Synthesis of Poly(*N*,*N*-dimethylacrylamide) via Nitroxide-Mediated Radical Polymerization

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ABSTRACT: Poly(*N*,*N*-dimethylacrylamide) (PDMA) with a low polydispersity was prepared via stable free radical polymerization (SFRP) using 2,2,6,6-tetramethyl-1-piperdinyloxy nitroxide (TEMPO). PDMA with a polydispersity of 1.55 (M_n = 10 600) was obtained for [TEMPO]/[AIBN] = 1.0 with quantitative monomer conversion; higher [TEMPO]/[AIBN] ratios decreased conversion. The polydispersity of PDMA was higher and polymerization times were shorter compared to SFRP of styrene or *n*-butyl acrylate. Attempts to prepare higher molecular weight PDMA with low polydispersity were unsuccessful. When polystyrene-TEMPO was used as a macroinitiator, *N*,*N*-dimethylacrylamide could be polymerized, but the conversion was low. Unlike styrene or acrylate polymerization, SFRP of *N*,*N*-dimethylacrylamide is not a living process, as evidenced by an unsuccessful incremental-monomer-addition experiment.

Introduction

A number of investigators have successfully prepared polymers with controlled molecular weight and narrow polydispersities via “living”/controlled radical polymerization.[1−6] Compared to other controlled polymerization methods such as anionic,[7] cationic,[8] and group transfer polymerization,[9] controlled radical polymerization does not require extraordinary conditions such as low temperature, inert atmosphere, or carefully purified reagents. The two most common types of controlled radical polymerization systems are (1) stable free radical polymerization (SFRP) using nitroxide additives such as 2,2,6,6-tetramethyl-1-piperdinyloxy nitroxide (TEMPO)[3] or (2) atom transfer radical polymerization (ATRP) using a transitional metal complex to generate radicals from a dormant alkyl halide by a reversible redox process.[4] Controlled styrene polymerization has been the hallmark of the nitroxide-mediated process where polystyrene with M_n = 141 000 and a polydispersity of 1.33 has been prepared.[10] Extension of SFRP to (meth)acrylates has been reported.[11−14] Listigovers et al.[11] prepared polyacrylates using 4-oxo-TEMPO; a 9 h polymerization time of 155 °C led to poly(*n*-butyl acrylate) with M_n = 10 500 and a polydispersity of 1.53. Higher molecular weights were reported (27 000), but the polydispersity was also higher.

ATRP has proven to be a versatile method for controlled radical polymerization. Matyjaszewski[15,16] has described the synthetic scope of ATRP and demonstrated the robust nature of ATRP in numerous publications. Recently, Grimaud and Matyjaszewski[17] reported ATRP of methyl methacrylate (MMA) to produce polymers with polydispersities as low as 1.1 (M_n = 20 000) and controlled molecular weights up to M_n = 180 000. The polymerizations were conducted at 90 °C over a period of 5−6 h. Matyjaszewski and co-workers[18] also prepared poly(acrylonitrile) using ATRP although the conversions and reported molecular weights were lower than MMA. While details were not given, Matyjaszewski[15] claimed the successful ATRP of (2-hydroxypropyl)methacrylamide in the bulk.

As part of our research program on water-soluble polymers, we initiated a research project to apply these controlled radical polymerization techniques to acrylamide monomers. Our goal was to prepare polyacrylamides with controlled molecular weights and narrow polydispersities. We were also attracted to the possibility of synthesizing amphiphilic block copolymers such as polystyrene-*b*-polyacrylamide.

We attempted ATRP of *N*,*N*-dimethylacrylamide using heterogeneous conditions (1-bromo-1-phenylethane, CuBr, 2,2′-bipyridine) in different solvents (toluene, diethyl carbonate) over the temperature range of 80−95 °C but did not obtain polymer.[19] However, we did obtain polymer using SFRP with TEMPO. In this communication, we report the TEMPO-mediated polymerization of *N*,*N*-dimethylacrylamide using AIBN as an initiator in an aromatic solvent (toluene or xylene).

Experimental Section

Materials. 2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich, 99%) was purified by recrystallization from methanol. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO, Aldrich) was used as received. *N*,*N*-Dimethylacrylamide (Aldrich) was purified by vacuum distillation to remove stabilizer. Styrene was purified by washing with 5% aqueous NaOH and water. The styrene phase was dried over anhydrous $MgSO_4$ and distilled over CaH_2 before use. Toluene (Aldrich, anhydrous grade) was used as received. Xylene (Aldrich) was purified by vacuum distillation.

Gel permeation chromatography (GPC) analysis of polyacrylamide samples was performed on a Waters HPLC system equipped with a Model 510 pump, Model 410 differential refractometer, and two PLGel columns (Polymer Labs, 1000 and 10 000 Å). The RI detector and columns were thermostated at 50 °C. The mobile phase was *N*,*N*-dimethylformamide (containing 1% lithium bromide), and the flow rate was 0.7 mL/min. The molecular weight and polydispersity were calculated with EZChrom GPC/SEC software (Scientific Software, Inc.) based on linear calibration curves using well-characterized poly(methyl methacrylate) standards (Polymer Labs). GPC analysis of polystyrene was performed on a similar HPLC system using THF as the eluent at 0.5 mL/min. Analysis was based on calibration curves using polystyrene standards.

^{1}H NMR spectra were recorded using a Varian 200 MHz spectrometer.

Polymerization. Polymerizations were carried out in sealed 20 mL vials that were placed in an oil bath at specified temperatures. AIBN and TEMPO were weighed into the vials

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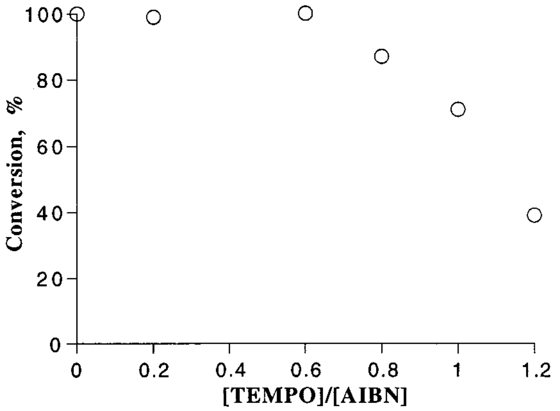

Figure 1. Dependence of conversion on the molar ratio of [TEMPO]/[AIBN] for the polymerization of *N*,*N*-dimethylacrylamide in toluene at 84 °C for 14 h. $[\mathrm{AIBN}]_0 = 0.024$ M, $[N,N\text{-dimethylacrylamide}]_0 = 2$ M.

followed by monomer and solvent. After the reaction mixture was degassed by bubbling with argon for 10 min, the vials were capped and sealed with PTFE tape and placed in the preheated oil bath. At the end of the polymerization, the polymer was precipitated in ether or hexane followed by vacuum-drying overnight at 50 °C. Monomer conversion was determined by gravimetry.

For kinetic studies, the polymerization was carried out in a 250 mL round-bottomed flask. After AIBN, TEMPO, solvent, and monomer were charged into the flask, the solution was degassed by two freeze−pump−thaw cycles. Then the flask was placed in the oil bath under the protection of argon. Aliquots were removed via syringe through the rubber septum.

TEMPO-terminated polystyrene (PS-TEMPO) was prepared in a 250 mL round-bottomed flask using 0.6 g (0.0248 mol) of BPO, 0.48 g (0.0031 mol) of TEMPO, and 79 g (0.759 mol) of styrene. After the mixture was degassed with two freeze−pump−thaw cycles, the flask was sealed with a rubber septum. The solution was heated at 95 °C for 3 h followed by 130 °C for 2 h. The polymer was precipitated twice in methanol. The conversion of styrene was 21%; $M_n = 7100$; $M_w/M_n = 1.18$ (GPC analysis in THF, calibrated against polystyrene). In a 100 mL flask, 6 g of PS-TEMPO was combined with 12 g (0.121 mol) of *N*,*N*-dimethylacrylamide. After purging with argon for 10 min, the flask was placed in an oil bath at 135 °C. After 24 h of heating, the product was precipitated in hexane.

Results and Discussion

Experiments were carried out in toluene at 84 °C using different molar ratios of [TEMPO]/[AIBN]. Figure 1 shows the conversions at different ratios after 14 h polymerization times. Quantitative conversions were achieved at 84 °C when [TEMPO]/[AIBN] ≤ 0.6. No polymer was obtained when the ratio exceeded 1.3. High TEMPO concentrations reduce the radical concentrations and thus effectively prevent propagation.

Figure 2 is the plot of M_n and M_w/M_n versus the initial [TEMPO]/[AIBN] ratio. It was found that both M_n and M_w/M_n decreased as the TEMPO concentration increased. The decrease in polydispersity is consistent with a suppression of spontaneous bimolecular termination. Also, the use of TEMPO minimizes the molecular weight broadening due to changing ratios of [monomer]/[initiator]. PDMA has a broad polydispersity (3.5) in the absence of TEMPO; the polydispersity decreased to 1.75 for [TEMPO]/[AIBN] = 0.8. Increasing the TEMPO concentration did not decrease the polydispersity of PDMA significantly. Figure 3 compares the GPC chromatograms of PDMA in the absence and presence of TEMPO. Compared to TEMPO-mediated polymerization of styrene and *n*-butyl acrylate,[11,12] TEMPO-mediated polymerization of *N*,*N*-dimethylacrylamide produced polymers with higher polydispersities. However, the polydispersity is lower and the conversions higher than that obtained for MMA polymerization.[14]

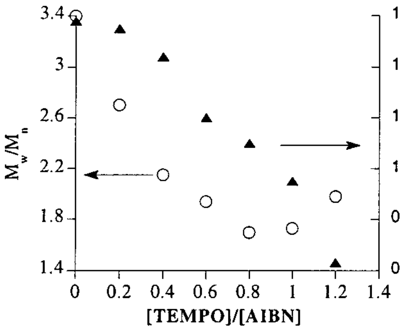

Figure 2. Dependence of M_n (▲) and M_w/M_n (○) on the molar ratio of [TEMPO]/[AIBN] for the polymerization of *N*,*N*-dimethylacrylamide in toluene at 84 °C for 14 h. $[\mathrm{AIBN}]_0 = 0.024$ M, $[N,N\text{-dimethylacrylamide}]_0 = 2$ M.

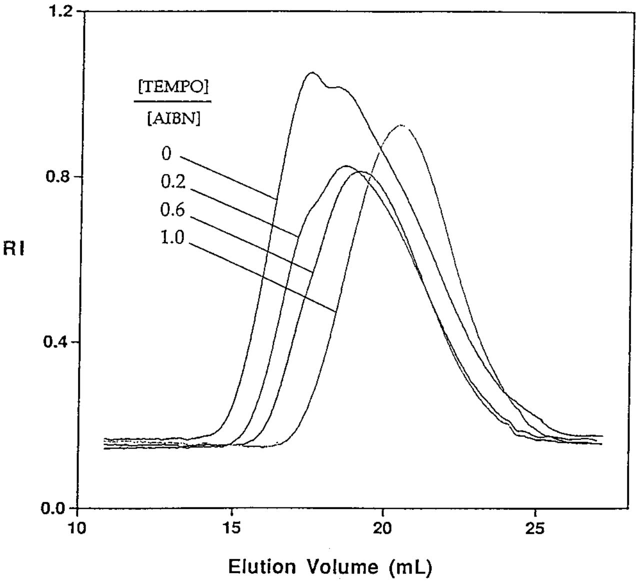

Figure 3. GPC chromatograms for poly(*N*,*N*-dimethylacrylamide) prepared with different molar ratios of [TEMPO]/[AIBN]. Polymerization performed in toluene at 84 °C for 14 h. $[\mathrm{AIBN}]_0 = 0.024$ M, $[N,N\text{-dimethylacrylamide}]_0 = 2$ M.

In TEMPO-mediated radical polymerization, there is an equilibrium between active radicals and the dormant, TEMPO-terminated chain ends.[20] This equilibrium can be affected by many factors such as temperature, solvent, monomer, and TEMPO concentration. Among these variables, temperature can play the most important role. The polymerization temperature should be high enough to cause homolytic dissociation of the TEMPO−chain end bond. Temperature also affects the decomposition kinetics of the initiator and the monomer propagation rate.

Table 1 summarizes the results of temperature experiments at a constant [TEMPO]/[AIBN] ratio of 1.0. Inspection of the data in Table 1 reveals that higher polymerization temperatures produced polymers with a lower polydispersity. This is consistent with an increase in the rate ratio of initiation to propagation. TEMPO-mediated polymerization of MMA (neat, [TEMPO]/[AIBN] = 1.5, 7 h, 125 °C) gave 17% conversion to poly(methyl methacrylate) with $M_n = 25\,000$ and a polydispersity of 1.80.[14] Compare this to PDMA

Table 1. Effect of Temperature on TEMPO-Mediated Polymerization of *N*,*N*-Dimethylacrylamide[a]

T, °C	M_n	M_w/M_n	conversion,[b] %
75	6540	1.84	50
84	9500	1.76	75
98	9800	1.67	98
120	10600	1.55	100

[a] $[AIBN]_o = 0.024$ M, $[TEMPO]_o/[AIBN]_o = 1.0$, $[monomer]_o = 2$ M, 14 h polymerization time; toluene was the solvent except for the 120 °C run, which was performed in xylene. [b] Product was precipitated in diethyl ether, which may not precipitate low molecular weight oligomers.

Table 2. Polymerization Results at Low AIBN Concentration[a]

$[TEMPO]_o/[AIBN]_o$	M_n	M_w/M_n	conversion,[b] %
0	27 000	2.68	100
0.2	27 300	2.48	100
0.4	26 500	2.41	100
0.6	25 500	2.44	100
0.8	25 400	2.40	100
1.0	25 200	2.38	100
1.2			0

[a] $[AIBN]_o = 0.006$ M, $[monomer]_o = 2$ M, 14 h polymerization time, toluene, 84 °C. [b] Product was precipitated in hexane.

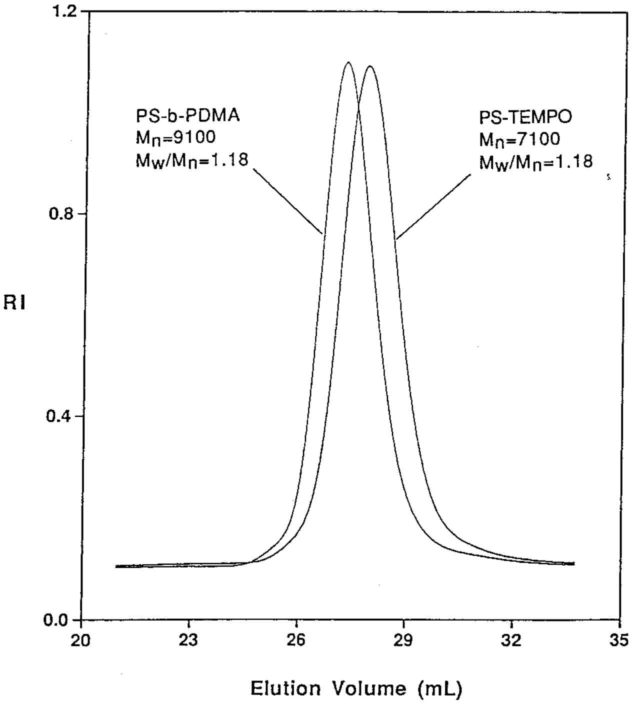

Figure 4. GPC chromatograms for PS-TEMPO and PS-*b*-PDMA.

produced at 120 °C, which was characterized by a lower polydispersity (1.55).

We attempted to study the evolution of M_n as a function of conversion. Although we used a 14 h polymerization time in routine experiments, we later observed that the polymerization of *N*,*N*-dimethylacrylamide is very fast. In fact, this monomer polymerizes much faster than styrene or acrylates.[9,10] For example, quantitative polymerization of *N*,*N*-dimethylacrylamide was achieved in less than 10 min at 98 °C for [TEMPO]/[AIBN] = 1.0. The fast polymerization times made it difficult to conveniently obtain time–conversion relationships at high temperatures. Attempts to extend the polymerization time by lowering the polymerization temperature or increasing the [TEMPO]/[AIBN] ratio were unsuccessful. No polymerization was observed at 70 °C with [TEMPO]/[AIBN] = 1.0, suggesting that the TEMPO–chain end bond is not labile below 70 °C.

For TEMPO-mediated *N*,*N*-dimethylacrylamide polymerization, the reaction mixture was orange before polymerization (the color of free TEMPO). As AIBN started to decompose, the orange color decreased in intensity and the solution eventually became colorless, indicating the absence of free TEMPO. The time for color loss depended on the polymerization temperature and TEMPO concentration. When the polymerization was carried out at 75 °C with [TEMPO]/[AIBN] = 1.0, the TEMPO color disappeared after 2 h. There was no polymerization prior to this time. A 50% conversion was observed 10 min after the loss of color; no additional polymerization was observed during the remainder of the 14 h polymerization time. Incomplete conversion may reflect bimolecular chain termination, which is consistent with the reappearance of the TEMPO color that we observed. Reappearance of the orange TEMPO color was also observed for polymerization at 98 °C, but conversion was quantitative. Several minutes after initial loss of the TEMPO color, the color reappeared, indicating chain termination. Addition of a second portion of monomer did not increase the molecular weight further.

It is difficult to obtain high molecular weight polymers in TEMPO-mediated acrylate polymerization.[11] For *N*,*N*-dimethylacrylamide polymerization at 120 °C with $[AIBN]_o = 0.024$ M, [TEMPO]/[AIBN] = 1.0, and $[N,N\text{-dimethylacrylamide}]_o = 2$ M, $M_n = 10\,600$ at 100% conversion. Attempts were made to prepare polymers with a higher molecular weight and low polydispersity by changing the AIBN and TEMPO concentrations. Table 2 summarizes the polymerization results. Table 2 indicates that by decreasing the AIBN concentration, the M_n of PDMA increased to 25 000 but polydispersity also increased to 2.38. Changing the [TEMPO]/[AIBN] ratio had a negligible effect on the polymerization results. Thus, like TEMPO-mediated acrylate polymerization, it is difficult to produce high molecular weight PDMA with low polydispersity.

Like other SFRP processes, the TEMPO-mediated polymerization of *N*,*N*-dimethylacrylamide is strongly affected by TEMPO concentration. In an attempt to more carefully control the TEMPO/chain end stoichiometry, we initiated the polymerization of *N*,*N*-dimethylacrylamide with PS-TEMPO ($M_n = 7100$). The target M_n of the PS-*b*-PDMA was 20 000. We isolated a product from this polymerization with $M_n = 9100$ and a polydispersity of 1.18. Figure 4 displays the GPC analysis of PS-TEMPO and the product from the *N*,*N*-dimethylacrylamide polymerization. To assess the amount of homopolymer present, the product was subjected to extraction with water (to remove PDMA homopolymer) for 24 h; this extraction resulted in 2% weight loss for the product. On the basis of ^{1}H NMR analysis of the block copolymer before and after water extraction, the molar composition of styrene to *N*,*N*-dimethylacrylamide units remained the same (70/30). Attempts to analyze the copolymer using potassium ionization of desorbed species (K^+IDS) mass spectrometry were unsuccessful. Steenbock et al.[14] used PS-TEMPO to initiate the polymerization of MMA but obtained bimodal GPC traces.

Although the polydispersity was low, the conversion of *N*,*N*-dimethylacrylamide was poor and, thus, the copolymer was primarily composed of styrene. An explanation for the low conversion of *N*,*N*-dimethylacrylamide might be bimolecular termination because the polymerization of *N*,*N*-dimethylacrylamide was performed at 130 °C (this high temperature is required to promote homolytic dissociation of the polystyrene−TEMPO bond).

Conclusions

The water soluble polymer poly(*N*,*N*-dimethylacrylamide) (PDMA) was synthesized using a TEMPO-mediated free radical polymerization. PDMA with a polydispersity of 1.55 and $M_n = 10\,600$ was obtained for the polymerization with [TEMPO]/[AIBN] = 1.0 (xylene, 120 °C) compared to PDMA with a polydispersity of 3.4 and $M_n = 16\,000$ for the polymerization without TEMPO (toluene, 84 °C). Higher polymerization temperatures decreased both polydispersity and M_n. Unlike the TEMPO-mediated polymerization of styrene or acrylates, polymerization of *N*,*N*-dimethylacrylamide was fast. However, incremental monomer addition experiments revealed that the polymers are not living. Attempts to achieve $M_n > 10\,000$ and maintain a low polydispersity were unsuccessful. A polymerization using a TEMPO-terminated polystyrene proceeded with low monomer conversion. Following extraction with water to remove PDMA homopolymer, NMR and GPC analysis indicated formation of a copolymer.

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