

Preparation of Polyacrylonitrile with Improved Isotacticity and Low Polydispersity

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ABSTRACT: The preparation of a polymer with both low polydispersity and high tacticity is one current challenge we face and warrants thorough investigation from both the theoretical and experimental standpoints. In this study, we synthesized polyacrylonitrile (PAN) with simultaneously controlled molecular weight and tacticity on the basis of the strategy of the atom transfer radical polymerization (ATRP) of acrylonitrile (AN) in the presence of Lewis acids. A new combined initiation system of 3-bromopropionitrile (3-BPN)/Cu₂O/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) was used for the ATRP of AN for the first time. When the polymerization was performed with the ratio [AN]₀/[Initiator]₀/[Cu₂O]₀/[TMEDA]₀ = 190/1/0.5/1.5 (where the subscript 0 indicates the initial conditions) in ethylene carbonate at 60°C for 48 h, the polydispersity of the

obtained PAN was 1.13, and the molecular weight was up to 13,710. The polymerization kinetics results show that the polymerizations proceeded with a living/controlled nature except that an induction period existed during the polymerization process because of the lower initiating activity of 3-BPN. Also, two kinds of Lewis acid, AlCl₃ and yttrium trifluoromethanesulfonate, were used in the ATRP system of AN for the tacticity control. The addition of 0.01 equiv (relative to AN) of the Lewis acid AlCl₃ in the polymerization afforded PAN with an improved isotacticity [meso/meso triad (mm) = 0.32] and a very narrow polydispersity (1.06). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2610–2616, 2010

Key words: atom transfer radical polymerization (ATRP); isotactic; molecular weight distribution

INTRODUCTION

The mechanical and chemical properties of polymers depend highly on their primary structures, such as tacticity, molecular weight, and polydispersity. Therefore, continuous interest and effort have been focused on the synthesis of polymers with controlled molecular weights and stereoregularity. For decades, the development of controlled/living radical polymerization has made it possible to synthesize polymers with targeted molecular weights and narrow polydispersities, which can be categorized into three processes: nitroxide-mediated polymerization,^{1–4} metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP),^{5–12} and reversible addition fragmentation chain transfer (RAFT) or macromolecular design via the interchange of xanthates.^{13–16} Meanwhile, the control of the stereochemistry in radical polymerization has

been achieved with special solvents, such as fluoroalcohols or Lewis acid additives, that can interact with the monomer or the growing radical via hydrogen bonding or coordination.^{17–19} Thus, controlled/living radical polymerization in solvents such as fluoroalcohols or in the presence of Lewis acids may afford the polymers with simultaneously controlled molecular weight and tacticity. For instance, Matyjaszewski, Sawamoto, and coworkers^{20–22} successfully synthesized well-defined isotactic poly(*N,N*-dimethylacrylamide), poly(*N*-methylmethacrylamide), and poly(*N*-isopropylacrylamide) by ATRP or reversible addition fragmentation chain transfer in the presence of the Lewis acids yttrium trifluoromethanesulfonate [Y(OTf)₃] or [Yt(OTf)₃] and ytterbium trifluoromethanesulfonate [Yb(OTf)₃].^{20–22} Okamoto, Kakuchi, and coworkers^{23–26} also reported the achievement of the stereospecific and controlled/living polymerizations of methyl methacrylate, vinyl acetate, and *N*-vinylpyrrolidone in fluoroalcohols such as (CF₃)₃COH, (CF₃)₂–CHOH, PhC(CF₃)₂OH, and *m*-C₆H₄[C(CF₃)₂OH]₂.

Polyacrylonitrile (PAN) is a commercially important polymer because of its unique and well-known properties, including hardness and rigidity, chemical resistance, compatibility with certain polar substances, and low gas permeability. In recent years, considerable efforts have been devoted to the molecular

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design and controlled synthesis of PAN for further extending its applications, among which the synthesis of well-defined PAN on the basis of the ATRP technique is the main one. According to reports on the ATRP of acrylonitrile (AN), 2-halidepropionitriles, such as 2-bromopropionitrile (2-BPN), 2-chloropropionitrile, and sulfonyl chlorides, were the only initiators used and were normally accompanied by the use of the catalyst CuCl/2,2'-bipyridyl (BPY) or Cu₂O/BPY.^{27–35} The development of some new activators could aid the synthesis of the well-defined PAN. Matyjaszewski et al.³⁶ recently devoted their activators regenerated by the electron-transfer ATRP of AN with Cu^{II}Cl₂/tris[(2-pyridyl)methyl]amine as a catalyst and both Sn(II) and glucose as organic reducing agents to yield PAN with a high molecular weight (>100,000) and low polydispersity (<1.30). However, because of the possible side reaction between the growing radicals and the copper catalysts, the existed methodologies on the ATRP of AN remain unsatisfactory.³⁷

Another attempt to improve the utility of PAN is to increase the tacticity of PAN. It is well-known that highly stereoregular PAN [meso/meso triad (mm) = 0.84] can be prepared by γ -ray irradiation on an AN urea canal complex at a low temperature, and the obtained PAN is essentially isotactic in its configuration.^{38–42} In 2000, Minagawa et al.⁴³ reported stereoregular PAN (mm = 0.68) prepared by electron-beam irradiation canal polymerization. Soon after that, Jung et al.⁴⁴ reported that PAN prepared with a zeolite as a host had an improvement in isotacticity from 0.26 to 0.34. It was not difficult to determine that all of these studies were based on a similar strategy for the achievement of stereoregular PAN, that is, the canal polymerization of AN under irradiation. To our knowledge, Lewis acids such as Y(OTf)₃, Yb(OTf)₃, and scandium trifluoromethanesulfonate [Sc(OTf)₃] have been reported to effectively control stereoregularity over the radical polymerization of methyl acrylamides, methacrylates, and α -(alkoxymethyl)acrylates with the mechanism of coordination between monomers and the propagating species during polymerization.^{20,45–49} However, there have been few reports on the use of such Lewis acids to control the stereoregularity of PAN.

Because the cyano group of AN is a strong polar group and may coordinate with Lewis acids added in the polymerization of AN, it is worthwhile to explore the possibility of synthesizing PAN with controlled tacticity by the addition of Lewis acids to the radical polymerization. Up to this point, stereospecific ATRP for the simultaneous control of the polydispersity and tacticity of PAN has not been reported.

In this study, we introduced 3-bromopropionitrile (3-BPN) as the initiator in the ATRP of AN for the

first time to investigate whether a compound with a remoter halogen atom from a cyano group could effectively initiate the ATRP of AN. In addition, Cu₂O/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) was first used as a catalyst system, coacting with 3-BPN, for the ATRP of AN because of its presumed higher catalytic activity. On the basis of the novel initiation system 3-BPN/Cu₂O/TMEDA, we obtained PAN with a high molecular weight and low polydispersity. Moreover, with the addition of the Lewis acid AlCl₃ in the ATRP system, we successfully accomplished the simultaneous control of the molecular weight and tacticity of PAN, obtaining PAN with an improved isotacticity (mm = 0.32), low polydispersity (1.06), and higher molecular weight (48,360).

EXPERIMENTAL

Materials

AN [Shanghai Chemical Reagents Co., Shanghai, China, analytical reagent (AR) grade] was vacuum-distilled from CaH₂ just before polymerization. 3-BPN and yttrium trifluoromethanesulfonate [Yt(OTf)₃] were obtained from Aldrich and were used without further purification. AlCl₃ (Shanghai Chemical Reagents Co., AR grade) were dried *in vacuo* (at 60°C) before use. Ethylene carbonate (Taixing Fengming Chemical Reagents Co., Taixing, Jiangsu Province, China, AR grade), methanol (Hangzhou Chemical Reagent Co., Ltd., Hangzhou, Zhejiang Province, China, AR grade), and TMEDA [Shanghai Qianjing Chemical Reagent Plant, Shanghai, China, biochemical reagent (BR) grade] were used as received. Cu₂O was synthesized according to the published literature.⁵⁰

Polymerization

A typical example of the general procedure was as follows: a dry tube was filled with Cu₂O, TMEDA, ethylene carbonate (EC), AlCl₃, 3-BPN, and AN at an appropriate ratio in turn. The tube was sealed under nitrogen after three freeze–vacuum cycles. The tube was then immersed in an oil bath and held at the desired temperature by a thermostat. After a definite polymerization time, we terminated the polymerization by taking out the tube and opening the flask to expose the reaction system to air. The polymerization product was dissolved in a mixture of dimethylformamide and HCl, and the resulting solution was then poured into a large amount of methanol for precipitation. After centrifugation, the precipitated polymer, PAN, was redissolved and reprecipitated, and then, the precipitate obtained was washed with a mixture of methanol and water several times and dried at 60°C *in vacuo* for 24 h.

TABLE I
ATRP of AN with 3-BPN as an Initiator Under Different Reaction Conditions^a

Run	[AN] ₀ /[Initiator] ₀	Catalyst/ligand	Temperature (°C)	Conversion (%) ^b	<i>M_n</i> , ^c	<i>M_n</i> ^d	<i>M_w</i> ^d	<i>M_w</i> / <i>M_n</i> ^d
1	190/1	Cu ₂ O/TMEDA	60°C	14.9	1,631	13,710	15,490	1.13
2	570/1	Cu ₂ O/TMEDA	60°C	28.6	8,774	26,860	33,670	1.25
3	570/1	Cu ₂ O/TMEDA	80°C	32.3	9,876	21,020	28,780	1.37

^a Polymerization in ethylene carbonate for 48 h.

^b Measured gravimetrically.

^c $M_{n,th} = [(Conversion \times M_{Monomer} \times [Monomer]_0) / [Initiator]_0] + M_{Initiator}$.

^d Determined on a Waters 1515 gel permeation chromatograph.

Characterization

The conversion of the monomer was determined gravimetrically, calculated via the equation:

$$\text{Conversion (\%)} = m_{\text{PAN}}/m_{\text{AN}}$$

where m_{PAN} and m_{AN} refer to the weights of the obtained PAN and the feeding monomer AN, respectively. ¹³C-NMR spectra was recorded on a Bruker DRX500 spectrometer (Karlsruhe, Baden-Württemberg, Germany) in hexadeuterated dimethyl sulfoxide at ambient temperature. The number-average molecular weight (M_n) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC). GPC was performed on a Waters (USA) 1515 gel permeation chromatograph equipped with a Waters 2414 refractive-index detector with three commercial columns (Waters Styragel) connected in series. The analysis was undertaken at 30°C with purified high-performance-liquid-chromatography-grade dimethylformamide as the eluent at a flow rate of 1 mL/min. Calibration was performed with standard polystyrenes.

RESULTS AND DISCUSSION

ATRP of AN: Control of the molecular weight

2-BPN is commonly used as an effective ATRP initiator (especially for the polymerization of AN), as it has been accepted that the radical stabilization provided by an α -nitrile group facilitates the initial atom transfer process that creates the initiating radical species. In this study, however, we introduced 3-BPN with a bromine atom on the β -carbon as the initiator in the ATRP of AN for the first time to explore whether a compound with a remoter halogen atom from a cyano group could effectively initiate the ATRP of AN. We expected that the experimental results might be a valuable hint for the use of ordinary haloalkanes as the initiators in the ATRP of AN. Of course, 3-BPN is relatively lower in cost and more easily available compared to 2-BPN. On the other hand, catalyst system cooperation with the given initiator is also a vital factor in a successful

ATRP. Cu₂O has shown a higher catalytic activity in the ATRP of AN than CuBr and CuCl.^{27–31} Moreover, TMEDA was assumed to be more efficacious for improving the solubility of Cu₂O in a polymerization system than BPY because of its linear structure similar to the monomer AN. Therefore, we first used Cu₂O/TMEDA as the catalyst system to join with 3-BPN for the ATRP of AN. Considering the insolubility of PAN in its monomer AN, we chose ethylene carbonate as the solvent of the polymerization to make polymerization system homogeneous. The ATRP of AN with 3-BPN as the initiator working with different catalyst systems was carried out in the solvent ethylene carbonate for 48 h. The effects of catalyst system, reaction temperature, and [AN]₀/[Initiator]₀ ratio (where the subscript 0 indicates the initial conditions) on the polymerization were investigated to optimize the reaction conditions. The results are summarized in Table I.

According to the work of Matyjaszewski et al.,²⁷ the polymerization of AN based on 2-BPN/CuBr/BPY within 23 h at 44°C led to PAN with a 38.3% conversion, a low polydispersity of 1.04, and a molecular weight up to 3160. By comparison, the novel combination 3-BPN/Cu₂O/TMEDA that we used in the ATRP of AN offered similar efficacy under the appropriate polymerization temperature to obtain a PAN with a low polydispersity. Beyond all doubt, when 3-BPN was applied instead of 2-BPN as the initiator in the ATRP of AN, it was not suitable to use CuBr/BPY as a catalyst sequentially because of its low initiating activity and low catalytic activity. Also, at the relatively low polymerization temperature of about 40°C, even the cooperation of 3-BPN/Cu₂O/TMEDA had no effect because of two reasons: (1) the temperature was not high enough for the cleavage of 3-BPN to generate original radicals and supply the required reaction energy for the propagation of PAN chains and (2) the low melting point of the solvent ethylene carbonate of 37°C limited the diffusion and polymerization of the monomer AN. However, we were gratified that when the feeding ratio AN/3-BPN/Cu₂O/TMEDA was 570/1/0.5/1.5 at the raised reaction temperatures 60 and 80°C, PAN was obtained with conversions of 28.60 and

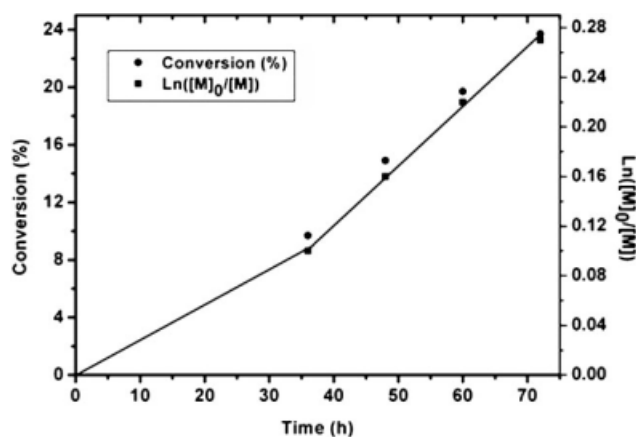


Figure 1 Plots of the conversion (%) and $\ln([M]_0/[M])$ versus the reaction time for the polymerization of AN in ethylene carbonate with an $[AN]_0/[3\text{-BPN}]_0/[Cu_2O]_0/[TMEDA]_0$ ratio of 190/1/0.5/1.5 at 60°C.

32.30%, respectively; this implied the availability of the newly combined activator 3-BPN/ Cu_2O /TMEDA.

The experimental molecular weights from the GPC of PAN obtained at 60 and 80°C were 26,860 and 21,020, respectively; both were much higher than the predicted $M_{n,th}$ (the theoretical number-average molecular weight) $\{M_{n,th} = [(Conversion \times M_{Monomer} \times [Monomer]_0/[Initiator]_0) + M_{Initiator}]$, where $M_{Monomer}$ and $M_{Initiator}$ are the molecular weights of acrylonitrile and 3-BPN, respectively}. This result was quite likely subjected to a low initiation efficiency during the reactions, which might have been due to the coupling/disproportionation of the initiating radicals.²⁶ Most probably, as the rate of activation in case of the initiator 3-BPN was low because of the lack of radical stability provided by the alkyl substituent, the high rate of propagation compared to the low rate of initiation was more likely responsible for this low initiation efficiency. On the other hand, the precipitation–washing cycles during purification possibly washed out the low-molecular-weight fraction of PAN, which could have also accounted for the occurrence that the factual conversion was not so high as expected and the experimental molecular weight of the obtained PAN was much higher than the theoretical $M_{n,th}$.

The polydispersity indices of the obtained PAN ranged from 1.13 to 1.37, depending on the different polymerization conditions; this manifested the acceptable controllability of the polymerization. Although it might be commonly accepted that slow initiation usually results in a broad molecular weight distribution, we hold that not only the initiator but also the concurrent cooperation between the initiator and the catalytic system determined the controllability of the polymerization. As for our polymerization system of AN, with the participation of the catalyst Cu_2O /TMEDA with a higher catalytic activity, the

cleavage of 3-BPN into the radicals by the redox reaction of Cu_2O /TMEDA with 3-BPN and the formation of monomer radical via the reaction of the radical with the monomer were collaborated and, thus, maintained the dynamic equilibrium between the initiation and propagation. On the other hand, PDI of PAN at 80°C reached 1.37; this indicated that the raised reaction temperature led to a deteriorated controllability of the polymerization, which might have been caused by the enhanced polymerization rate at the raised temperature.

To determine more about the polymerization system, the polymerization kinetics of AN were carried out in ethylene carbonate with an $[AN]_0/[3\text{-BPN}]_0/[Cu_2O]_0/[TMEDA]_0$ ratio of 190/1/0.5/1.5 at 60°C. As shown in Figure 1, an induction period existed during the polymerization process. After the induction period, the conversion increased with time, and the semilogarithmic plot of $\ln([M]_0/[M])$ [original concentration/current concentration] versus time showed a significant first-order linearity with respect to the polymerization time. This induction period, however, was attributed to the slow initiation reaction as a result of the lower initiating activity of the initiator 3-BPN.

The M_n values of the polymers measured by GPC increased linearly with monomer conversion (Fig. 2), although M_n at lower conversion (9.7%) showed little deviation from first order, which was because of the slow initiation. The PDI [weight-average molecular weight (M_w)/ M_n] values of the resulting polymers remained low, ranging from 1.13 to 1.36. These results indicate that this polymerization proceeded by normal ATRP with a living/controlled nature.

Additionally, when we performed the ATRP of AN with 2-BPN as an initiator instead of 3-BPN under the same conditions, expecting to reveal some possible different initiation behavior between the

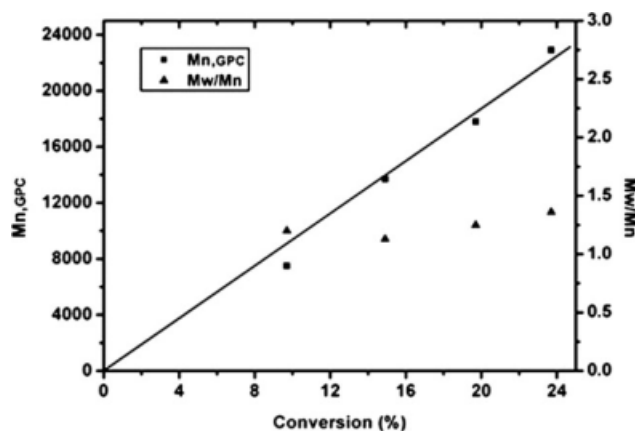


Figure 2 Relationship between the molecular weight ($M_{n,GPC}$) and polydispersity (M_w/M_n) with conversion (%) for the polymerization of AN in ethylene carbonate with an $[AN]_0/[3\text{-BPN}]_0/[Cu_2O]_0/[TMEDA]_0$ ratio of 190/1/0.5/1.5 at 60°C.

TABLE II
 ATRP of AN in the Presence of Yt(OTf)₃ or AlCl₃ with 3-BPN/Cu₂O/TMEDA Initiating System in Ethylene Carbonate at 60°C for 48 h^a

Run	Lewis acid	[Lewis acid] ₀ /[Monomer] ₀	Conversion (%) ^b	$M_{n,th}$ ^c	M_n ^d	M_w ^d	M_w/M_n ^d	rr ^e	mr ^e	mm ^e
1	Yt(OTf) ₃	0.005	0	—	—	—	—	—	—	—
2	AlCl ₃	0	14.9	1,631	13,710	15,490	1.13	23.1	51.0	25.9
3	AlCl ₃	0.005	4.9	621	46,730	53,750	1.15	22.9	45.9	31.2
4	AlCl ₃	0.01	3.2	455	48,360	51,270	1.06	25.1	42.4	32.5
5	AlCl ₃	0.015	0	—	—	—	—	—	—	—

^a Feeding ratio [AN]₀/[Initiator]₀/[Cu₂O]₀/[TMEDA]₀ = 190/1/0.5/1.5.

^b Measured gravimetrically.

^c $M_{n,th} = [(Conversion \times M_{Monomer} \times [Monomer]_0) / [Initiator]_0] + M_{Initiator}$.

^d Determined on a Waters 1515 gel permeation chromatograph.

^e Measured by ¹³C-NMR spectra with a Bruker DRX500 spectrometer.
 rr, racemo/racemo triad; mr, meso/racemo triad.

two initiators, the polymerization remained sluggish, and no better results were eventually obtained compared with the polymerization with 3-BPN as the initiator. We ascribed this to a consequence of the more active cleavage of 2-BPN and the high catalytic activity of Cu₂O/TMEDA. The initiation step included the cleavage of 2-BPN into radicals by the redox reaction of Cu₂O/TMEDA with the initiator and the formation of a monomer radical via the reaction of the radical with the monomer. With the participation of Cu₂O/TMEDA in the polymerization, the original radical stabilization provided by the α-nitrile group in 2-BPN possibly deteriorated because of the activity of catalyst and meanwhile, the initiation could not be balanced by a parallel bromine-transfer reaction.

Among all of the published works concerning traditional ATRP of AN, the ATRP of AN initiated by 2-BPN/Cu₂O/BPY with [AN]₀/[Initiator]₀ feeding ratios of 130/1 and 2000/1 led to PANs with molecular weights of 8400 and 38,400, respectively.^{27–35} Although in our study, with [AN]₀/[Initiator]₀ feeding ratios of 190/1 and 570/1, the molecular weights of the obtained PAN were 13,710 and 26,860, respectively. These results indicate that 3-BPN suffered a lower initiating activity than 2-BPN, but the combination of 3-BPN with the higher active catalyst system Cu₂O/TMEDA was an attractive alternative as the initiation system for the ATRP of AN to obtain PANs with higher molecular weights and low polydispersities.

Effects of the Lewis acids in the ATRP of AN

Simultaneous control of the molecular weights and tacticity of PAN

To obtain well-defined, stereoregular PAN, the ATRP of AN in ethylene carbonate in the presence of AlCl₃ or Yt(OTf)₃ was carried out with the 3-BPN/Cu₂O/TMEDA initiating system with an [AN]₀/[Initiator]₀/[Cu₂O]₀/[TMEDA]₀ feeding ratio

of 190/1/0.5/1.5. As shown by the polymerization results shown in Table II, the addition of Lewis acids had a dramatic influence on the polymerization of AN. On one hand, no PAN was observed in the polymerizations with Yt(OTf)₃. This was presumably due to the fact that the Lewis acid Yt(OTf)₃ was a strong Lewis acid, which might have destroyed the ATRP catalytic system of AN and, consequently, handicapped the polymerization of AN. On the other hand, the introduction of AlCl₃ into the ATRP of AN decreased the polymerization rate tremendously compared with that in the absence of the Lewis acid, which afforded PAN in a very low amount. When the amount of AlCl₃ added reached 0.015 equiv (relative to the monomer), no PAN was obtained. We supposed that this decreased rate might have arisen from the intermediate acidity of AlCl₃ and possible deactivation of the catalytic system. To the best of our knowledge, the acidity of a Lewis acid depends on the central metals and the ligands, and it increases as the ionic radius of the metal decreases or with the more electron-withdrawing ligands the Lewis acid has. Compared with Yt(OTf)₃, AlCl₃ enjoyed such an intermediate acidity that the addition of AlCl₃ led to a relatively slighter deactivation of the catalytic system in the ATRP of AN, which made the polymerization system tolerate a certain amount of added AlCl₃.

Interestingly, although the addition of AlCl₃ in the ATRP of AN greatly decreased the yield of PAN, the polydispersities of the polymers obtained remained low, ranging from 1.03 to 1.15. Furthermore, we observed that the molecular weights of the resulting PAN of the ATRP of AN in the presence of AlCl₃ were higher (46,730 and 48,360, depending on different [Lewis acid]₀/[Monomer]₀ ratios) than that of the PAN obtained in the absence of AlCl₃, which was only 13,710. Also, the molecular weights of the resulting PAN obtained in both cases, with or without AlCl₃, as measured via GPC, were higher than their respective theoretical molecular weights. We

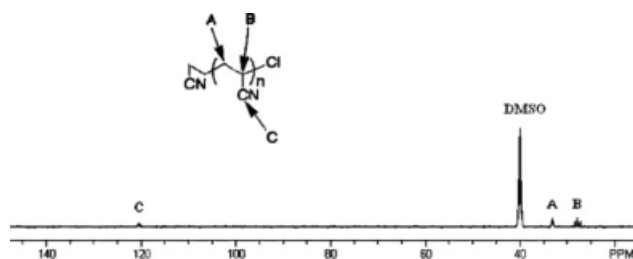


Figure 3 ^{13}C -NMR spectrum of PAN obtained by ATRP of AN with the 3-BPN/ Cu_2O /TMEDA initiating system in ethylene carbonate at 60°C for 48 h with a feeding ratio $[\text{AN}]_0/[\text{Initiator}]_0/[\text{Cu}_2\text{O}]_0/[\text{TMEDA}]_0$ of 190/1/0.5/1.5.

thought that when the Lewis acid AlCl_3 was introduced into the ATRP of AN, it would possibly inactivate the catalyst system and further decrease the initiating efficiency and the amount of radicals, which might have resulted in the increased molecular weight of PAN and an enormous disparity between the predicted molecular weights ($M_{n,\text{th}}$'s) and experimental molecular weights ($M_{n,\text{GPC}}$'s), where $M_{n,\text{GPC}}$ refers to the number-average molecular weight obtained via GPC. The addition of AlCl_3 led to PAN with a higher isotacticity, although the accurate amount of AlCl_3 responsible for the improvement of isotacticity in the reaction might have been smaller than that of AlCl_3 added in the system because the polymerization system in the presence of AlCl_3 was heterogeneous. When 0.005 or 0.01 equiv of the Lewis acid AlCl_3 (relative to the monomer) was applied in the polymerization, the resulting PAN had increasing mm contents of 31.2 and 32.5%, respectively, whereas the mm content of PAN obtained without AlCl_3 added was only 25.9%.

The tacticity of the PAN prepared by the ATRP of AN with the 3-BPN/ Cu_2O /TMEDA initiating system in the presence or absence of AlCl_3 was examined by ^{13}C -NMR spectroscopy. Figure 3 shows the ^{13}C -NMR spectra of PAN obtained by the ATRP of AN with the 3-BPN/ Cu_2O /TMEDA initiating system in ethylene carbonate at 60°C with an $[\text{AN}]_0/[\text{Initiator}]_0/[\text{Cu}_2\text{O}]_0/[\text{TMEDA}]_0$ feeding ratio of 190/1/0.5/1.5. Three kinds of carbon species, methine

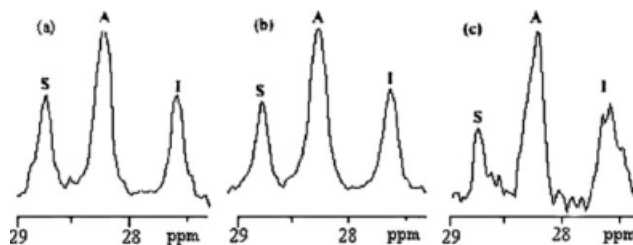
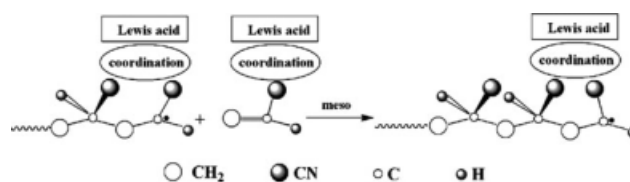


Figure 4 Expanded methine signals of the ^{13}C -NMR spectra of (a) PAN obtained in the absence of AlCl_3 , (b) PAN obtained with a ratio $\text{AlCl}_3/[\text{AN}]_0$ of 0.5/100, and (c) PAN obtained with a ratio $\text{AlCl}_3/[\text{AN}]_0$ of 1/100 (S = syndiotactic, A = atactic, and I = isotactic).



Scheme 1 Radical propagation in the presence of a Lewis acid.

(CH), methylene (CH_2), and nitrile carbon (CN), were observed with decreasing magnetic field.^{38–40} Both the signals of methine and nitrile carbon can be used to determine the tacticity of PAN;^{51,52} however, in this study, only the methine signals were investigated. The methine $-\text{CH}$ carbon gave rise to three well-resolved peaks centered at 27.8 ppm due to triad chemical shift sensitivity. The isotactic signal appeared at 27.2 ppm followed by atactic and syndiotactic signals at lower magnetic fields, respectively. Figure 4 demonstrates the expanded methine signals of the ^{13}C -NMR spectra of the PAN prepared in the absence of AlCl_3 (Table II, run 2) and in the presence of AlCl_3 with different AlCl_3 concentrations (Table II, runs 3 and 4). The tacticity of the obtained PAN was calculated from the relative intensities of the respective peaks of methine, as shown in Table II. The increased isotacticity might have been due to the fact that during the polymerizations in the presence of AlCl_3 , the Lewis acid might have coordinated with the pendent groups of the polymer terminal and the monomer and forced them into the meso configuration during monomer addition; this led to a stereocontrolled polymerization, which is illustrated in Scheme 1.²⁰

CONCLUSIONS

In conclusion, we developed the novel initiating system 3-BPN/ Cu_2O /TMEDA to successfully synthesize PAN with a higher molecular weight and narrow polydispersity. This may shed some light on the exploration of new combinations of initiator and catalyst for the ATRP of the given monomers. Isotactic PAN (mm = 32%) with a low polydispersity (1.06) was prepared for the first time by the ATRP of AN in the presence of AlCl_3 . The ^{13}C -NMR results show that the isotacticity of PAN obtained in the presence of AlCl_3 was higher than that of PAN prepared in the absence of AlCl_3 and was affected by the amount of AlCl_3 added.

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