— on residue groups (F).
B	5.1–5.3	H atom on terminal units (T_m), —CH_2—CH(Br)—CN.
C	4.3–4.5	H atom of —CH_2—CH_2— on BPEA units and —$OCOCH$(Br)CH_3 on linear units (L_v) and terminal units (T_l).
D	2.8–3.2	—CH— of PAN units.
E	2.3–2.8	—CH— and —CH_2— on the main chain of poly(BPEA) units.
F	1.8–2.3	—CH_2— of PAN units.
G	1.7–1.8	—CH_3 of —$OCOCH$(Br)CH_3 on terminal units (T_l) and linear units (L_v).
H	1.1–1.3	—CH_3 of —$OCOCH$(CH_3)— on branch points (B), linear unts (L_c), and residue groups (F).

[a] The terms in parenthesis stand for the structure units shown in Scheme 2.

residue group (F), which meant that there were three average branch points (B) and linear units (L_c) on one macromolecular chain. Peak G was the signals of —CH_3 on terminal unit (T_1) and pendent unit (L_v), whose area was 2.7 times of that of peak A, so there were 2.7 pendent and terminal BPEA units on an average on one macromolecule chain. The polymerization degree of AN was calculated to be 121 through the area ratio of the sum of D and F to A. So the molar ratio of AN unit to BPEA unit was 18.1, which was consistent with the value calculated through the feed ratio and the conversion of AN, 17.6. The number-average molecular weight of Sample 7 was calculated to be about 8100 through the average unit numbers of AN and BPEA in the macromolecular chain. Meanwhile, the apparent number-average molecular weight of Sample 7 measured by GPC calibrated with linear PAN broad standards was 5100, which was smaller than that calculated through ^{1}H NMR data. This was due to the compact conformation of the branched polymer in solution, which led to a longer elution time in GPC trace than that of its linear analogue and resulted in a lower apparent molecular weight.

The average degree of branching ($\overline{DB}$) is one of the most important molecular parameters, which determines many physical properties of the branched polymers. It can be defined as follows[23,25]:

$$\overline{DB} = \frac{2(\text{number of branching units})}{(\text{total number of units1})} \quad (1)$$

However, the number of branching units was hard to be calculated from NMR spectrum data directly. For equal reactivity of all active sites, $\overline{DB}$ was given by[23]:

$$\overline{DB} = \frac{2z_A(x_M - z_A)}{1 - (1 - x_M)(1 + z_A)} \quad (2)$$

where z_A is the fraction of A* in the active centers and x_M is the conversion of AN. z_A cannot be calcu-

lated through NMR spectrum data directly. For equal reactivity of all active sites, it can be estimated as follows[19]:

$$z_A = \frac{b}{\gamma + 1} \quad (3)$$

where b is the fraction of b group in the BPEA units in the copolymer and γ is the feed ratio of monomer to inimer, $[AN]_0/[BPEA]_0$. For Sample 7, b was 0.597 (i.e., 4/6.7), and γ was 30, thus z_A was calculated to be 0.019. For Sample 7, the conversion of AN, x_M, was 58.6%. The values of z_A and x_M were inserted into eq. (2) and $\overline{DB}$ was calculated to be 0.038. The average degree of branching of other samples was calculated in the same way and the values were listed in Table I. Because of the dilution of the AN units in the copolymer chains, the values of $\overline{DB}$ were low. Under the same polymerization condition (from Sample 1 to 6), $\overline{DB}$ nearly kept constant along with the increase of AN conversion, which coincided with the result of literature.[23]

To clarify the branched architectures of the products more clearly, we measured the absolute weight-average molecular weight of Sample 8 which owned the largest apparent molecular weight (given by GPC) by static light scattering and compared it with the value given by GPC. The dn/dc value of PAN solution in DMF at 25°C was measured to be 0.0807 mL/g by a differential refractometer at a wavelength of 632.8 nm. This value was consistent with that of linear PAN, 0.078 mL/g, found in literature,[26] which suggested that low BPEA content had little influence on the value of dn/dc. The absolute molecular weight was measured with SLS in DMF at 25°C with different concentrations (1.01 g/L, 3.00 g/L, 5.02 g/L, 7.04 g/L, and 9.02 g/L, respectively) and scattering angles (from 30° up to 150° with a step length of 5°). The weight-average molecular weight of Sample 8 obtained was 63,000 when Zimm plot was employed (Fig. 4), which was much larger than the value got from GPC was 26,100. This result indicated that this polymer adapted a compact conformation.

The intrinsic viscosity of the branched PAN and that of the linear analogue that had the same molecular weight as branched PAN was also compared. The intrinsic viscosity of Sample 8 was measured with an Ubbelohde viscometer in DMF at 25°C (Fig. 5). The value measured was 47 mL/g. The intrinsic viscosity of linear PAN which had the same molecular weight as that of Sample 8 can be estimated through Mark-Houwink equation:

$$[\eta] = K \times M_v^{\alpha} \tag{4}$$

where M_v stands for the viscosity-average molecular weight. For linear PAN,[27] $K = 0.0243$ and $\alpha = 0.75$, i.e., $[\eta]_{linear} = 0.0243 \times M_v^{0.75}$, in which the molecular weights of linear PAN standards were measured by SLS. Through this equation, one could calculate the intrinsic viscosity of the linear PAN that had the same molecular weight as that of branched Sample 8. To minimize the influence of the broad distribution, a correction was necessary[28]:

$$[\eta]_{linear} = K_w \times M_w^{\alpha} \tag{5}$$

where $K_w = K \times (M_w/M_n)^{0.5\alpha(\alpha-1)} = 0.0221$

$$\text{So} \quad [\eta]_{linear} = 0.0221 \times M_w^{0.75} \tag{6}$$

If $M_w = 63,000$, then $[\eta]_{linear}$ was calculated to be 88 mL/g.

It was noteworthy that the intrinsic viscosity of the branched polymer (Sample 8), 47 mL/g, was much lower than that of its linear analogue, 88 mL/g. The contraction factor g' of Sample 8 was evaluated at follows:

$$g' = [\eta]_{branched}/[\eta]_{linear} = 0.53$$

The decrease of the solution intrinsic viscosity and the low contraction factor could be interpreted as
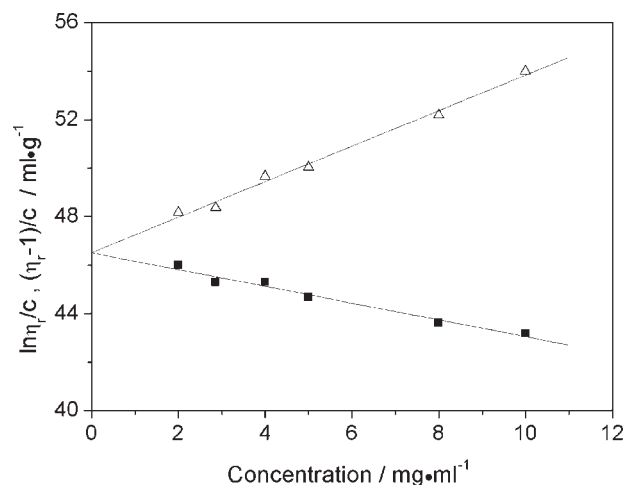
Figure 5 The intrinsic viscosity of branched PAN (Sample 8) in DMF at 25°C.

the result of compact conformation of the branched structure. It was interesting that just a small amount of BPEA could lead to such a dramatic decrease of intrinsic viscosity. Simon et al.[20,21] have prepared branched PMMA by self-condensing group transfer copolymerization of MMA and 2-(2-methyl-1-triethylsiloxy-1-propenyloxy)ethyl methacrylate (inimer) and also found that even small amounts of inimer led to a dramatic decrease in the solution viscosity. However, Pitto et al.[7] have synthesized well-defined star PAN with 3, 4, and 6 arms and measured the Mark-Houwink exponents of the samples through the double logarithmic plot of intrinsic viscosity against molecular weight. Through the comparison of the exponents of star and linear polymers, they concluded that the star PAN still adapted a disturbed stiff rod-like shape. As for star polymers, there exists only one branch point (focal unit) along each chain, thus the properties of star polymers are mainly governed by its arms and the Mark-Houwink exponent of star polymer should be similar with that of linear polymers.[1] We employed the same method as the previous method is to calculate the Mark-Houwink exponents of the branched products. Figure 6 showed the double logarithmic plot of intrinsic viscosity of the samples against their molecular weight given by NMR spectra. The Mark-Houwink exponent α, i.e., the slope of the plot, was 0.61, which was smaller than the value of linear PAN given by Pitto,[7] 0.74. That was coincident with the point of Burchard[1] that the exponent of randomly branched polymer was smaller than that of its linear analogues. From the comparison of the exponents of our products and linear PAN, the molecular chains of the products were considered to adapt a relatively compact conformation in the solution, and the products owned a branched architecture.
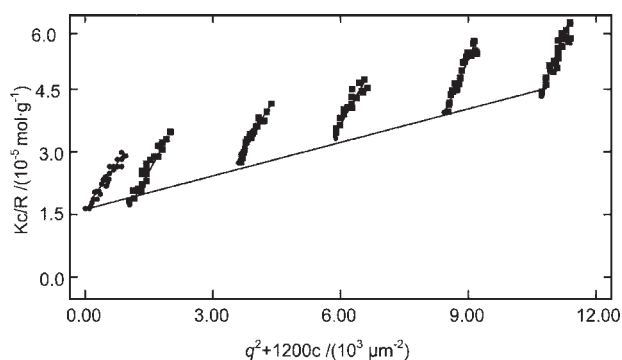

Figure 4 Zimm plot of laser light scattering of branched PAN (Sample 8) prepared through SCVCP of AN and BPEA. The concentrations of PAN in DMF solution (from right to left) were 9.02 g/L, 7.04 g/L, 5.02 g/L, 3.00 g/L, and 1.01 g/L.
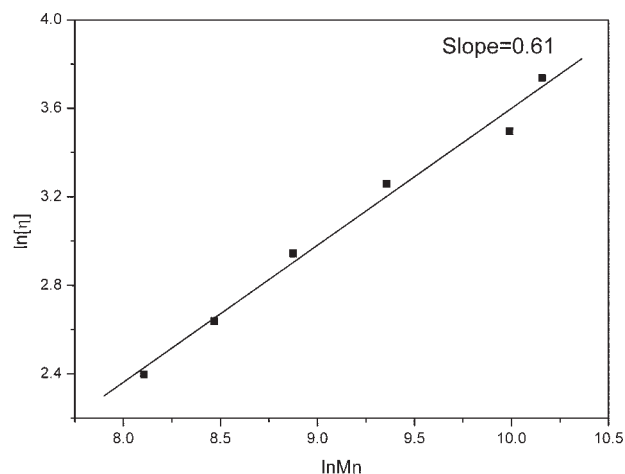
Figure 6 The Mark-Houwink plot of the hyperbranched PAN (Sample 1–6) for the evaluation of α.

The shear viscosity of Sample 8 was investigated by an ARES rheometer. For the purpose of comparison of the shear viscosity of polymers with different topologies, linear PAN samples with a similar molecular weight to that of branched PAN should be prepared through free radical polymerization of AN. Among several linear PAN samples prepared, sample with appropriate molecular parameters ($M_w = 60600$, $M_w/M_n = 1.38$, measured by GPC calibrated with linear PAN) was chosen to make the comparison. Under the same shear rate (8 rad s^{-1}) and concentration (60.5 mg/mL) in DMF, the shear viscosity of the branched PAN was 0.008 Pa s, evidently lower than that of linear PAN, 0.056 Pa s. In the results of Simon et al.,[21] the branched PMMA was fractionated into eight fractions with narrow polydispersity and the shear viscosities of each fraction were far lower than that of their linear analogues owning the similar molecular weight. In our experiments, it was considered that the decrease of viscosity was attributed to the branched architecture of PAN.

CONCLUSIONS

Branched PAN was prepared through self-condensing atom transfer radical copolymerization of AN and BPEA. The branched architecture of the product was proven by ^{1}H NMR analysis and solution prop-

erties. Thus, prepared PAN has obviously low intrinsic viscosity and shear viscosity compared with its linear analogue. This property could be important for the spinning process in the production of Acrylon.

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