Synthesis and Characterization of 2-(Dimethylamino)ethyl Methacrylate Homopolymers via aqueous RAFT Polymerization and Their Application in Miniemulsion Polymerization

Qingfeng Xiong, Peihong Ni (✉) , Feng Zhang, and Zhangqing Yu

School of Chemistry and Chemical Engineering and the Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, Suzhou 215006, China

E-mail: phni@suda.edu.cn

Summary

Homopolymers of 2-(dimethylamino)ethyl methacrylate (DMAEMA) have been synthesized directly in aqueous media by reversible addition-fragmentation chain transfer polymerization (RAFT) using 4,4'-azobis(4-cyanopentanoic acid) (V501) as a water-soluble azo initiator and 4-cyanopentanoic acid dithiobenzoate (CPADB) as a chain transfer agent. The resulting polymers were controlled in the range of narrow molecular weight distributions, with $\overline{M}_w/\overline{M}_n$ lower than 1.3. Using the produced dithioester-capped DMAEMA homopolymer as a macro chain transfer agent, miniemulsion RAFT polymerization of methyl methacrylate and styrene were carried out, respectively. ^{1}H NMR analysis showed that the diblock copolymer PDMAEMA-*b*-PMMA in the form of stable latices was obtained as expected.

Introduction

In the past decade, controlled radical polymerization (CRP) has been the focus of intense research owing to its versatility and potential commercial applications, such as controlled molar mass, narrow molecular weight distribution and well-defined architecture and functionalities [1-4]. In these techniques, some definite initiator systems have been used, for example, stable nitroxyl radicals for nitroxide-mediated polymerization (NMP) [5], transition metal complexes for atom transfer radical polymerization (ATRP) [6-8], and dithioester derivatives for reversible addition-fragmentation radical polymerization (RAFT) [4,9,10].

Almost all of CRPs are interested in bulk and organic solution polymerization. In recent years, many efforts have directed toward controlled polymerization in aqueous media, especially for RAFT polymerization [9]. Rizzardo's group [10] reported the preparation of poly[*p*-styrenesulfanic acid sodium sait] (stySO$_3$Na) with a narrow polydispersity of 1.13 via RAFT polymerization in water media. Other groups extended some water-soluble monomers into this system. McCormick and coworkers

[11] synthesized homopolymers and block copolymers based on a water-soluble styrenic monomers, such as sodium 4-styrenesulfonate, sodium 4-styrenecarboxylate, *N,N*-dimethylvingbenzylamine and (ar-vinylbenzyl) trimethylammonium chloride, via RAFT. Several functional polymers from anionic acrylamido monomers were also prepared by the same group [12-14]. Claverie et al. presented the RAFT polymerization of the acrylic acid (AA) screened various chain transfer agents (CTAs). The polymerization of AA could be controlled in alcohol and water [15]. Matyjaszewski et al. conducted ATRP in aqueous media [16-18] and obtained amphiphilic diblock copolymer containing DMAEMA and other units.

Poly[(dimethylamino)ethyl methacrylate] and its derivatives are an extremely important species of synthetic polymers used widely in industry. The syntheses of DMAEMA homopolymer and copolymers have been investigated with several living polymerizations, including ATRP [19], group transfer polymerization (GTP) [20-21], and oxyanion-initiated polymerization [22-23]. As far as we are aware, only little literature regarding the RAFT polymerization of DMAEMA in aqueous solution, except for the report by Rizzardo et al., who prepared PDMAEMA in organic solution [10].

In the work reported here, DMAEMA homopolymers were synthesized in water by RAFT. We demonstrate that molecular masses of homopolymers were controlled by varying the ratio of monomer to CTA. The resulting dithiobenzoate-terminated poly(DMAEMA) with near monodisperse was employed as a macro-CTA in miniemulsion polymerization of oil-soluble monomers such as methyl methacrylate and styrene, and led to the production of diblock copolymer.

Experimental

Materials

2-(Dimethylamino)ethyl methacrylate (DMAEMA), styrene, and methyl methacrylate (MMA) were obtained from Shanghai Chemical Reagent Co., China. These monomers were purified in turn by treatment with basic alumina to remove inhibitor and distilled under reduced pressure prior to use. 4,4'-azobis(4-cyanopentanoic acid) (V501, 75%) was purchased from Aldrich and used as received. Sodium dodecyl sulfate (SDS), hydroquinone, hexadecane (HD) were synthetic grade and used without further refining. The chain transfer agent (CTA), 4-cyanopentanoic acid dithiobenzoate (CPADB), was prepared according to the previous literature reported by Tang et al. [24]. Deionized water was utilized throughout this work.

Homopolymer syntheses

2-(Dimethylamino)ethyl methacrylate (5 g), 4-cyanopentanoic acid dithiobenzoate (0.15 g), were dissolved in 45 g deionized water, then transferred to a 100 mL three-neck glass flask equipped with magnetic stirrer, reflux condenser, thermometer and inlet system for nitrogen. The mixture was deoxygenated by purging with nitrogen for 30 min, and heated to 70 °C with agitation. V501 (0.05 g) was added. Maintaining the polymerization temperature at 70 °C for 10 h, samples were taken at regular time intervals and inhibited immediately by hydroquinone through the reaction for analysis.

Conversions were determined by gravimetry. The poly(DMAEMA) solution was obtained and stored for miniemulsion polymerization. Each sample corresponding to the gravimetrical analysis was diluted and analyzed by aqueous gel permeation chromatography (GPC) to give the molecular weights and molecular weight distributions.

Miniemulsion polymerization of oil-soluble monomers in the presence of poly(DMAEMA)-based macro-CTA

Crude emulsions were prepared as the following description: an organic phase containing St (or MMA) and HD was added dropwise into a water phase, which was composed of above synthetic poly(DMAEMA) solution (solid content of 10 %), surfactant SDS and trace amount of V501. The mixing solution was stirred by magnetic bar at ambient temperature for 30 min. Miniemulsification was carried out using ultrasonication (CPS-2, Shanghai Branson Ultrasonic Co. China) at 60% of output in pulse mode for 5 min. Immediately after sonication, the resultant miniemulsion was transferred into a 100 mL three-neck flask equipped with a magnetic stirrer, nitrogen inlet and reflux condenser. The miniemulsion was purged with nitrogen for 10 min while it was heated to a given reaction temperature. The polymerization temperature was kept constant at 70 °C. When the polymerization was completed, the reaction mixture was added dropwise into methanol to precipitate the polymers and filtered with a Buchner funnel with glass frit. To assure separating homopolymer and unreacted monomers from the crude product, the sample was washed extensively with methanol at least three times to remove unconverted oil-soluble monomers (MMA or St), and then washed by deionized water to remove water-soluble poly(DMAEMA) homopolymer. The final samples were dried in vacuum oven for 3 days.

Characterization

Molecular weight and molecular weight distribution (polydispersity index, PDI) were measured by aqueous gel permeation chromatograph (GPC) (HP-1100 instrument) equipped with a W300 TSK and W6000xl columns connected to a refractive-index detector (G 1362A) and a UV detector (G 1315A). 0.1 M $NaNO_3$ was used as eluant at a flow rate of 0.5 mL/min at 40 °C, with poly(ethylene glycol) and poly(ethylene oxide) standards were used for calibration. ^{1}H NMR spectra were obtained from an INVOA-400 nuclear magnetic resonance instrument using $CDCl_3$ as solvent.

Results and Discussion

Homopolymerization of DMAEMA

DMAEMA was polymerized in aqueous solution with V501 as the free radical initiator and CPADB as RAFT agent at 70 °C. The effect of the molar ratio of initiator to CTA on the RAFT polymerization was investigated by varying the ratio in the range of from 1:1 to 1:5. The optimum condition was chosen by keeping the [initiator]:[CTA] ratio at 1:3. A series of near mono-dispersed poly(DMAEMA)s were obtained by changing the monomer-initiator ratio. Table 1 summarizes the molar ratio

[V501]:[CTA]:[M], the molecular weights and PDI, as well as the final conversions. The homopolymers by RAFT show narrow polydispersity in the range of 1.04-1.31, lower than the theoretical limit of 1.5 for classical free-radical polymerization.

Table 1. RAFT Polymerization of DMAEMA in Water under Different Initiated Conditions

Sample No.	[V501]/[CTA]/[M]	T (°C)	Time (h)	Conv. (%)	$\overline{M}_w$ [a]	$\overline{M}_n$ [a]	PDI [a]
1	1 : 1 : 178	70	10	98.6	25530	18890	1.35
2	1 : 2 : 178	70	10	99.3	1580	1520	1.04
3	1 : 3 : 178	70	10	99.8	6300	5380	1.17
4	1 : 5 : 178	70	10	67.1	7670	5970	1.28
5	1 : 3 : 50	70	10	95.9	2310	1860	1.24
6	1 : 3 : 552	70	10	93.5	17350	13900	1.25
7	1 : 2 : 357	70	10	78.4	17800	13550	1.31

a)   measured by aqueous GPC

Figure 1 shows the GPC profiles of the evolving poly(DMAEMA) from the original oligomer sample to the final homopolymer corresponding to the samples of conversion of gravimetrical analysis. It is very obvious that the molecular weights increase with the increasing conversions in the experimental condition, suggesting the propagation of living chain with time.
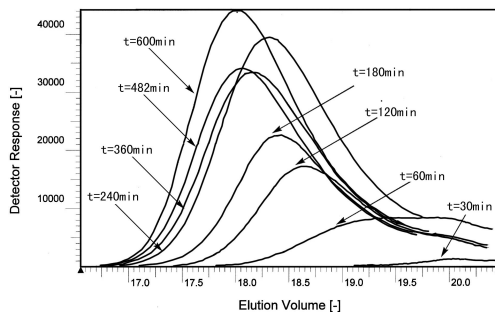

Figure 1. A typical aqueous GPC profiles of evolving poly(DMAEMA) corresponding to the samples in kinetics studies, prepared by RAFT at 70 °C in the presence of 4-cyanopentanoic acid dithiobenzoate with $[M]_0$/[CTA]/[V501]=178:3:1.

Figure 2 shows the time-conversion relationship for the homopolymer as well as the pseudo-first-order kinetic plots. For the 4-cyanopentanoic acid dithiobenzoate-midiated polymerization, 80% conversion is achieved after 4 h. The first order kinetics does appear to be a slight deviation. The plots of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ versus conversion are also shown in Figure 3. The molecular weights increase in a linear fashion which is essential consistent with a controlled/"living" polymerization. The measured PDI are very low, change slightly with conversion from an initial value of 1.08 to a final value of 1.20. Again, this is a characteristic of controlled/"living" polymerization.
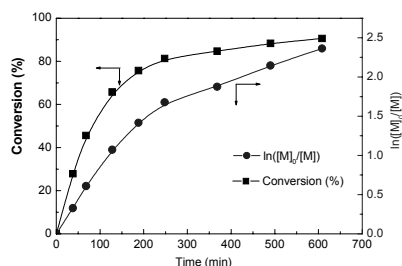
Figure 2. Monomer conversion and ln([M_0]/[M]) *vs* time plots for DMAEMA polymerization at 70 °C in the presence of CPADB with $[M]_0/[CTA]/[V501]=178:3:1$.
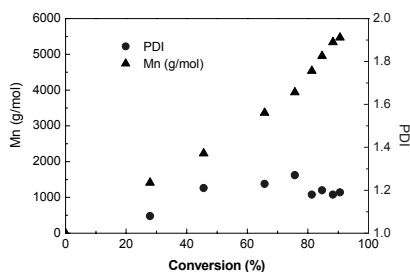
Figure 3. Number-average molecular weight $\overline{M}_n$ (GPC) and PDI *vs* monomer conversion polts for DMAEMA polymerization at 70 °C in the presence of CPADB with $[M]_0/[CTA]/[V501]=178:3:1$.

Miniemulsion polymerization of MMA and St via RAFT using macro-CTA

Miniemulsion polymerizations of MMA or styrene were studied using the recipe in Table 2. The homopolymer of DMAEMA bearing a dithioester terminal group not only acted as a macro-RAFT agent to control the living free-radical polymerization, but also as an efficient steric stabilizer for polymer latex in heterogeneous polymerization due to the protonated tendency of dimethylamino groups at neutral and acidic media. This synthetic technique would lead to a novel architecture design of block copolymers. In the process of miniemulsion polymerization, theoretically, each monomer droplet was a separate reaction locus. Trace amount of water-soluble initiator was utilized in the system. When the radical produced from V501 entered into the droplets of oil-soluble monomer, RAFT polymerization mechanism may be dominant in the miniemulsion polymerization due to the existence of poly(DMAEMA)-based CTA. Moreover, the latter possessed much higher concentration than that of the added initiator. Therefore, the chain transfer reaction would occur between the free radicals and the macro-CTAs. A successive reversible-addition-fragmentation-transfer process would take place and generate a diblock copolymer on the basis of original dithioester-terminated poly(DMAEMA).

Table 2. Miniemulsion Polymerization Recipe

Ingredient	Amount (g/100g solution)
Aqueous PDMAEMA solution	90 (solid content 10%)
Monomer (MMA or styrene)	10
Surfactant (SDS)	0.25
Initiator (V501)	Trace amount
Co-stabilizer (HD)	0.1

Several researchers have already approached this subject [25], but the polymer as steric stabilizer in their work was water-soluble anionic polyacrylic acid (PAA), and PAA-*b*-PBA diblock copolymer was generated in conventional emulsion polymerization. In our work, the dithioester-capped poly(DMAEMA) is likely to yield

partial protonation of the dimethylamino group at neutral and acidic media and provide cationic steric stabilizer for polymer latex. The overall composition of the macro-RAFT agent was the same so that the length of amphiphilic polymer was uniform.

^{1}H NMR technique can be used to study the composition of polymer latex and prove both the existence of the hydrophilic shell and hydrophobic core in latices [26]. The compositions of PDMAEMA-*b*-PMMA diblock copolymer were determined from the integration ratio of the six protons of dimethylamino (δ=2.2-2.4 ppm) for DMAEMA to that of the three protons of methyloxy (δ=3.6 ppm) for MMA (Figure 4). The results were in good agreement with the micro-RAFT agent and MMA monomer feed ratio. This proved the incorporation of dithioester-terminated poly(DMAEMA) with MMA. The conversions of the second monomer were in the range of 87 to 91%. The RAFT controlled polymerization occurred at two loca, i.e. the interface between water phase and the organic monomer phase, and inside latex particle.

Figure 5 shows the ^{1}H NMR spectrum of the dried latices of polystyrene prepared by miniemulsion polymerization in the presence of dithioester-terminated poly(DMAEMA). From Figure 5, one can find that the integration ratio of aromatic protons of phenyl (δ=7.2-7.4 ppm) of polystyrene to that of six dimethylamino protons of DMAEMA units (δ=2.2-2.4 ppm) is not agreement with the initial poly(DMAEMA)-styrene feeding ratio. This result can be explained by a postulate that only small amount of the hydrophilic micro-RAFT agent was absorbed onto the surface of styrene drops due to the stronger hydrophobicity of styrene than that of MMA.
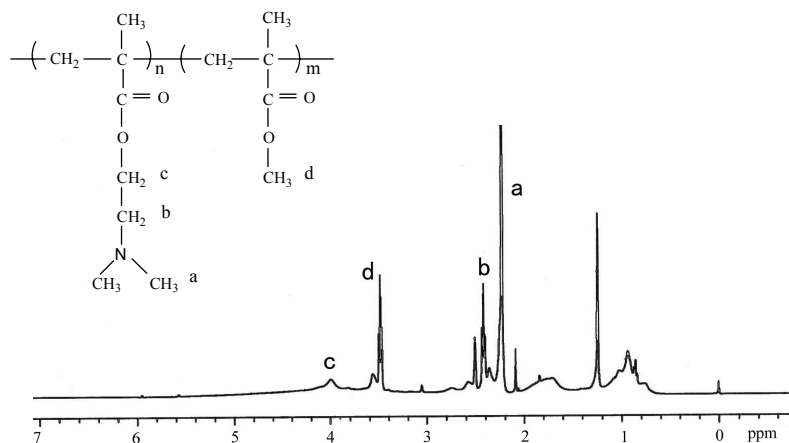

Figure 4. ^{1}H NMR spectrum of PDMAEMA-*b*-PMMA prepared by miniemulsion polymerization in the presence of poly(DMAEMA)-based macro-RAFT agent in deuterated DMSO.
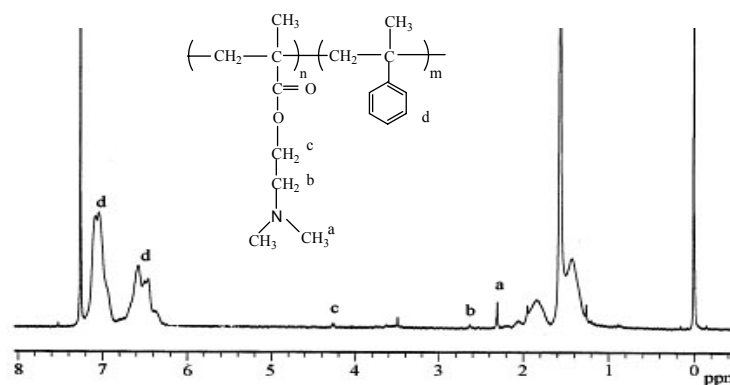
Figure 5. ^{1}H NMR spectrum of polystyrene prepared by miniemulsion polymerization in the presence of poly(DMAEMA)-based macro-RAFT agent in CDCl₃.

Conclusion

In a first part, the synthesis of a hydrophilic poly(DMAEMA) via aqueous RAFT polymerization was studied. It was confirmed that the plots of $\overline{M}_n$ vs conversion and the pseudo-first-order rate plot were near linear. The polydispersity indexes of these polymers were in the range of 1.04~1.35.

In a second part, using the DMAEMA homopolymer as both a macro-CTA and a steric stabilizer, miniemulsion RAFT polymerization of MMA was carried out successfully and formed diblock copolymer PDMAEMA-*b*-PMMA. In styrene system, any satisfied RAFT polymerization was not achieved ultimately via miniemulsion polymerization.

References

1. Matyjaszewski K, Ed. (1998) Controlled Rdical Polymerization, ACS Symposium Series. Vol 685; American Chemistry Society: Wanshington DC

2. Matyjaszewski K, Ed. (2000) Controlled/Living Radical Polymerization Progress in ATRP, NMP and RAFT, ACS Symposium Series. Vol 768; American Chemistry society: Wanshington, DC

3. Matyjaszewski K, Ed. (2003) Advanced in Controlled/Living Radical Polymerization ACS Symposium Series. Vol 854; American Chemistry society: Wanshington DC

4. Matyjaszewski K, Davis T P, Eds. (2002) Handbook of Radical Polymerization; John Willy & Sons, Hoboken

5. Hawker CJ, Bosman AW, Harth E (2001) Chemical Review 101: 3661

8

6. Wang JS, Matyjaszewski K (1995) Journal of American Chemical Society 117: 5614

7. Matyjaszewski K, Xia JH (2001) Chemical Review, 101: 2921

8. Kamigaito M, Ando T, Sawamoto M (2001) Chemical Review 101: 3689

9. McCormick CL, Lowe AB (2004) Accounts of Chemical Research 37: 312

10. Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery L, Le TP, Mayadunne RTA, Meijs GF, Moad CL, Moad G, Rizzardo E, Thang SH (1998) Macromolecules 31: 5559

11. Mitsukami Y, Donovan MS, Lowe AB, McCormick CL (2001) Macromolecules 34: 2248

12. Sumerlin BS, Donovan MS, Mitsukami Y, Lowe AB, McCormick CL (2001) Macromolecule 34: 6561

13. Thomas DB, Sumerlin BS, Lowe AB, McCormick CL (2003) Macromolecules 36: 1436

14. Sumerlin BS, Lowe AB, Thomas DB, McCormick CL (2003) Macromolecules 36: 5982

15. Catherine L, Nicole D, Jérôme PC (2001) Macromolecules 34: 5370

16. Gaynor SG, Qiu J, Matyjaszewski K (1998) Macromolecules 31: 5951

17. Qiu J, Aynor SG, Matyjaszewski K (1999) Macromolecules 32: 2872

18. Lee SB, Russell AJ, Matyjaszewski K (2003) Biomacromolecules 4:1386

19. Zeng FQ, Shen YQ, Zhu SP, Robert P (2000) Macromolecules 33: 1628

20. Vamvakaki M, Billingham NC, Armes SP Polymer (1999) 40: 5161

21. Patrickios CS, Hertler WR, Abbott NL, Hatton TA (1994) Macromolecules 27: 930

22. Báñez MV, Robinson KL, Butum V, Armes P (2001) Polymer 42: 29

23. Nagasaki Y, Sato Y, Kato M (1997) Macromol Rapid Commun 18: 827

24. Tang SH, Chong (Bill) YK, Mayadunne RTA, Moad G, Rizzardo E (1999) Tetrahedron Letters 40: 2435

25. Ferguson CJ, Hughes RJ, Pham BTT, Hawkett BS, Gilbert RG, Serelis AK, Such CH (2002) Macromolecules 35: 9243

26. Agosto FD, Charreyre MT, Pichot C, Gilbert RG (2003) Journal of Polymer Science: Part A: Polymer Chemistry 41: 1188