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High Molecular Weight and Low Dispersity Polyacrylonitrile by Low Temperature RAFT Polymerization

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ABSTRACT: High molecular weight polyacrylonitrile (PAN) with low dispersity has been successfully synthesized utilizing reversible addition-fragmentation chain transfer (RAFT) polymerization. A comprehensive study was performed to understand the influence of reaction temperature, RAFT agent structure, and $[M]_0:[CTA]_0:[I]_0$ on the polymerization kinetics, molecular weight, and dispersity. Enhanced control is attributed to reduction of side reactions by conducting the polymer-

ization at lower temperature, and optimizing the radical exchange between active and dormant states via appropriate selection of RAFT agent and initiator. © 2015 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 553–562

KEYWORDS: kinetics (polyn); molecular weight distribution; reversible addition fragmentation chain transfer (RAFT); synthesis

INTRODUCTION Polyacrylonitrile (PAN)-containing copolymers are the leading precursor materials for carbon fiber production, comprising approximately 90% of all production world wide.¹ PAN-based carbon fibers are recognized for their outstanding tensile strength as compared to other precursor materials² and are, therefore utilized in a variety of industries, including aerospace, automotive, wind turbines, and sports and leisure. Although PAN-based carbon fibers have impressive mechanical properties, their measured value of tensile strength falls well below that from theoretical predictions due to impurities and defects.³ It is known that the polymerization of acrylonitrile and the precursor polymer characteristics are of critical importance to the carbon fiber properties.⁴ Since the first report of PAN-based carbon fibers by Shindo in 1961,⁵ PAN precursors have been polymerized primarily by solution and suspension polymerization, with solution polymerization being most favorable due to immediate manufacture of spinning dopes.^{4,6} The two main drawbacks to solution polymerized precursors are that monomer conversion is typically only 50–70%, and that conventional solvent systems are characterized by high transfer constants leading to undesirable side reactions during polymerization.⁶

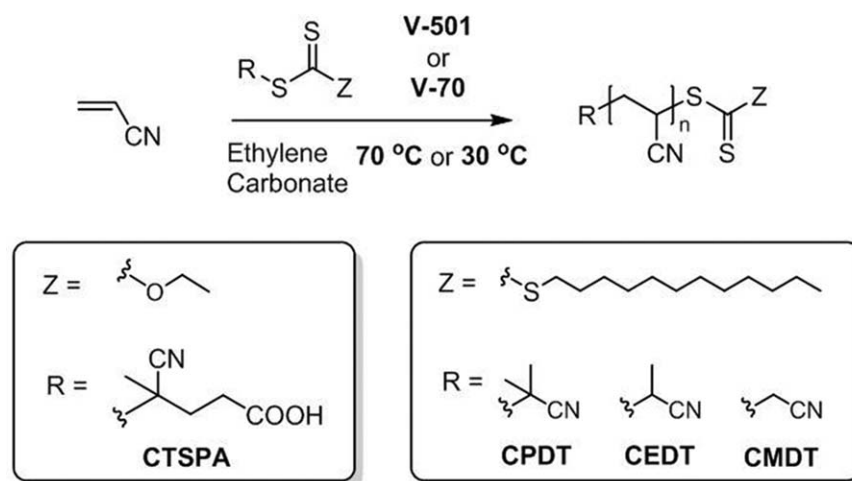
With the advent of contemporary reversible-deactivation radical polymerization (RDRP) methods, several attempts have been reported to control the polymerization of AN and its comonomers utilizing atom transfer radical polymerization

(ATRP),^{7–10} activators regenerated by the electron transfer (ARGET) ATRP,¹¹ and reversible addition-fragmentation chain transfer (RAFT) polymerization.^{12–19} Despite these efforts, there has been limited success in obtaining high molecular weight PAN with narrow dispersities. Suitable molecular weights for carbon fiber production typically range between 70,000–200,000 g/mol.² Meanwhile, the dispersity (\mathcal{D}_M), M_w/M_n , typically ranges from 1.5 to 3.0.^{2,20} Molecular weight and molecular weight distribution have been shown to influence the microstructure of resulting carbon fiber.^{17,21,22} Specifically, Lin et al.²² and Tsai et al.²³ have shown that higher molecular weight leads to grooved surfaces and changes in the cross-section of the fiber. Moreover, the high molecular weight fractions in uncontrolled free radical polymerizations tend to be insoluble and cause problems such as gelation during fiber spinning and filtration.^{19,24} Therefore, controlling molecular weight and \mathcal{D}_M of PAN is essential before considering other precursor properties, such as comonomer selection and tacticity, to avoid confounding variables.

Dong et al.¹¹ utilized ARGET ATRP at long reaction times (>90 h) to prepare PAN with molecular weights above 200,000 g/mol (SEC-MALLS) with relatively high \mathcal{D}_M of 1.45. Yet, at shorter reaction times (<90 h) conversions remained below 60% and molecular weights below 100,000 g/mol. Also, ATRP necessitates the use of a metal catalyst, which can be difficult to remove and the residual metal ions are

This article was published online on 28 August 2015. An error was subsequently identified. This notice is included in the online and print versions to indicate that both have been corrected on 30 September 2015.

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SCHEME 1 General synthetic route for the RAFT polymerization of acrylonitrile.

detrimental to carbon fiber fabrication.¹⁸ Pan et al.²⁵ recently reported on the photoinduced metal-free ATRP of acrylonitrile, but the resulting polymers were of low molecular weight (<15,000 g/mol) and broad D_M (>1.5).

Alternatively, RAFT polymerization is a versatile RDRP technique with excellent functional group tolerance²⁶ and shows promise for the production of carbon fiber precursor materials with controlled molecular weights and narrow dispersities. Niu et al.¹⁸ utilized a bifunctional dithiocarbamate to achieve relatively high molecular weight (>100,000 g/mol) and low D_M (<1.4) PAN using RAFT. More recently, Spörl et al.^{19,24} demonstrated high conversion (>80%) of AN in less than 7 h with the use of 2-cyano-2-propyl dodecyltrithiocarbonate (CPDT) at 90 °C. However, References ([18, 19 and 24]) report molecular weights relative to polymethylmethacrylate (PMMA) standards, which overestimate the molecular weight of PAN.¹¹ In addition, these studies show nonlinear first-order kinetics for reaction times beyond 8 h.

It was first shown in 1995 by Kim et al.²⁷ that the low decomposition temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (V-70), could be used to polymerize acrylonitrile under conventional free-radical solution conditions at 30 °C. Higher molecular weights were indicated by increased inherent viscosities as compared to those initiated by 2,2'-azobis(isobutyronitrile) (AIBN) at 50 °C. Similarly, high conversions and narrow dispersities have been achieved during the room temperature RAFT polymerizations of acrylamide, *N,N*-dimethylacrylamide, and *N*-isopropylacrylamide using V-70 as the initiator.^{28,29} In addition, Dong et al. demonstrated that lowering the temperature of the ATRP of AN from 65 to 40 °C resulted in narrower dispersities.¹¹

In this study, our goals were to synthesize PAN with high molecular weight and low dispersity via RAFT polymerization. We investigated the effects of RAFT agent structure, reagent concentrations, and temperature on the molecular weight, dispersity, and kinetics of polymerization. Significantly, we show that low temperature polymerizations improve molecular weight control in the RAFT polymeriza-

tion of acrylonitrile. Using the commercially available RAFT agent, CPDT at 30 °C, PAN with high molecular weight, and low dispersity was successfully prepared. The ability to synthesize precisely controlled molecular weight and dispersity PAN and PAN copolymers provides a new platform for studying carbon fiber precursor chemistries of interest to the global carbon fiber scientific community.

EXPERIMENTAL

Materials

Acrylonitrile (AN, 99%, 35–45 ppm monomethyl ether hydroquinone inhibitor (MEHQ), Sigma-Aldrich Chemical) was passed through a neutral aluminum oxide (50–200 μm) column to remove the inhibitor immediately prior to use. Ethylene carbonate (EC, 99%, Alfa Aesar), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT, 97%, Sigma-Aldrich Chemical), cyanomethyl dodecyl trithiocarbonate (CMDT, 98%, Sigma-Aldrich Chemical), 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako Pure Chemical Industries), and 4,4'-azobis(4-cyanopentanoic acid) (V-501, 99%, Sigma-Aldrich Chemical) were used as received. Cyanoethyl dodecyl trithiocarbonate (CEDT) and 4-cyano-4-((thioethoxy)sulfanyl)pentanoic acid (CTSPA) were synthesized according to literature procedures and purified via column chromatography.^{30,31}

RAFT Polymerization

A representative RAFT polymerization of AN at $[\text{AN}]_0: [\text{CPDT}]_0: [\text{V-501}]_0 = 2,000:1:0.4$ was conducted as follows: ethylene carbonate (32.0 g), acrylonitrile (7.97 g, 150 mmol, 20 wt %), CPDT (26.0 mg, 0.075 mmol, 1300 μL of a 20 mg/mL stock solution in dimethylformamide (DMF)), and V-501 (8.4 mg, 0.030 mmol, 420 μL of a 20 mg/mL stock solution in DMF) were charged into a 100 mL round bottom flask equipped with a rubber septum and magnetic stir bar. For polymerizations conducted at 30 °C, a stock solution of V-70 (20 mg/mL) in tetrahydrofuran (THF) was used. The reaction flask was cooled to 0 °C and subsequently purged with N_2 for 60 min prior to heating in an oil bath at 70 °C. At timed intervals, 1 mL aliquots were drawn and analyzed

by $^1\text{H-NMR}$ (DMSO-d_6) by comparing the relative integral areas of ethylene carbonate (δ (ppm): s, 4.50, CH_2) to the vinyl protons of AN (δ (ppm): d, 6.22; d, 6.36, CH_2 ; quad, 6.00, CH). SEC-MALLS (DMF 20 mM LiBr) was used to monitor molecular weight progression and \bar{D}_M during each polymerization.

Characterization

$^1\text{H-NMR}$ experiments were recorded with a Bruker AcendTM 600 MHz spectrometer at 30 °C with 5 wt % solutions in DMSO-d_6 using 32 scans and a 1 s relaxation delay. Monomer conversion was followed throughout the reaction by tracking the relative monomer concentration (δ (ppm): d, 6.22; d, 6.36; quad, 6.00) with respect to the ethylene carbonate (δ (ppm): s, 4.50).

Number average molecular weight (M_n), weight average molecular weight (M_w), and \bar{D}_M of the polymer materials were measured using a GPC system consisting of a Waters Alliance 2695 separation module, online multiangle laser light scattering (MALLS) detector fitted with a gallium arsenide laser (20 mW power) operating at 690 nm (MiniDAWN Wyatt Technology), an interferometric refractometer (Optilab DSP, Wyatt Technology), and two Agilent PLgel mixed-C columns connected in series. HPLC grade N,N' -dimethylformamide (DMF) with 20 mM LiBr served as the mobile phase and was delivered at a flow rate of 0.5 mL/min while operating at 60 °C. Sample concentrations were prepared at approximately 5 mg/mL with an injection volume of 100 μL . The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology). The dn/dc for PAN (0.084 mL/g) in the above eluent was determined offline from the slope of the refractive index versus polymer concentration plot generated from refractive index measurements made at five polymer concentrations between 1 and 10 mg/mL. The measured dn/dc value was in excellent agreement with the dn/dc value calculated from the response of the interferometric refractometer, assuming 100% mass recovery (0.086 mL/g). Molecular weights were also determined relative to polymethyl methacrylate (PMMA) standards.

RESULTS AND DISCUSSION

The general RAFT polymerization of AN is outlined in Scheme 1. Ethylene carbonate was utilized as the solvent to minimize chain transfer to solvent.^{15,32} The effects of RAFT agent structure $[M]_0:[\text{CTA}]_0:[I]_0$, and polymerization temperature on molecular weight, \bar{D}_M , and polymerization rate were investigated. Judicious selection of the RAFT agent is necessary to achieve successful polymerization control of a given monomer. The free radical leaving R-group determines the fragmentation efficiency,³³ while the Z-group modifies the reactivity of the thiocarbonylthio compound and the derived adduct radical.³⁴ There are established classes based on R- and Z-groups of suitable RAFT agents for select monomers,^{26,35} and the homopolymerization of AN has been conducted using dithiobenzoates,^{12,13,15} trithiocarbonates,^{13,19,24} as well as dithiocarbamates.¹⁸ However, to date there are no reported examples of xanthate-mediated RAFT polymeriza-

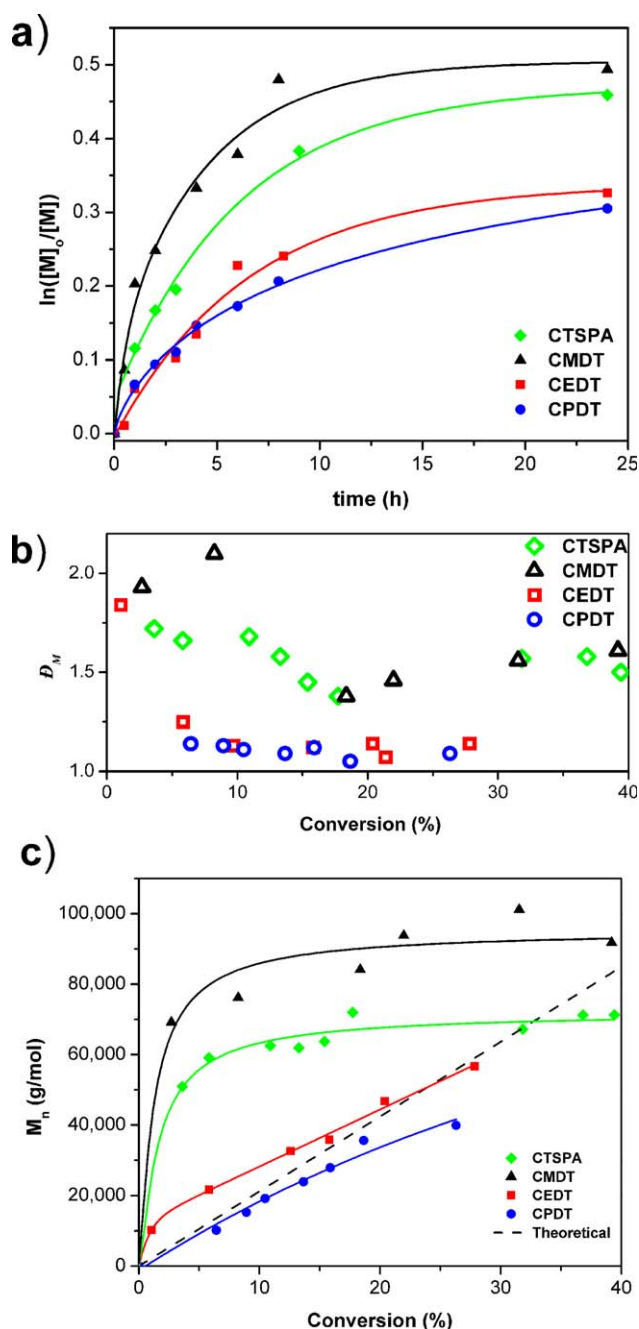


FIGURE 1 (a) $\ln([M]_0/[M])$ versus time plots, (b) \bar{D}_M versus conversion, and (c) M_n (SEC-MALLS) versus conversion plots for selected RAFT agents at 70 °C and $[M]_0:[\text{CTA}]_0:[I]_0 = 4,000:1:0.4$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tions of AN. Xanthates provide more active intermediate radicals by a lower chain transfer constant, which could increase conversions and molecular weights as compared to trithiocarbonates.³⁴ Thus, we first investigated xanthate-mediated polymerization of AN and subsequently studied the effects of R-group $[M]_0:[\text{CTA}]_0:[I]_0$, and temperature on achieving high molecular weight, low dispersity PAN.

TABLE 1 Conversion, Molecular Weight, and \bar{M}_n Data for the RAFT Polymerization of AN Conducted at 70 °C

Entry ^a	RAFT agent	$[M]_0:[CTA]_0:[I]_0$	Time (h)	Conv. ^b (%)	$M_{n,th}$ (g/mol) ^c	$M_{n,exp}$ (g/mol) ^d	$M_{n,PMMA}$ (PMMA eq.) ^e	\bar{M}_n^d
1a	CTSPA	4,000:1:0.4	3	18	38,200	72,000	214,300	1.38
1b	CTSPA	4,000:1:0.4	6	32	67,900	67,300	207,300	1.57
1c	CTSPA	4,000:1:0.4	24	37	78,800	74,600	191,000	1.58
2a	CMDT	4,000:1:0.4	3	22	46,400	93,800	365,800	1.46
2b	CMDT	4,000:1:0.4	6	32	67,600	83,400	330,900	1.81
2c	CMDT	4,000:1:0.4	24	36	76,700	77,300	310,200	1.42
3a	CEDT	4,000:1:0.4	3	10	20,900	35,900	117,700	1.13
3b	CEDT	4,000:1:0.4	6	20	43,600	46,800	144,300	1.14
3c	CEDT	4,000:1:0.4	24	28	59,400	56,700	152,300	1.14
4a	CPDT	4,000:1:0.22	3	9	19,500	15,200	47,400	1.24
4b	CPDT	4,000:1:0.22	6	12	25,900	18,100	49,300	1.08
4c	CPDT	4,000:1:0.22	24	16	33,200	21,500	54,300	1.10
5a	CPDT	4,000:1:0.4	3	10	22,600	22,300	58,500	1.09
5b	CPDT	4,000:1:0.4	6	16	34,000	27,900	81,300	1.08
5c	CPDT	4,000:1:0.4	24	26	56,200	39,900	113,600	1.14
6a	CPDT	4,000:1:0.67	3	12	25,800	29,600	81,700	1.12
6b	CPDT	4,000:1:0.67	6	22	48,100	43,900	117,500	1.08
6c	CPDT	4,000:1:0.67	24	41	86,800	51,000	143,500	1.18

^a Polymers synthesized in ethylene carbonate at 20 wt % monomer concentration under a nitrogen atmosphere with V-501 as the initiator.

^b Conversions were determined by ¹H-NMR spectroscopy recorded in DMSO-*d*₆.

^c Theoretical number average molecular weights were calculated according to the following equation: $M_n = (\rho \cdot MW_{mon} \cdot [M]/[CTA]) + MW_{CTA}$

where ρ is the fractional monomer conversion, MW_{mon} is the molecular weight of the monomer, and MW_{CTA} is the molecular weight of the CTA.

^d Number average molecular weight (M_n) as determined by SEC (0.5 mL/min, 60 °C, polymer labs PL gel 5 μ m mixed-C column, DMF with 20 mM LiBr eluent) equipped with RI and MALLS detectors.

^e M_n expressed as equivalents of PMMA standards.

RAFT Polymerizations of AN at 70 °C

We first compared the effect of Z-group on the RAFT polymerization of AN using the xanthate CTSPA, and the commercially available trithiocarbonate CPDT; the latter has been shown to successfully control the RAFT polymerization of AN.¹⁹ Figure 1 shows $\ln([M]_0/[M])$ versus time [Fig. 1(a)], \bar{M}_n versus conversion [Fig. 1(b)], and M_n versus conversion [Fig. 1(c)] plots for the CTSPA- and CPDT-mediated polymerizations of AN in ethylene carbonate at 70 °C ($[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.4$). The results for polymerizations performed at 70 °C are summarized in Table 1.

As observed in Figure 1(a), the kinetic plots for both the CTSPA- and CPDT-mediated polymerizations of AN deviate significantly from pseudo-first-order behavior beyond approximately 4 h. The slope of the kinetic plot is linear when the rate of polymerization (R_p) is first order with respect to $[M]$ while $k_p[P_n]$ is constant where k_p is the propagation rate constant and $[P_n]$ is the concentration of propagating radicals.³⁶ This indicates that the propagating radical concentration is likely diminishing over time due to deleterious chain transfer and/or radical termination events. Limited monomer conversion was observed beyond 10 h during CTSPA- and CPDT-mediated polymerization of AN which has been in part attributed to the reduced radical flux observed as initiator concentration decreases after prolonged reaction times,³⁷ but also suggests irreversible side reactions. Figure

1(b,c) show the influence of RAFT agent Z-group on molecular weight progression during the CTSPA- and CPDT-mediated polymerizations of AN at 70 °C. The CPDT-mediated polymerization of AN shows linear progression in molecular weight with conversion while experimentally determined molecular weights ($M_{n,exp}$) are in good agreement with the theoretical molecular weights ($M_{n,theory}$) calculated from monomer conversion [Fig. 1(c), dashed line]. In addition, dispersities remained low ($\bar{M}_n < 1.20$) throughout the CPDT-mediated polymerization of AN at 70 °C (Table 1; entries 5a–c). In contrast, the CTSPA-mediated polymerization of AN results in $M_{n,exp}$ values exceeding the $M_{n,theory}$ values at low monomer conversions while dispersities increase with conversion ($\bar{M}_n > 1.50$) (Table 1, entries 1a–c). The poor control exhibited during the CTSPA-mediated polymerization of AN is likely due to the lower chain transfer constant of xanthates as compared to analogous trithiocarbonates, which give higher probability for the propagating chain to add to monomer than for addition to the CTA.³⁴ The difference in molecular weight control is demonstrated by the progressive refractive index (RI) traces obtained from SEC analysis for CPDT- [Fig. 2(a)] and CTSPA- [Fig. 2(b)] mediated polymerizations.

The SEC chromatogram overlay for the CPDT-mediated polymerization of AN [Fig. 2(a)] shows a distinct shift in the RI peaks toward shorter elution times as the reaction progresses, consistent with the RAFT process in the absence of

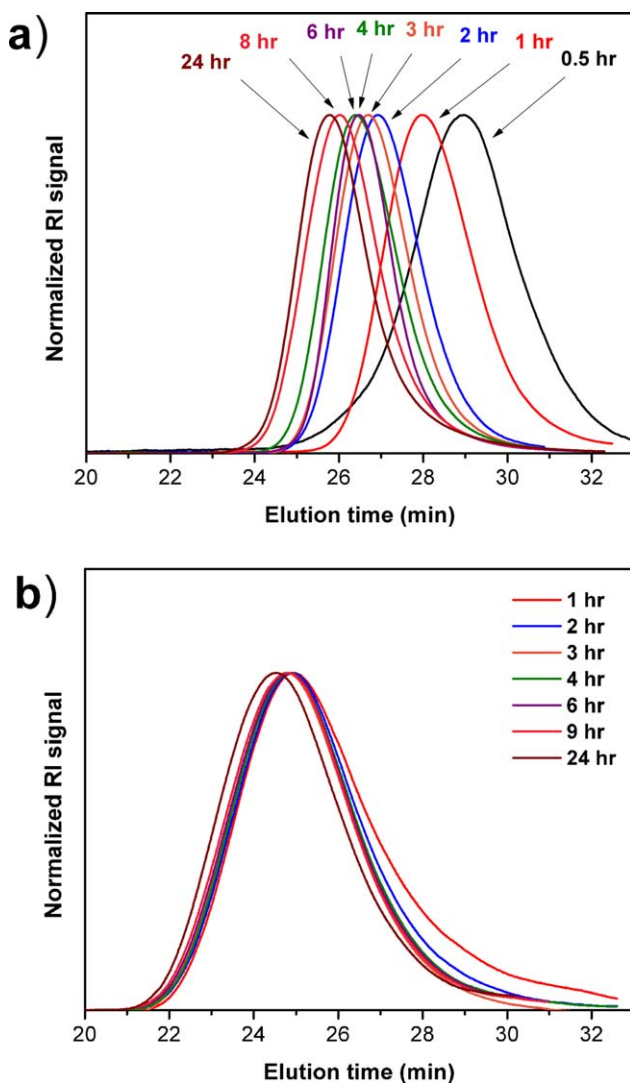


FIGURE 2 Progressive RI traces for the polymerization of AN using (a) CPDT and (b) CTSPA at 70 °C with $[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.4$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

significant termination and/or undesirable chain transfer events. However, beyond 8 h, a minimal increase in monomer conversion and molecular weight was observed, indicating a loss in the “livingness” of the polymerization at longer reaction times. In comparison, the CTSPA-mediated polymerization of AN results in a rapid increase in molecular weight at low conversions [Fig. 1(c)] with little change in the elution time of the SEC chromatogram RI traces [Fig. 2(b)] suggesting that CTSPA does not adequately mediate the polymerization of AN under the chosen conditions.

We chose to utilize trithiocarbonate CTAs in subsequent efforts to achieve high molecular weight, low dispersity PAN. We first evaluated the effect of the trithiocarbonate R-group on the RAFT polymerization of AN at 70 °C. It has been reported previously that the R-group can have a significant

role in the re-initiating ability of *N,N*-dimethylacrylamide utilizing dithiobenzoates.³⁸ Thus, we explored three different cyanoalkyl R-groups ranging from primary radical (CMDT) to tertiary radical (CPDT) leaving groups (Table 1, entries 2–3). The kinetic plot [Fig. 1(a)] for CEDT-mediated polymerization of AN exhibits very similar behavior to CPDT in that rapid monomer conversion is achieved early in the reaction, followed by a decrease in the rate of monomer consumption after 4 h. In contrast, the CMDT-mediated polymerization shows a faster initial rate of polymerization [Fig. 1(a)] but lacks control with broad dispersity [Fig. 1(b)] and nonlinear progression of molecular weight with conversion [Fig. 1(c)] as compared to the CEDT- and CPDT-mediated polymerizations. This is attributed to poor fragmentation and slow reinitiation by the primary cyanomethyl radical, thus increasing the likelihood of monomer propagation before complete initialization of the RAFT agent.³⁹ This effect is also observed to some extent during the CEDT-mediated polymerization of AN, which shows an initial overshooting of $M_{n,exp}$ relative to $M_{n,theory}$ but a linear progression in $M_{n,exp}$ that tends towards the theoretical values at higher conversions [Fig. 1(c)]. The CPDT-mediated polymerization of AN offered promising molecular weight control, prompting our investigation of the effect of $[CTA]_0:[I]_0$ on the molecular weight progression (Fig. 3 and Table 1, entries 4–6).

Typically, an increase in initiator concentration results in a higher concentration of initiator-derived polymer chains, which leads to deviation from pseudo-living behavior and an increased D_M .¹⁵ In this case, the theoretical molecular weight ($M_{n,th}$) is determined by³⁷ in which $[M]_0$ and $[CTA]_0$ are the initial concentrations of monomer and chain transfer agent (CTA), respectively, M_{MW} and CTA_{MW} are the molecular weights of the monomer and CTA, respectively, ρ is the fractional monomer conversion, and $[P_n]$ are chains derived from the initiator species:

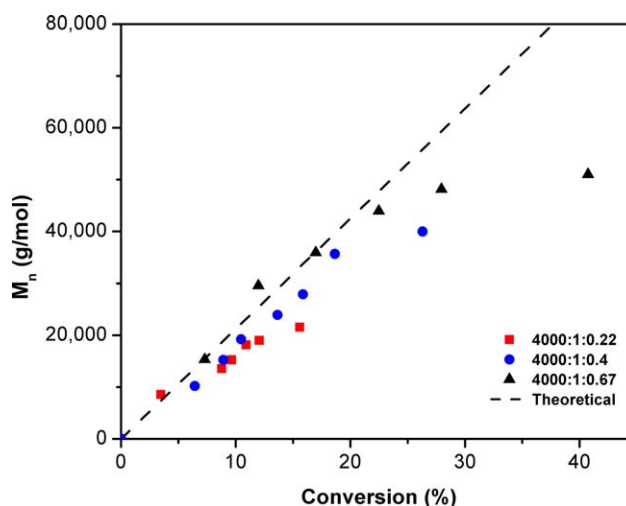


FIGURE 3 M_n (SEC-MALLS) versus conversion for the CPDT-mediated RAFT polymerization of AN at 70 °C at various $[CTA]_0:[I]_0$ ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

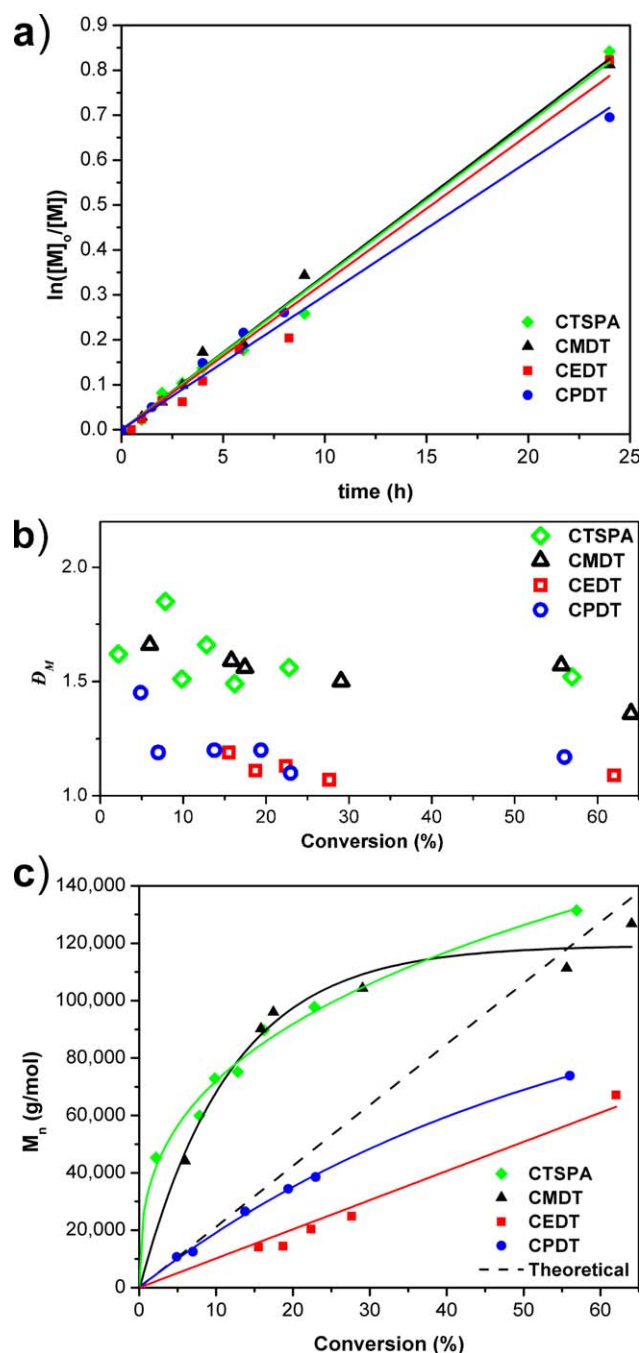


FIGURE 4 (a) Kinetic plots, (b) \bar{D}_M versus conversion, and (c) molecular weight (SEC–MALLS) versus conversion for polymerization of AN utilizing selected RAFT agents at 30 °C and $[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.4$. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

$$M_{n,th} = \frac{M_{MW}[M]_0 \cdot \rho}{[CTA]_0 + [P_n]} + CTAMW \quad (1)$$

$[P_n]$ increases as $[CTA]_0:[I]_0$ decreases due to the lower probability of initiator adding to CTA and establishing the RAFT equilibrium. However, when the $[CTA]_0:[I]_0$ is suitably large, $[P_n]$ is expected to be negligible. Interestingly, increasing the

$[CTA]_0:[I]_0$ to 1:0.67 under these reaction conditions resulted in minimal deviation from $M_{n,th}$ while conversion increased to over 40% after 24 h.

Evident from Table 1, the polymerizations of AN mediated by CPDT and CEDT exhibit lower molecular weight distributions than those mediated by CTSPA and CMDT. Also, the conversions for entries 1–5 remained below 40% after 24 h of polymerization. It was found that conversion and molecular weight could be increased by more than 10% at the expense of increasing \bar{D}_M by decreasing the $[CTA]_0:[I]_0$ (Table 1, entries 6a–c). Molecular weights were also reported relative to PMMA standards for comparison with literature reported values due to the issues of performing SEC on PAN.¹¹

Thus far, our efforts to achieve high molecular weight and low \bar{D}_M PAN by varying the CTA structure and $[M]_0:[CTA]_0:[I]_0$ were unsatisfactory. It has been shown that conversion and molecular weight of conventional solution polymerization of AN can be increased by utilizing lower temperature polymerizations.^{27,40} Moreover, other issues commonly associated with polymerization of acrylamides, such as nonuniform \bar{D}_M , have been addressed with low temperature RAFT polymerization.^{28,29} Therefore, we explored the effects of lowering the reaction temperature on achieving high molecular weights while maintaining low \bar{D}_M .

RAFT Polymerizations of AN at 30 °C

The polymerization temperature of 30 °C was selected based on the decomposition temperature of the initiator, V-70, which has the same initiator efficiency as V-501 at 70 °C. The RAFT polymerization conditions for AN at 30 °C were otherwise analogous to those at 70 °C. The kinetic plots, \bar{D}_M versus conversion, and M_n versus conversion plots at $[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.22$ are shown in Figure 4(a–c).

As seen in Figure 4(a), the kinetic plots for all CTAs used exhibit pseudo-first-order behavior up to 24 h, which indicates a constant $k_p[P\cdot]$ at 30 °C and that monomer is still being consumed at long reaction times. For thermally initiated polymerizations, the kinetic chain length, ν , is expressed as R_p/R_t , where R_p is the rate of propagation and R_t is the rate of termination. R_p decreases with decreasing temperature, however, R_t typically decreases at a much faster rate than R_p .⁴¹

Figure 4(b) and (c) are consistent with the 70 °C results showing that CEDT and CPDT are the most effective CTAs in controlling molecular weight and \bar{D}_M of PAN. Furthermore, at 24 h, the conversions reach about 60% for all CTAs studied and molecular weights determined by SEC–MALLS were in excess of 60,000 g/mol. The RI traces for the CPDT-mediated polymerization of AN at 30 °C (Fig. 5) are unimodal and shift to lower elution times with increasing conversion up to 24 h. Table 2 summarizes the results of the polymerizations performed at 30 °C.

The data in Table 2 show that reducing the polymerization temperature to 30 °C allows for higher conversions and

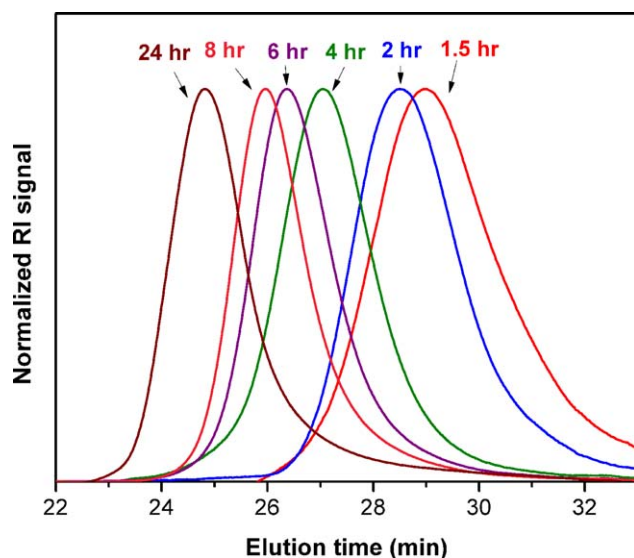


FIGURE 5 RI traces for the CPDT-mediated polymerization of AN at 30 °C with $[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.4$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular weights to be reached. Entries 10–12, which parallel entries 4–6, show that as $[CTA]_0:[I]_0$ decreases, higher conversions can be achieved at the expense of increasing D_M

and a greater deviation in $M_{n,exp}$ and $M_{n,th}$ values. Figure 6 shows the respective kinetic and molecular weight versus conversion plots of the CPDT-mediated polymerizations of AN at 30 and 70 °C. Figure 6(a) shows that the conversion at 30 °C surpasses that of the polymerization at 70 °C at about 6 h. It is suggested that fewer radicals are lost by chain termination and chain transfer events at 30 °C,^{27–29} and that the reduced radical flux at prolonged reaction times at 70 °C results in a slowing of the polymerization rate, or a decrease in the slope.³⁷ Figure 6(b) shows that after 6 h, conversion at 30 °C surpasses conversion obtained during the analogous reaction at 70 °C.

High Molecular Weight RAFT Polymerizations of AN at 30 °C

The above results show AN polymerizations mediated by CPDT or CEDT at 30 °C exhibit controlled molecular weights while maintaining low D_M up to 24 h. At long reaction times $M_{n,exp}$ deviates from $M_{n,th}$, but polymerizations still show higher conversions as compared to the analogous 70 °C reactions at 24 h. Commercially used PAN-based carbon fiber precursors traditionally have molecular weights above 100,000 g/mol. Therefore, we investigated the effect of $[M]_0:[CTA]_0:[I]_0$ on achieving molecular weights greater than 100,000 g/mol for reaction times up to 48 h.

TABLE 2 Conversion, Molecular Weight, and D_M for the RAFT Polymerization of AN Conducted at 30 °C

Entry ^a	RAFT Agent	$[M]_0:[CTA]_0:[I]_0$	Time (h)	Conv. ^b (%)	$M_{n,th}$ (g/mol) ^c	$M_{n,exp}$ (g/mol) ^d	$M_{n,PMMA}$ (PMMA eq.) ^e	D_M
7a	CTSPA	4,000:1:0.4	4	13	27,600	75,200	254,200	1.66
7b	CTSPA	4,000:1:0.4	6	16	34,000	89,700	273,700	1.49
7c	CTSPA	4,000:1:0.4	24	57	121,000	131,500	237,800	1.52
8a	CMDT	4,000:1:0.4	4	16	33,600	90,200	309,500	1.59
8b	CMDT	4,000:1:0.4	6	18	37,900	96,000	342,200	1.56
8c	CMDT	4,000:1:0.4	24	64	136,200	126,600	318,070	1.36
9a	CEDT	4,000:1:0.4	4	19	40,000	20,300	68,800	1.13
9b	CEDT	4,000:1:0.4	6	28	59,000	24,900	54,600	1.07
9c	CEDT	4,000:1:0.4	24	62	131,900	70,300	196,200	1.09
10a	CPDT	4,000:1:0.22	4	12	25,800	21,000	54,000	1.11
10b	CPDT	4,000:1:0.22	6	18	38,500	25,800	71,700	1.11
10c	CPDT	4,000:1:0.22	24	40	84,800	69,000	183,300	1.07
11a	CPDT	4,000:1:0.4	4	14	29,300	27,700	69,000	1.47
11b	CPDT	4,000:1:0.4	6	19	41,200	36,000	96,300	1.20
11c	CPDT	4,000:1:0.4	24	57	121,300	73,900	201,900	1.17
12a	CPDT	4,000:1:0.67	4	19	41,100	34,400	93,600	1.08
12b	CPDT	4,000:1:0.67	6	24	50,900	43,300	128,100	1.11
12c	CPDT	4,000:1:0.67	24	63	134,200	84,800	301,500	1.24

^a Polymers synthesized in ethylene carbonate at 20 wt.% monomer concentration under a nitrogen atmosphere with V-70 as the initiator.

^b Conversions were determined by ¹H-NMR spectroscopy recorded in DMSO-d₆.

^c Theoretical number average molecular weights were calculated according to the following equation: $M_n = (\rho \cdot MW_{mon} \cdot [M]/[CTA]) + MW_{CTA}$

where ρ is the fractional monomer conversion, MW_{mon} is the molecular weight of the monomer, and MW_{CTA} is the molecular weight of the CTA.

^d Number average molecular weight (M_n) as determined by SEC (0.5 mL/min, 60 °C, polymer labs PL gel 5 μ m mixed-C column, DMF with 20 mM LiBr eluent) equipped with RI and MALLS detectors.

^e M_n expressed as equivalents of PMMA standard.

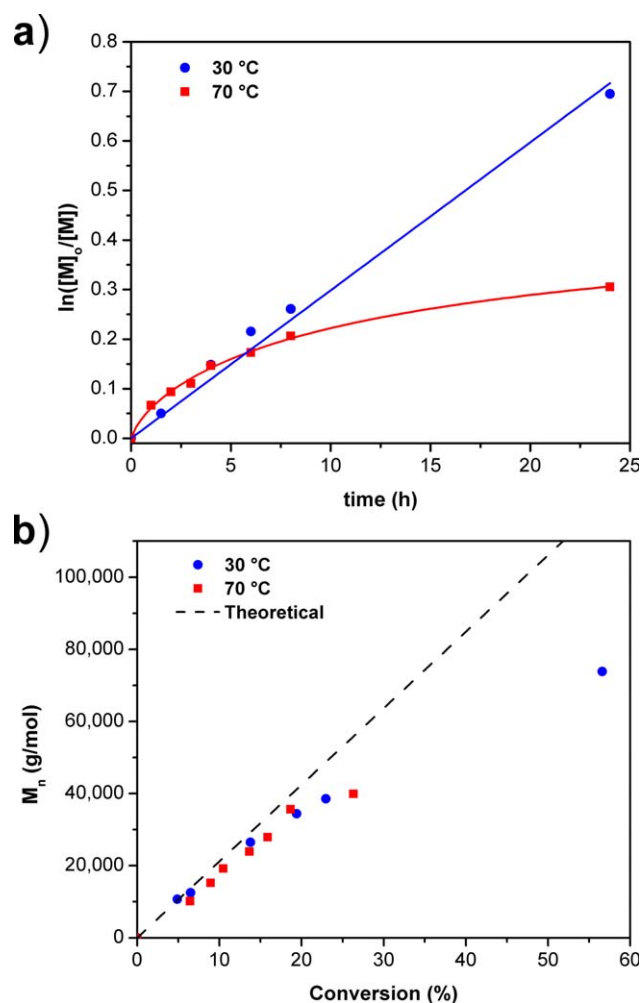


FIGURE 6 (a) Kinetic plots and (b) M_n (SEC–MALLS) versus conversion for CPDT-mediated polymerization of AN ($[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.4$) at 30 and 70 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in Table 3 $[CTA]_0:[I]_0$ ratios of 1:0.22, 1:0.4, and 1:0.67 were used. Lowest molecular weight distributions were achieved in entries 13–14 with $[CTA]_0:[I]_0$ of 1:0.22

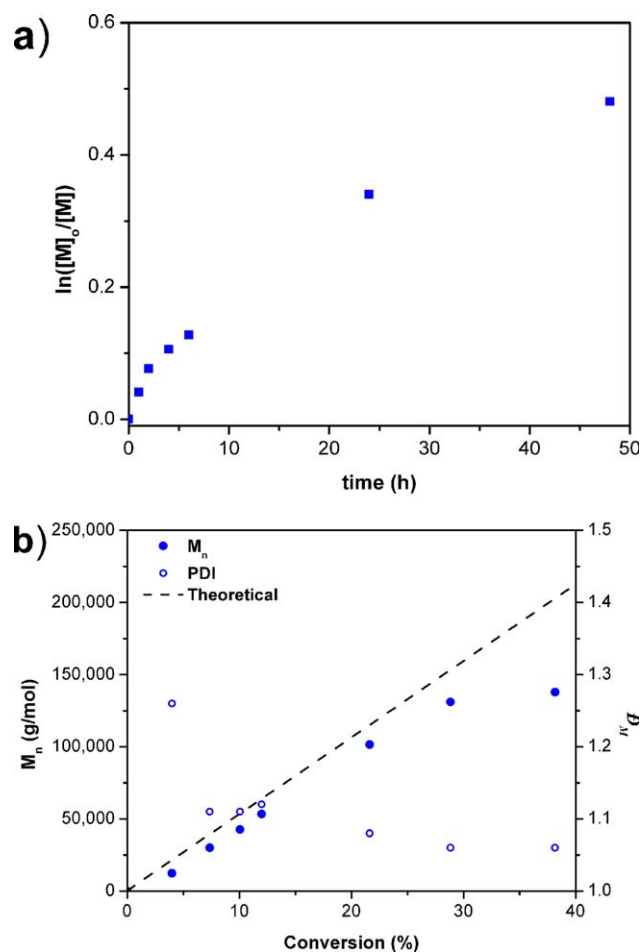


FIGURE 7 (a) Kinetic plot and (b) molecular weight and \mathcal{D}_M (SEC–MALLS) versus conversion plots for the polymerization of AN with CPDT at $[M]_0:[CTA]_0:[I]_0 = 10,000:1:0.22$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

while the highest conversions at 48 h are represented by entries 16–17. Entry 14 shows conditions for synthesizing PAN with M_n of 137,900 g/mol and \mathcal{D}_M of 1.06 at 38% conversion. Decreasing $[CTA]_0:[I]_0$ led to conversions above 70%

TABLE 3 Conversion, Molecular Weight, and \mathcal{D}_M data for the RAFT Polymerization of AN Conducted at 30 °C and High $[M]_0:[CTA]_0$

Entry ^a	RAFT Agent	$[M]_0:[CTA]_0:[I]_0$	Time (h)	Conv. ^b (%)	$M_{n,th}$ (g/mol) ^c	$M_{n,exp}$ (g/mol) ^d	$M_{n,PMMA}$ (PMMA eq.) ^e	\mathcal{D}_M ^d
13	CPDT	8,000:1:0.22	48	31	130,100	97,600	234,200	1.06
14	CPDT	10,000:1:0.22	48	38	202,900	137,900	330,100	1.06
15	CPDT	8,000:1:0.4	48	51	216,100	125,000	274,800	1.12
16	CPDT	10,000:1:0.67	48	71	377,070	131,400	423,100	1.27
17	CPDT	13,333:1:0.67	48	70	495,570	168,600	564,800	1.25

^a Polymers synthesized in ethylene carbonate at 20 wt % monomer concentration under a nitrogen atmosphere with V-70 as the initiator.

^b Conversions were determined by ¹H-NMR spectroscopy recorded in DMSO-*d*₆.

^c Theoretical number average molecular weights were calculated according to the following equation: $M_n = (\rho \cdot MW_{mon} \cdot [M]/[CTA]) + MW_{CTA}$

where ρ is the fractional monomer conversion, MW_{mon} is the molecular weight of the monomer, and MW_{CTA} is the molecular weight of the CTA.

^d Number average molecular weight (M_n) as determined by SEC (0.5 mL/min, 60 °C, polymer labs PL gel 5 μ m mixed-C column, DMF with 20 mM LiBr eluent) equipped with RI and MALLS detectors.

^e M_n expressed as equivalents of PMMA standards.

and a slight increase in \bar{D}_M (1.27) with a similar M_n of 131,400 g/mol as seen in entry 16. These results demonstrate conditions for preparing high molecular weight and low \bar{D}_M PAN with polymer conversions similar to those prepared by conventional solution polymerization. Although polymers were quenched at 48 h, conversions should continue to increase for longer reaction times if the radical concentration is preserved.

As an example of high $[M]_0:[CTA]_0$ polymerizations, the kinetic plot and molecular weight versus conversion plot are shown for entry 14 in Figure 7(a,b), respectively.

Figure 7(a) exhibits continued monomer conversion for 48 h. Moreover, Figure 7(b) shows that ideal chain growth continues up to 30% conversion at 24 h, indicating the existence of living chain ends for long reaction times, followed by non-linear behavior beyond 24 h.

CONCLUSIONS

Polymerization of AN has been performed in the presence of a series of RAFT agents at selected temperatures and reactant concentrations with the purpose of synthesizing PAN with high molecular weight and low \bar{D}_M . It was found that

1. neither CTSPA nor CMDT provide adequate control for RAFT-mediated polymerization of AN as compared to CEDT and CPDT;
2. decreasing the $[CTA]_0:[I]_0$ ratio in CPDT-mediated polymerizations yields higher molecular weight and higher conversion at the cost of broader molecular weight distributions and larger deviations from M_n theory; and
3. lowering the polymerization temperature to 30 °C is an effective approach for increasing molecular weight and conversion.

It is suggested that chain termination reactions are suppressed at 30 °C, permitting monomer conversion up to 48 h. Utilizing CPDT as the RAFT agent at $[M]_0:[CTA]_0:[I]_0 = 10,000:1:0.67$ and 30 °C in ethylene carbonate, PAN of molecular weight $\approx 170,000$ g/mol and $M_w/M_n = 1.25$ was obtained at 70% conversion. In comparison, a change in molar ratios to $[M]_0:[CTA]_0:[I]_0 = 10,000:1:0.22$, PAN of molecular weight $\approx 137,000$ g/mol and $M_w/M_n = 1.06$ was obtained at 38% conversion.

Of significance to composite technology, controlling molecular weight and dispersity of PAN via low temperature CPDT-mediated polymerization provides means to synthesize an array of well-defined carbon fiber precursor architectures. We have recently applied this method to synthesize a series of PAN copolymers in order to study the effects of molecular weight, \bar{D}_M , and precursor compositions on white-fiber spinning and carbon fiber oxidation/stabilization processes. It is our belief that such well-defined PAN-based polymers provide a new approach for the scientific community to link precursor molecular design with optimized carbon fiber morphologies and ultimate mechanical properties.

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