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ICAR ATRP OF ACRYLONITRILE UTILIZING A MODERATE TEMPERATURE RADICAL INITIATOR*

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Abstract Initiators for continuous activator regeneration atom transfer radical polymerization (ICAR ATRP) of acrylonitrile was first conducted at various ambient temperatures (30–45 °C). The key to success is ascribed to the usage of an appropriate low temperature radical initiator (2,2′-azobis(2,4-dimethylvaleronitrile)) and a high reactivity catalytic system ($CuBr_2$/Me_6TREN). The molar ratio of Cu catalyst to AN as low as 1:20000 was used to prepare well-defined polyacrylonitrile with controlled molecular weight and a narrow polydispersity index range of 1.08–1.30, while the monomer conversion was up to *ca*. 98%. The apparent activation energy of the polymerization was calculated to be 128.45 kJ/mol, suggesting that the polymerization strongly depended on reaction temperature. The very high chain-end functionality of the resultant polymer was confirmed by ^{1}H-NMR and GPC analyses as well as chain extension reaction.

Keywords: Living polymerization; ICAR ATRP; Acrylonitrile; Ambient temperature.

INTRODUCTION

Atom transfer radical polymerization (ATRP) has received considerable attention over the past decades because it is applicable to a wide range of monomers under a variety of reaction conditions and can produce a number of complex polymer architectures[1−12]. The basic principle of ATRP process is to protect the majority of active propagating species from bimolecular termination reactions through a reversible redox reaction between a low oxidation state metal and an organic halide (Scheme 1). Besides normal ATRP technique, the techniques reported recently are believed to be more promising, *e.g*., the initiators for continuous activator regeneration (ICAR) ATRP, due to lower catalyst loading and better tolerance towards oxygen[13−19]. A typical ICAR ATRP system consists of an alkyl halide initiator, very small amounts of a higher oxidation state transition metal and a thermal radical initiator (for monomers that do not undergo thermal initiation) such as azobis(isobutyronitrile) (AIBN). Based on the mechanism of ICAR ATRP, the activators, lower oxidation state transition-metal complex, are produced by an *in situ* reduction with the radical initiator (Scheme 2). To date, the ICAR ATRP processes were usually performed at a relatively high reaction temperature (≥ 60 °C) with low polymerization rates and mild monomer conversions. The report on the ambient temperature ICAR ATRP was rather rare[19]. First, conducting the polymerization at ambient temperature means reducing energy consumption and volatility of organic reagents. Secondly, low reaction temperature is possibly favorable to decrease the side reactions, *e.g*., termination and chain transfer reactions. With this regard, the ICAR ATRP carried out at mild conditions is worthy to be studied in depth.

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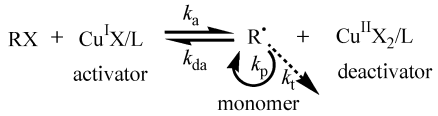


Scheme 1 Mechanism of ATRP

Living radical polymerization (LRP) of AN is challenging to control owing to its high reactivity and the poor solubility of polyacrylonitrile (PAN) in both monomer and solvents typically used in LRP[20–29]. Recently, we have reported controlled synthesis of PAN *via* the ICAR ATRP process. Utilizing $CuBr_2$/2,2′-bipyridine (bpy) as the catalyst, ethyl 2-bromoisobutyrate (EBiB) as the halogen initiator, and AIBN as the radical initiator, the polymerization proceeded in a living/controlled manner and the resulting polymer displayed a high chain-end functionality[18]. However, the monomer conversions were limited to *ca*. 80% with a long reaction duration, and the apparent molecular weight values showed large differences between the theoretical ones. Alternatively, another strategy is applied to improve the ICAR ATRP of AN, and thus to produce PAN with controlled molecular weight, even at high monomer conversion. However, the high reactivity of AN monomer facilitates it to polymerize at a high propagation rate. This high propagation rate readily leads to the occurrence of a large amount of termination reaction, which causes a broad molecular weight distribution. On the other hand, for a typical ICAR ATRP system, it includes both a halogen initiator and a radical initiator. Especially for the high reactivity AN monomer, there will be unavoidably an enhanced amount of bimolecular termination. Therefore, we reason whether by optimizing the catalytic systems and experimental parameters, the biradical termination reactions can be efficiently lowered and a higher control of the polymerization is achieved.

The present contribution reports that a moderate temperature radical initiator, 2,2′-azobis(2,4-dimethylvaleronitrile), aided with a high reactivity catalytic system, $CuBr_2$/Me_6TREN, can successfully mediate the ambient temperature ICAR ATRP of AN. The polymerization kinetics studies and the detailed end-group analyses of the resultant polymer confirmed the typical living/controlled characteristics.

EXPERIMENTAL

Materials

After thorough drying over anhydrous sodium sulfate, AN was distilled prior to use. $CuBr_2$ (99%; Aldrich), *N,N,N′,N′,N′*-pentamethyldiethylenetriamine (PMDETA, 99%; Aldrich), Hexamethylenetetramine (HMTA, 99.5%; Aladdin) and EBiB (98%; Aldrich) were obtained and used as received. Dimethyl sulfoxide (DMSO) was dried over anhydrous magnesium sulfate and distilled under reduced pressure. Bpy and 2,2′-azobis(2,4-dimethylvaleronitrile) (ABVN) were purified by recrystallizing twice from acetone and ethanol, respectively. Hexamethylated tris(2-aminoethyl)amine (Me_6TREN) was synthesized according to literature procedures[30, 31].

Polymerization

A typical polymerization procedure is as follows: a dry Schlenk tube was charged with AN monomer (1 mL), DMSO (1 mL), Me_6TREN (0.18 mg, 0.00076 mmol), $CuBr_2$ (0.17 mg, 0.00076 mmol), ABVN (4 mg, 0.0152 mmol) and EBiB (14.9 mg, 0.076 mmol). The reaction mixture was deoxygenated by three standard freeze-pump-thaw cycles, charged with nitrogen and sealed. The Schlenk tube with reaction mixture was placed in an oil bath at the predetermined reaction temperature. After a desired reaction time, the content was diluted with dimethylformamide (DMF). When the mixture becomes a homogenous solution, the polymer was precipitated in a large excess of methanol. The resultant polymer was filtered and dried at 40 °C in vacuo. The monomer conversions were determined by gravimetry.

Chain Extension of PAN

The following chain-extension recipe was used: a predetermined quantity of obtained PAN (263 mg, 0.076 mmol) and AN (1 mL) were dissolved in DMSO (1 mL). The mixture was stirred magnetically for 30 min to prepare a homogeneous solution in Schlenk tube, and then Me_6TREN (0.18 mg, 0.00076 mmol), $CuBr_2$

(0.17 mg, 0.00076 mmol) and ABVN (4 mg, 0.0152 mmol) were rapidly added. The tube was tightly sealed with a rubber septum. The rest procedure was the same as ICAR ATRP of AN.

Characterization

The number-average molecular weight (M_n) and PDI of PAN were measured on a gel permeation chromatography (GPC) system, consisting of a Waters 510 HPLC pump, three Waters Ultrastyragal columns (500, 10^3, and 10^5) and a Waters 2414 DRI detector. DMF was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight analyses were performed at 40 °C based on the universal calibration procedure with poly(methyl methacrylate) (PMMA) narrow standards. The Mark-Houwink constants used are $K = 1.32 \times 10^{-4}$ dL/g, $a = 0.674$ (PMMA)[32] and $K = 3.17 \times 10^{-4}$ dL/g, $a = 0.746$ (PAN)[33].

RESULTS AND DISCUSSION

$CuBr_2$/Me_6TREN-mediated ICAR ATRP of AN Utilizing a Moderate Temperature Radical Initiator

As noted previously, various ligands, *i.e.*, bpy, PMDETA, HMTA and Me_6TREN, have been successfully used to mediate radical polymerization of AN in a living/controlled fashion[20–22, 27, 29, 34–36]. Therefore, the $CuBr_2$-catalyzed AN polymerizations in DMSO at 35 °C were first carried out with the ligands reported, and the typical results are summarized in Table 1. The molar ratio of AN/EBiB/$CuBr_2$/Ligand/ABVN was set as 200:1:0.01:0.01:0.2. Obviously, Me_6TREN provided the highest rate of polymerization under the similar conditions (77% conversion for Me_6TREN versus 67%, 55%, and 44% conversions for bpy, PMDETA and HMTA). Importantly, compared with the other three ligands, Me_6TREN shows better control of the molecular weight and PDI. On one hand, with bpy, PMDETA, or HMTA as the ligand, there is a large difference between the apparent molecular weight and the theoretical ones. On the other hand, a higher PDI value is observed for these ligands. Only Me_6TREN yielded a controlled molecular weight close to the theoretical one (M_n (GPC) = 8510 versus $M_{n,th}$ = 8057) and a low PDI value of 1.20. The results suggest that the AN polymerization mediated by Me_6-TREN possessed a faster activation but also a sufficiently faster deactivation compared with those mediated by bpy, PMDETA or HMTA. In addition, for an efficient ligand PMDETA, the decrease in rate of polymerization is also due to the strong coordination of copper center with CN group of AN compared with the interactions of Cu with PMDETA. The interactions may either deactivate the catalyst (Cu/PMDETA) or lower its effective concentration in the reaction mixture[36]. Therefore, Me_6TREN was the optimal ligand in terms of rate of polymerization as well as control of molecular weight and PDI.

Table 1. Effect of the ligand on ICAR ATRP of AN[a]

No.	Ligand	Conv. (%)	$M_{n,th}$ (Da)	$M_{n,GPC}$ (Da)	PDI
1	bpy	67	7325	24500	1.48
2	PMDETA	55	5983	43600	1.50
3	HMTA	44	4905	36700	1.62
4	Me_6TREN	74	8057	8510	1.20

[a] [AN]/[EBiB]/[$CuBr_2$]/[L]/[ABVN] = 200:1:0.01:0.01:0.2, $[AN]_0$ = 7.63 mol/L, AN/DMSO = 1:1 (*V*/*V*), *T* = 35 °C, reaction time = 19 h

To further confirm the living/controlled nature of Me_6TREN system, the $CuBr_2$/Me_6TREN-catalyzed polymerizations of AN in DMSO were investigated in detail. Clearly, there appears a two-stage polymer kinetics curve (Fig. 1), *i.e.*, the rate of polymerization at the early stage is obviously lower than that at the latter stage. This rate retardation may be ascribed to the slow reduction of Cu(II) to Cu(I) by the resulting radicals from ABVN or residual traces of oxygen retained in the mixture in spite of three freeze-pump-thaw cycles. However, for both stages, a pseudo first-order linear polymerization kinetics was observed. A lower rate of polymerization at the early stage can be attributed to a small concentration of radicals derived from ABVN under the conditions ($t_{1/2}$ = 40 h, $k_d = 4.32 \times 10^{-6}$ s^{-1} for 35 °C)[37] and an excess of the deactivator Cu(II) relative to the radicals. An increase in rate of polymerization at the latter stage is due to the decrease of the deactivator Cu(II) concentration and the accumulated radicals from ABVN.

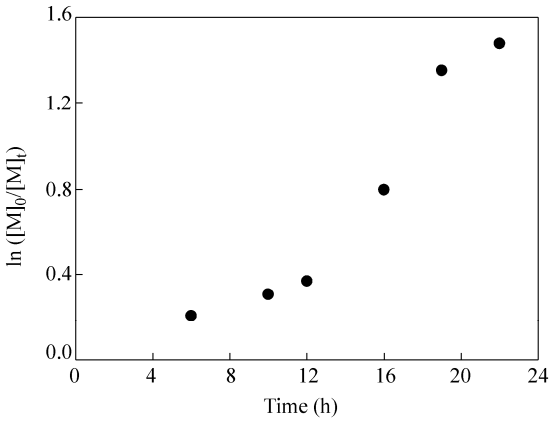


Fig. 1 Plot of $\ln([M]_0/[M]_t)$ versus reaction time for ICAR ATRP of AN ([AN]/[EBiB]/[$CuBr_2$]/[Me_6TREN]/[ABVN] = 200:1:0.01:0.01:0.2, $[AN]_0$ = 7.63 mol/L, AN/DMSO = 1:1 (*V*/*V*) and *T* = 35 °C.)

The theoretical number-average molecular weight ($M_{n,\,th}$) of PAN was predicted according to the following equation:

$$M_{n,th} = \frac{[AN]_0 \times Conv. \times M_{AN}}{[EBiB]_0 + 2f([ABVN]_0 - [ABVN]_t)} + M_{EBiB}$$

where AN, EBiB, and ABVN correspond to AN monomer, halogen initiator, and radical initiator, respectively. The radicals from ABVN is assumed to completely react with Cu(II) and would not initiate the radical polymerization of AN directly. Thus the initiator efficiency for ABVN, *f*, is close to unity. In addition, halogennitrile formed from the reaction of I radical and Cu(II) is assumed to be not a potential initiator for an ATRP process. In an ideal ICAR ATRP system, polymer directly derived from the initiator is thought to be minimal, and thus the right-hand side of the denominator becomes negligible.

The plots of M_n (GPC) and PDI (GPC) versus monomer conversion are shown in Fig. 2. Clearly, the measured M_n (GPC) values increase linearly in direct proportion to monomer conversions. Particularly, the M_n (GPC) values are close to the theoretical ones predicted by the ratio of consumed AN to EBiB, implying the negligible number of chains formed from the biradical termination. Concerning the PDI (GPC) values, they tended to lower with increasing monomer conversion, and ranged from 1.30 to 1.20. The corresponding GPC curves are shown in Fig. 3. They shift cleanly and completely, suggesting the increase of the M_n (GPC) values with monomer conversions. All these results powerfully demonstrate that the radical polymerization of AN mediated by $CuBr_2$/Me_6-TREN in DMSO at 35 °C possessed typical LRP characteristics[38].

Influence of Increased Radical Initiator Concentration

According to the ICAR ATRP mechanism, to achieve the highest living/controlled nature, it is recommendatory to use the minimal concentration of radical initiator, *i.e*., to minimize the number of polymer chains originated from radical initiator. The polymerizations with varied radical initiator concentrations were performed, and the results are presented in Table 2. The conventional radical polymerization of AN in the absence of EBiB/$CuBr_2$/Me_6TREN reached 33% monomer conversion after 16 h and produced PAN with M_n = 280000 and PDI = 2.96 (entry 1). In the case of the polymerizations initiated from EBiB/$CuBr_2$/Me_6TREN, an increase in rate of polymerization with the increasing ABVN concentration was observed. For example, the polymerization in the absence of ABVN did not occur and no polymer yielded after 22 h (entry 2). The polymerization with a ratio of [ABVN]/[EBiB] = 0.5 reached 94% monomer conversion after the same duration. The results indicate that radical initiator ABVN is necessary for the radical polymerization of AN using EBiB/$CuBr_2$/Me_6TREN as the initiating system at ambient temperatures. Concerning the molecular weight values, they enhanced with the increase of the ABVN concentration. However, an enlarged difference between the experimental molecular

weight values and the theoretical ones was observed. Additionally, PDI values showed an increasing tendency. Thus, an increase in the ABVN concentration would lead to a loss of the control over the polymerization.

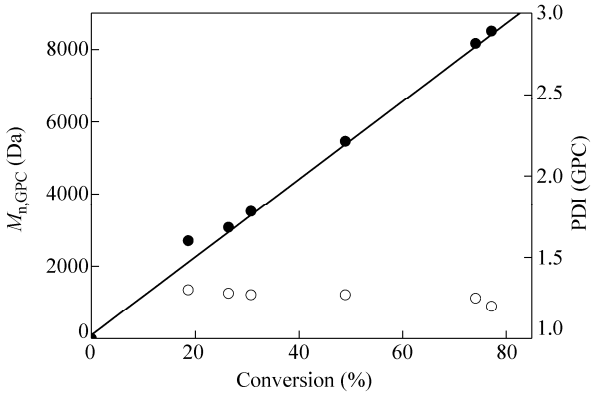


Fig. 2 Evolution of $M_{n,GPC}$ (•) and PDI (o) with conversion for ICAR ATRP of AN ([AN]/[EBiB]/[$CuBr_2$]/[Me_6TREN]/[ABVN] = 200:1:0.01:0.01:0.2, $[AN]_0$ = 7.63 mol/L, AN/DMSO = 1:1 (*V*/*V*) and *T* = 35 °C)

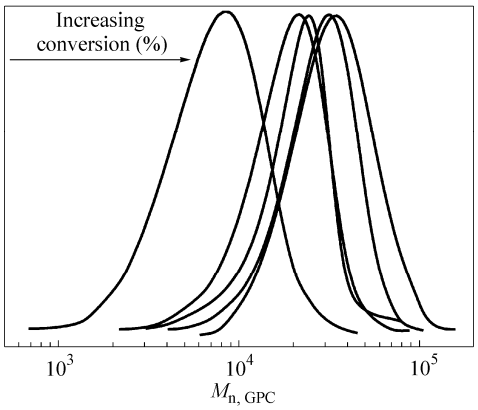


Fig. 3 Evolution of GPC traces for ICAR ATRP of AN ([AN]/[EBiB]/[$CuBr_2$]/[Me_6TREN]/[ABVN] = 200:1:0.01:0.01:0.2, $[AN]_0$ = 7.63 mol/L, AN/DMSO = 1:1 (*V*/*V*) and *T* = 35 °C.)

Table 2. Effect of increased free-radical initiator concentration on ICAR ATRP of AN[a]

No.	[AN]/[EBiB]/[$CuBr_2$]/[Me_6TREN]/[ABVN]	Time (h)	Conv. (%)	$M_{n,th}$ (Da)	$M_{n,GPC}$ (Da)	PDI
1	200:0:0:0:0.1	16	33	–	280000	2.96
2	200:1:0.01:0.01:0	22	0	–	–	–
3	200:1:0.01:0.01:0.1	22	18	2065	3500	1.16
4	200:1:0.01:0.01:0.2	22	77	8379	8510	1.20
5	200:1:0.01:0.01:0.4	22	87	9428	10100	1.22
6	200:1:0.01:0.01:0.5	22	94	10048	12200	1.36

[a] $[AN]_0$ = 7.63 mol/L, AN/DMSO = 1:1 (*V*/*V*) and *T* = 35 °C

Influence of Catalyst Concentration

In general, the molar ratio of Cu(I)/Cu(II) determines the rate of polymerization, while absolute Cu(II) concentration significantly influences PDI. Therefore, it is necessary to examine the influence of catalyst concentration on the polymerization by varying Cu concentrations, *i.e.*, the molar ratio of [$CuBr_2$]/[AN] was changed from 1:20000 to 16:20000 (Table 3). As foreseen, with the increase of Cu concentrations, the rate of polymerization displayed an obvious decrease. At the lowest molar ratio of [$CuBr_2$]/[AN] (1:20000), a polymer yield of 77% conversion was obtained after 22 h (entry 1). At the highest molar ratio of [$CuBr_2$]/[AN] (16:20000), a polymer yield of 48% conversion was obtained under similar reaction conditions (entry 5). Furthermore, the excellent controls of the molecular weights were observed in all cases. Especially, the PDI values remained in a narrow range of 1.20–1.08, and higher copper concentrations induced a slight decrease in PDI value.

Table 3. Effect of catalyst concentration on ICAR ATRP of AN[a]

No.	[AN]/[EBiB]/[$CuBr_2$]/[Me_6TREN]/[ABVN]	Conv. (%)	$M_{n,th}$ (Da)	$M_{n,GPC}$ (Da)	PDI
1	200:1:0.01:0.01:0.2	77	8379	8510	1.20
2	200:1:0.02:0.02:0.2	72	7835	7900	1.21
3	200:1:0.04:0.04:0.2	60	6505	6220	1.19
4	200:1:0.08:0.08:0.2	53	5849	6010	1.13
5	200:1:0.16:0.16:0.2	48	5255	5150	1.08

[a][AN] = 7.63 mol/L, AN/DMSO = 1:1 (*V*/*V*), *T* = 35 °C and reaction time = 22 h

Influence of Reaction Temperature

On the basis of the ICAR ATRP process, the reaction temperature influences the decomposition of radical initiator, and thus changing this parameter can regulate the number of the radicals. The typical polymerization results at varied reaction temperatures (30–45 °C) are shown in Table 4 and Fig. 4. Figure 4 exhibits linear first-order kinetic plots for four investigated reaction temperatures, indicating negligible biradical termination reactions. The k_p^{app} values for 30, 35, 40 and 45 °C were 5.61×10^{-6}, 1.99×10^{-5}, 4.81×10^{-5} and 5.99×10^{-5} s^{-1}, respectively. Clearly, the rate of polymerization enhanced with the increasing reaction temperature from 30 to 45 °C. At 30 °C, a lower monomer conversion of 45% is obtained after 32 h (entry 1). In stead, at 45 °C a higher monomer conversion of 92% is obtained after 12 h (entry 4). The strong increase in rate of polymerization was possibly due to a high concentration of primary radicals at early stage and the increase of all rate constants excited by the enhanced reaction temperature. For the molecular weight results, the differences between the experimental values and theoretical ones enlarged with the increasing reaction temperature. The increasing trend was also reflected in PDI results. It may originate from a higher level of primary radical concentration and termination reactions under this condition.

Table 4. Effect of reaction temperature on ICAR ATRP of AN[a]

No.	Temperature (°C)	Time (h)	Conv. (%)	$M_{n,th}$ (Da)	$M_{n,GPC}$ (Da)	PDI	$k_p^{app} \times 10^5$ (s^{-1})
1	30	32	45	5012	5100	1.10	0.56
2	35	22	77	8379	8510	1.20	1.99
3	40	22	97	10510	11200	1.25	4.80
4	45	12	92	9951	15800	1.30	5.99

[a][AN]/[EBiB]/[$CuBr_2$]/[Me_6TREN]/[ABVN] = 200:1:0.01:0.01:0.2, $[AN]_0$ = 7.63 mol/L, AN/DMSO = 1:1 (*V*/*V*) and *T* = 35 °C

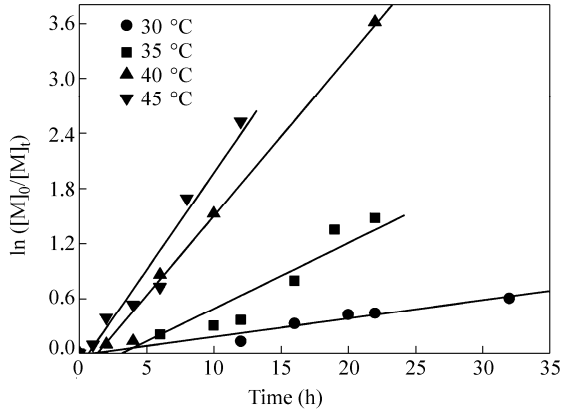


Fig. 4 Kinetics plots of $\ln([M]_0/[M])$ versus reaction time for ICAR ATRP of AN ([AN]/[EBiB]/[$CuBr_2$]/[Me_6TREN]/[ABVN] = 200:1:0.01:0.01:0.2, $[AN]_0$ = 7.63 mol/L and AN/DMSO = 1:1 (*V*/*V*))

Figure 5 exhibits the Arrhenius plot of $\ln k_p^{app}$ versus 1000/*T* for $CuBr_2$/Me_6TREN-mediated ICAR ATRP of AN utilizing ABVN. The apparent activation energy ($\Delta E_{app}^{\neq}$) for the polymerization was calculated to be 128.45 kJ/mol utilizing the Eqs. (1) and (2)[39, 40]. Higher $\Delta E_{app}^{\neq}$ value indicates that the polymerization reaction initiated from EBiB/$CuBr_2$/Me_6TREN/ABVN was strongly dependent of the reaction temperature, demonstrating the increase of rate of polymerization with an enhancement in reaction temperature.

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p[P^\bullet]t = k_p^{app}t \quad (1)$$

$$\ln k_p^{app} = \ln A_{app} - \frac{\Delta E_{app}^{\neq}}{RT} \quad (2)$$

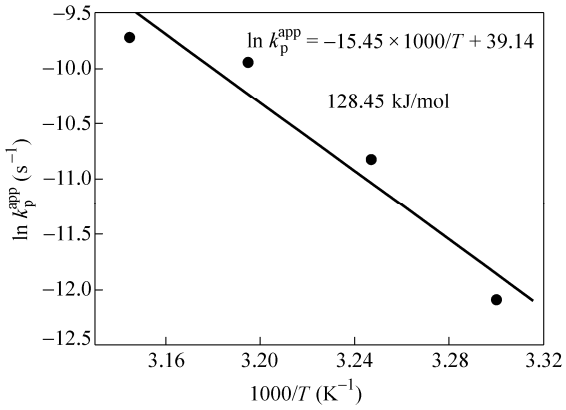


Fig. 5 Plot of apparent rate constant versus reaction temperature ([AN]/[EBiB]/[$CuBr_2$]/[Me_6TREN]/[ABVN] = 200:1:0.01:0.01:0.2, $[AN]_0$ = 7.63 mol/L, AN/DMSO = 1:1 (*V*/*V*))

Chain-end Functionality

Compared with classical radical polymerization, one of the most important LRP features is to generate well-defined polymers with high chain-end functionality. The end-structure of the PAN obtained was analyzed by ^{1}H-NMR and chain extension experiments. As illustrated in Fig. 6, the signals at δ = 1.1–1.3 and δ = 3.9–4.2 corresponded to the methyl (peaks a and c) and the methylene (peak b) protons of EBiB, respectively, providing clear evidence for the incorporation of the EBiB fragments as polymer end groups. Importantly, the signal at δ = 5.0–5.4 corresponds to the methine proton (peak f) of AN unit adjacent to bromine function. The integration

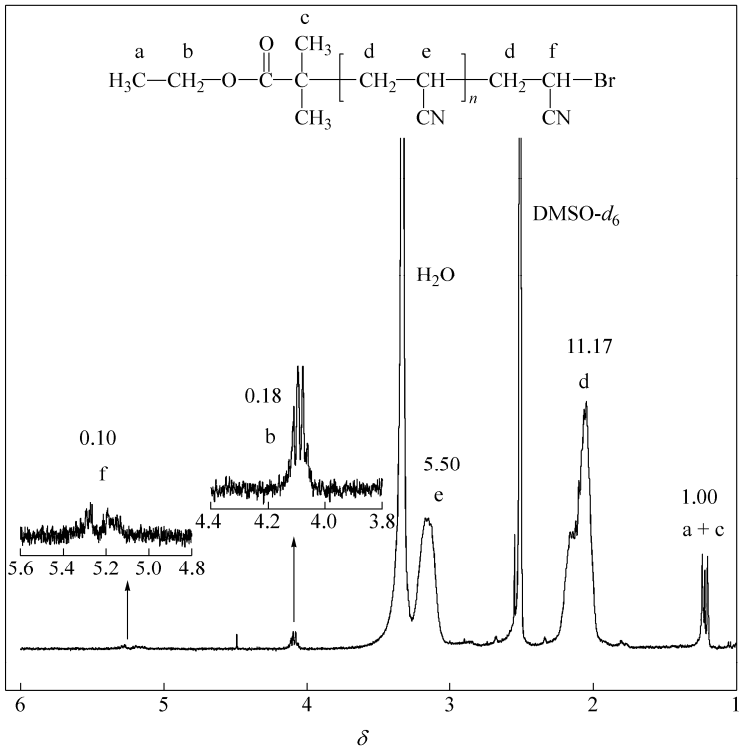


Fig. 6 ^{1}H-NMR spectrum of PAN mediated by ICAR ATRP of AN ([AN]/[EBiB]/[$CuBr_2$]/[Me_6TREN]/[ABVN] = 200:1:0.01:0.01:0.2, $[AN]_0$ = 7.63 mol/L, AN/DMSO = 1:1 (*V*/*V*), *T* = 35 °C and monomer conversion = 19%)

ratio of f/b/a + c is close to 1:2:9. The molecular weight of PAN sample calculated from the ^{1}H-NMR data ($M_{n,NMR}$) was 2623, which was close to the theoretical one ($M_{n,th}$ = 2174). The results prove that the EBiB moieties have been successfully attached to the PAN chain ends, and thus the resultant PAN can be used as the macroinitiator of the chain-extension reaction.

The chain-extension reaction was performed using the same strategy, *i.e.*, the $CuBr_2$/Me_6TREN-mediated ICAR ATRP of AN using ABVN as the radical initiator in DMSO. Figure 7 shows the GPC traces of the original PAN and the chain-extended product. An clear peak shift from the original PAN macroinitiator (M_n (GPC) = 5100, PDI (GPC) = 1.26) to the chain-extension product (M_n (GPC) = 15600, PDI (GPC) = 1.28) was observed. The monomodal GPC trace and low PDI value of the chain-extension product imply the successful chain extension reaction. The results confirm the living/controlled nature of the radical polymerization of AN initiated from EBiB/$CuBr_2$/Me_6TREN/ABVN.

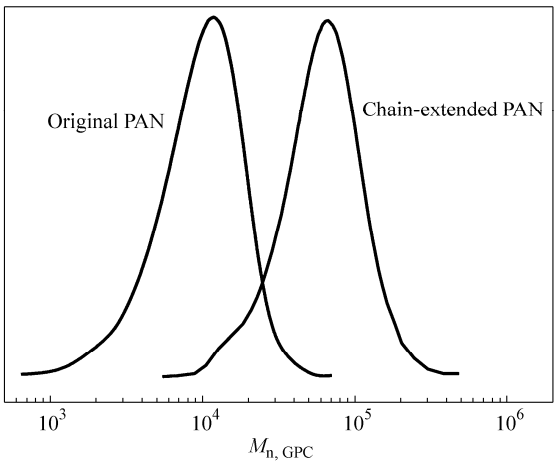
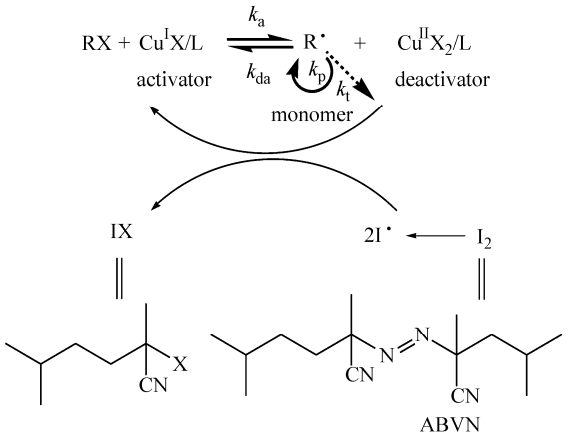


Fig. 7 GPC curve for the original and chain-extended PAN samples ([AN]/[PAN]/[$CuBr_2$]/[Me_6TREN]/[ABVN] = 200:1:0.01:0.01:0.2, $[AN]_0$ = 7.63 mol/L, AN/DMSO = 1:1 (*V*/*V*), *T* = 45 °C, reaction time = 21 h and monomer conversion = 78%.)

Mechanism of AN Polymerization Initiated via EBiB/$CuBr_2$/Me_6TREN/ABVN

As demonstrated above, the $CuBr_2$/Me_6TREN-mediated radical polymerization of AN in presence of ABVN possessed typical living/controlled behaviors, though the initiating system consists of two kinds of initiators, EBiB and ABVN. First, the half-lives of ABVN are *ca.* 84, 44, 23, and 12 h for 30, 35, 40, and 45 °C, respectively. The reaction durations for the four investigated temperatures are 32, 22, 22, and 12 h. Consequently, the decomposed ABVN amounts at the stop of the polymerization are 23%, 29%, 48%, and 50% of the original ABVN amounts for 30, 35, 40, and 45 °C, respectively. Additionally, the radicals from ABVN can not be instantly trapped by the deactivator Cu(II) and transformed into halogen compound I-X, simultaneously generating Cu(I) because the $CuBr_2$/AN molar ratios are very low (*i.e.*, 1:20000–16:20000). As a result, ABVN would potentially contribute to formation of the polymer chains because the amount of ABVN can not be negligible. To simplify the initiating system and conveniently calculate the theoretical molecular weight of the resultant polymer, a mechanism is proposed to explain the polymerization and is shown in Scheme 2. First, a low concentration of the moderate temperature radical initiator, ABVN, worked solely and effectively for reducing Cu(II) to Cu(I) species at various ambient temperatures. Furthermore, with the assistance of high reactivity catalytic system ($CuBr_2$/Me_6TREN) and low reaction temperatures (30–45 °C), the bimolecular termination was efficiently suppressed, and the polymerization even with a low molar ratio of [$CuBr_2$]/[AN] = 1:20000 proceeded in a living/controlled way up to a high monomer conversion than 97%, as evidenced by the controlled molecular weight, low PDI and high chain-end functionality.



Scheme 2 Mechanism of ICAR ATRP

CONCLUSIONS

The ICAR ATRP of AN has been successfully carried out at various ambient temperatures (30–45 °C) using an appropriate moderate temperature radical initiator, ABVN. ABVN, associating with a high reactivity catalytic system (*i.e.*, $CuBr_2/Me_6TREN$), efficiently prompts the polymerization to proceed in a living/controlled manner. The control of the polymerization was studied in terms of ligand, ABVN concentration, copper concentration and reaction temperature. Me_6TREN was demonstrated to provide better control of the polymerization than other ligands suitable for AN, such as bpy, PMDETA and HMTA. The increase of ABVN concentration and reaction temperature induces a dramatic rate increase, while still keeping low PDI, suggesting a strong dependence of two experimental parameters. In contrast, the increase of the $CuBr_2$/AN molar ratio from 1:20000 to 16:20000 decreased the rate of polymerization but improved the control of molecular weight and PDI. GPC and ^{1}H-NMR analytic techniques as well as the chain-extension reaction confirmed the very high chain-end functionality of the resulting polymers.

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