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Articles

Controlled/Living Ring-Closing Cyclopolymerization of Diallyldimethylammonium Chloride via the Reversible Addition Fragmentation Chain Transfer Process

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ABSTRACT: For the first time, controlled/living free-radical polymerization of a cyclopolymerizing monomer, that is diallyldimethylammonium chloride (DADMAC), was achieved via reversible addition fragmentation chain transfer (RAFT) chemistry in the presence of both trithiocarbonate and xanthate RAFT/macromolecular design via the interchange of xanthate (MADIX) agents in aqueous solution at 60, 80, and 90 °C. The structural characterization of the polymers was achieved via nuclear magnetic resonance spectrometry, indicating that during the RAFT polymerization of DADMAC, identical to its equivalent conventional free radical polymerization, five-membered rings are formed almost exclusively. In the case of the trithiocarbonate agent, there was excellent agreement between the theoretical and experimental number average molecular weights, M_n, with narrow polydispersities (approaching polydispersity index (PDI) $\approx$ 1.10) being observed (2100 g mol^{-1} < M_n < 51 000 g mol^{-1}). Chain extension was carried out by sequential batchwise addition of the monomer, confirming the living character of the system. However, the increase in M_n with respect to conversion was not linear in the case of the xanthate agent, yet the PDIs were as low as 1.12, indicating that control was achieved. The inclusion of NaCl into the reaction mixture reduces of the rate of polymerization for both RAFT agents. Such an observation supports the hypothesis that electrostatic repulsion is crucial to fragmentation of the primary propagating radicals from the adduct RAFT radical; that is, it appears that an electrostatic interaction is affecting the (chemical) RAFT equilibrium.

Introduction

Butler and co-workers demonstrated the formation of water-soluble linear polymers as compared to the formation of highly cross-linked quaternary ammonium polymers during the conventional free-radical polymerization of diallylquaternaryammonium salts.[1] These initial observations were followed by the proposal of an alternating intramolecular−intermolecular chain propagation mechanism,[2] now commonly referred to as cyclopolymerization, through which a wide variety of nonconjugated divinyl monomers have been converted to characteristic cyclopolymers.[3,4] Poly(diallyldimethylammonium chloride) (PDADMAC) is one such polymer. It has been widely used in many industrial and biological applications, for example, as flocculants in wastewater treatment, antimicrobial biocide and biocatalyst agents in biological, medical, food applications,[5] and layer-by-layer assembly.[6] The kinetics and mechanism of homo- and copolymer syntheses, chemical structures, polyelectrolyte behavior in solution, molecular characterization, and interactions in solution and at interfaces has been reviewed by Hunkeler et al.[7] The use of conventional free-radical polymerization is able to provide homopolymers or random copolymers of DADMAC but via this method one is quite limited with regard to the formation of more complex macromolecular architectures that allow for finely controlled property modification.[8,9] Poly(ethylene glycol)(PEG)-PDADMAC block copolymers (ABA type) containing nearly equal numbers of both monomer units were synthesized by free-radical polymerization using macroazoinitiators obtained from 2,2′-azobisisobutyronitrile (AIBN) and PEG.[10]

In the past two decades, many techniques have been developed to control free radical polymerization processes, leading to the synthesis of well-defined architectures with predictable and narrowly distributed molecular weights. Several key methods of achieving living free-radical polymerization have emerged. Nitroxide mediated or stable free-radical polymerization (SFRP) was first reported in the late 1980s and has been shown to be particularly effective in the synthesis of controlled styrenic-based (co)polymers.[11,12] Atom transfer radical polymerization (ATRP) was developed independently by Sawamoto[13−15] and Matyjaszewski and co-workers.[16−18] Like SFRP, ATRP

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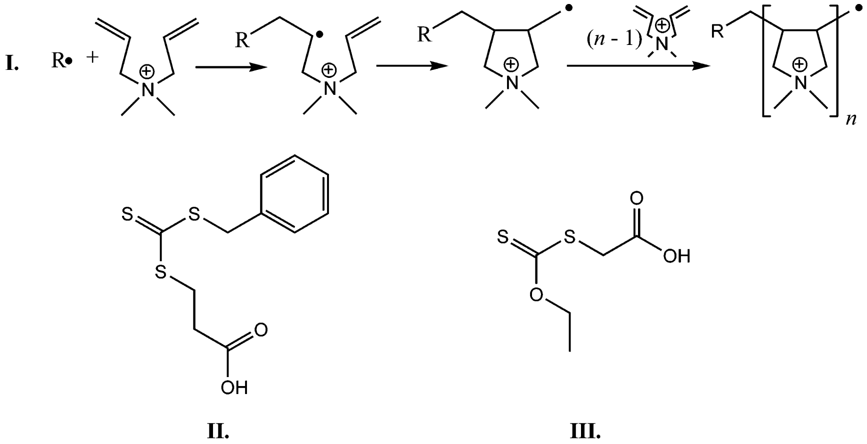
Scheme 1. Ring-closing Cyclopolymerization of Diallyldimethylammonium Chloride (I) Using RAFT Agents 3-Benzyltrithiocarbonyl Propionic Acid (II) and Ethylxanthogenacetic Acid (III)



works well for styrenic and (meth)acrylate-based monomers. Later, the CSIRO group reported a living/controlled polymerization technique they have termed the reversible addition fragmentation chain transfer (RAFT) process.[19,20] RAFT in some instances has advantages over SFRP or ATRP in that it is applicable to a wide range of monomers,[21] can be performed in a wide variety of solvents (including water), and can tolerate a broad range of experimental conditions[20,22,23] as well as allow for the targeted construction of complex macromolecular architectures.[24−26]

In the current work, the applicability of RAFT for control of a cyclopolymerization is demonstrated using diallyldimethylammonium chloride (DADMAC) as a representative example. Control over the growth of chains is evidenced by the linear relationship between conversion and the number average molecular weight, M_n, low polydispersities, and the increased molecular weight of the polymers upon subsequent batchwise addition of the monomer. To the best of our knowledge, the present study represents the first example of molecular weight control, with living characteristics, of a cyclopolymerizing monomer under RAFT conditions. The methods explored in this publication should provide for tailored and complex macromolecular architectures that will find uses in the existing areas of application of poly(diallyldimethylammonium chloride), for example, in the paper industry, in flocculation, in complexation, and in several other areas.

Experimental

Materials. Diallyldimethylammonium chloride (DADMAC) 65% water solution, ammonium persulphate (APS, ≥ 98%), ethylxanthogenacetic acid, and 4,4′-azobis(4-cyanovaleric acid) (ACVA, ≥ 98.0%) were purchased from Aldrich and used as received. Ethylxanthogenacetic acid is from Aldrich's rare chemicals library and comes with no purity information; however, it was pure within the detection limits of ^{1}H- and ^{13}C NMR spectroscopy. Dimethylformamide (DMF) and acetone were distilled before use. 3-Benzyltrithiocarbonyl propionic acid was prepared according to the literature.[27] In the remainder of this document, 3-benzyltrithiocarbonyl propionic acid and ethylxanthogenacetic acid will be referred to simply as trithiocarbonate and xanthate RAFT agents, respectively.

Procedure for the RAFT Polymerization of DADMAC. Monomer solution (2 mL, 2.1 mol L^{-1}), 3-benzyltrithiocarbonyl propionic acid (RAFT agent, 0.01 g), solvent (deionized H_2O, 2 mL) and initiator ammonium persulfate (0.01 g) were weighed and mixed to generate a solution that contained 2.1 mol L^{-1} monomer, 9.6×10^{-3} mol L^{-1} RAFT agent, and 1.1×10^{-2} mol L^{-1} initiator. These were added to a Schlenck tube containing a magnetic stirring bar. The system was degassed by three freeze−pump−thaw cycles and subsequently placed in an oil bath at 60 °C. After 12 h the contents of the tube were dissolved in water, and the polymer was precipitated in acetone. The polymer was collected by filtration and dried in a vacuum oven at 50 °C for 48 h. The ^{1}H and ^{13}C NMR spectra of the obtained polymer appear in Figures 1 and 2 and the molecular weight distribution (MWD) appears in Figure 3. Details of the polymerization times, conversions, and molecular weight measurements of all reactions are given Tables 1 to 4.

For trithiocarbonate mediated experiments, conversion was determined gravimetrically using

$$\text{Conversion} = [(W_m - W_p)/W_m] \times 100\% \tag{1}$$

where W_p and W_m are, respectively, the mass of the obtained polymer and the mass of monomer used. Xanthate mediated polymerizations had their conversion measured by ^{1}H NMR spectroscopy, in which the terminal aryl protons of the monomer and their polymerization product protons occupy different regions of the spectrum to any other protons in the molecule, allowing for unambiguous conversion measurements by integration. The ^{1}H chemical shifts of these protons for the monomer and polymer respectively are $\delta = 5.5-5.7$ ppm (multiplet) and 1.2−1.7 ppm (broad doublet).

Chain Extension Polymerization. PDADMAC formed from trithiocarbonate RAFT polymerization (run 5, Table 1, $M_n = 17\,200$ g mol^{-1}, PDI = 1.19) was used as a macro-RAFT agent for further chain extension. Macro-RAFT agent (0.25 g) and APS (0.01 g) were dissolved in a mixture of H_2O and DMF (1:1 vol). The polymerization was carried out at 60 °C for 20 h. All other parameters and procedures were the same as in procedure for the RAFT polymerization of DADMAC above. The results of this experiment are not tabulated but appear in the text of the Results and Discussion section and also in Figure 5.

Polymerization in the Presence of NaCl. Solid NaCl was added in an excess such that undissolved NaCl was observable, even at 60 °C, indicating a saturated solution. All other parameters and procedures were the same as in procedure for the RAFT polymerization of DADMAC above. The relevant results are depicted in Table 5.

Characterization. Molecular weight distributions (MWDs) of the polymers were determined by gel permeation chromatography (GPC) in a setup comprising a Knauer pump equipped with one NOVEMA column (particle size 10 μm, dimension 8.00mm × 300.00 mm, porosity 1000 Å) calibrated with poly(2-vinylpyridine)-(P2VP) standards and a differential refractive index detector using 0.1 N NaCl acidified with 1% trifluoroacetic acid as eluent with a flow rate of 0.2 mL min^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-300 NMR instrument using D_2O as the solvent. Theoretical M_n (from this point onward denoted M_{nth}) was calculated according to

$$M_{\mathrm{nth}} = (\text{conversion} \times W_{\mathrm{m}}/N_{\mathrm{RAFT}}) + M_{\mathrm{RAFT}} \qquad (2)$$

where W_{m} is the initial weight of monomer, N_{RAFT} and M_{RAFT} are initial moles and molecular weight of RAFT agent, respectively.

Results and Discussion

Polymer Structure and Molecular Weight Evolution. DADMAC was polymerized in aqueous solution under two sets of conditions: (a) using 3-benzyltrithiocarbonyl propionic acid (Scheme 1II) as the chain transfer agent and ammonium persulphate (APS) as a free radical initiator and (b) using ethylxanthogenacetic acid (Scheme 1III) as the chain transfer agent and 4,4′-azobis(4-cyanovaleric acid) (ACVA) as the initiator (Tables 1 and 2, respectively). Structural characterization of the obtained polymers was achieved via NMR spectroscopy.

Figures 1 and 2 contain representative ^{1}H and ^{13}C NMR spectra of both RAFT produced PDADMAC (see entry 6 in Table 1) and commercially obtained PDADMAC.[28] In the case of the trithiocarbonate mediated polymers, examination of the ^{1}H NMR spectra showed some extra peaks in the aromatic region due to the chain end phenyl groups from the RAFT agent. Splitting of the peaks in ^{1}H and ^{13}C NMR was also observed, indicating the presence of cis and trans configurations, as reported earlier for conventionally free radically polymerized PDADMAC.[9,29] The peak assignments are identical to those allocated in earlier studies[9] and confirm the structure of the polymer to be linear with five-membered rings having been formed exclusively or almost exclusively, identical to what is observed when PDADMAC is polymerized under conditions of conventional free-radical polymerization. All the polymers synthesized in the current study are soluble in water, further re-enforcing the notion that the divinyl functionality of the monomers has led to intramolecular propagation rather than cross-linking.

The ring-closing polymerization of DADMAC was carried out in the presence of both the trithiocarbonate and xanthate RAFT agents (see Tables 1 and 2, respectively). Using the xanthate RAFT agent a narrow polydispersity (as low as PDI = 1.12) was achieved, however the molecular weights did not evolve with conversion as might be expected from a successful RAFT polymerization (see Table 2). This is a surprising result: On the one hand the chain transfer agent has clearly led to a degree of control since PDIs significantly less than 1.5 cannot be achieved via a conventional radical polymerization process. However, chain growth appears to stop suddenly at the observed chain length, without the possibility for extension, and this result is not yet fully understood. This is similar to what has been observed in ethylene RAFT polymerizations, that is, narrow polydispersities without evolution of molecular weight.[30] Several example MWDs for a xanthate mediated polymerization are depicted in Figure 3B.

For the trithiocarbonate RAFT agent, there was a shift of GPC elugrams to lower elution volumes (higher molecular weights) with increasing conversion. The obtained M_{n} of the polymers (by calibration with P2VP polymer standards) increased linearly with the conversion, and the polydispersity remained low (1.09−1.25) with unimodal GPC curves throughout the reaction (Figures 3 and 4 and Table 1). The cyclopolymerization of DADMAC using concentrated monomer solution (4.2 mol L^{-1}) led to a very high polydispersitiy (see entry 11, Table 1). While the PDIs were low, some tailing is visible at both the high- and low-molecular-weight extremes of the main peaks.

Table 1. Times, Conversions, and Molecular Weights for Reversible Addition Fragmentation Chain Transfer (RAFT) (3-Benzyltrithiocarbonyl Propionic Acid) Mediated Cyclopolymerization of Diallyldimethylammonium Chloride (DADMAC)[a]

run no.	time (h)	conversion (%)	$M_{\mathrm{n,GPC}}$ (g mol^{-1})	M_{nth} (g mol^{-1})	PDI
1	0.5	6	2100	2390	1.12
2	1	16	6500	5900	1.11
3	2	26	12100	9400	1.25
4	4	38	14700	13700	1.19
5	8	49	17200	17600	1.19
6	12	65	22500	23200	1.09
7	16	76	25600	27100	1.19
8	20	81	28000	29000	1.15
9	24	86	29400	30600	1.13
10	36	85	30000	30300	1.14
11	20[b]	100	51000	35600	2.72

[a] Reaction run at 60 °C (using 2.1 mol L^{-1} monomer, 9.6 × 10^{-3} mol L^{-1} RAFT agent, 1.1 × 10^{-2} mol L^{-1} ammonium persulfate). This data is plotted in Figure 4. [b] Reaction run using 4.2 mol L^{-1} monomer, 19.2 × 10^{-3} mol L^{-1} RAFT agent, 2.2 × 10^{-2} mol L^{-1} ammonium persulfate.

Table 2. Times, Conversions, and Molecular Weights for Cyclopolymerization of Diallyldimethylammonium Chloride (DADMAC) with (A) No Reversible Addition Fragmentation Chain Transfer (RAFT) Agent, (B) 4.6 × 10^{-3} mol L^{-1} xanthate RAFT Agent, (C) 9.2 × 10^{-3} mol L^{-1} xanthate RAFT Agent[a]

conditions	run no.	time (h)	conversion (%)	$M_{\mathrm{n,GPC}}$ (g mol^{-1})	M_{nth} (g mol^{-1})[b]	PDI
A	1	1.8	9	37000	n/a	1.94
A	2	3.1	13	51000	n/a	2.18
A	3	4.4	15	44000	n/a	1.80
A	4	6.0	24	41400	n/a	1.72
B	1	2.3	9	16700	8800	1.19
B	2	3.2	11	21700	10500	1.22
B	3	4.6	14	19500	13700	1.25
B	4	6.0	21	19500	20400	1.25
C	1	2.8	10	20000	5000	1.20
C	2	4.7	16	23000	8000	1.17
C	3	6.6	20	24600	9900	1.12
C	4	7.8	26	26000	12700	1.14

[a] Reaction run with both at 60 °C with 2.7 mol L^{-1} monomer and 1.5 × 10^{-3} mol L^{-1} 4,4′-azobis(4-cyanovaleric acid). It is noted that, in contrast to the trithiocarbonate mediated system, there is not good agreement between experimental and theoretical M_{n} values, despite the presence of molecular weight control evidenced by low PDIs. [b] n/a = Not applicable.

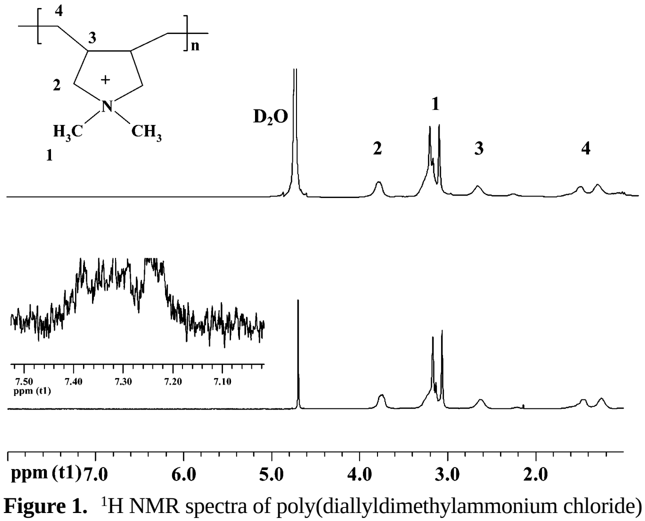


Figure 1. ^{1}H NMR spectra of poly(diallyldimethylammonium chloride) (PDADMAC) in D$_2$O: (top) commercial sample from Aldrich; (bottom) PDADMAC prepared via RAFT (run 6, Table 1).

Aromatic protons and carbons were observed in the ^{1}H and ^{13}C NMR spectra of the resulting polymer (not visible with the scale used for the spectrum), demonstrating fidelity of the end

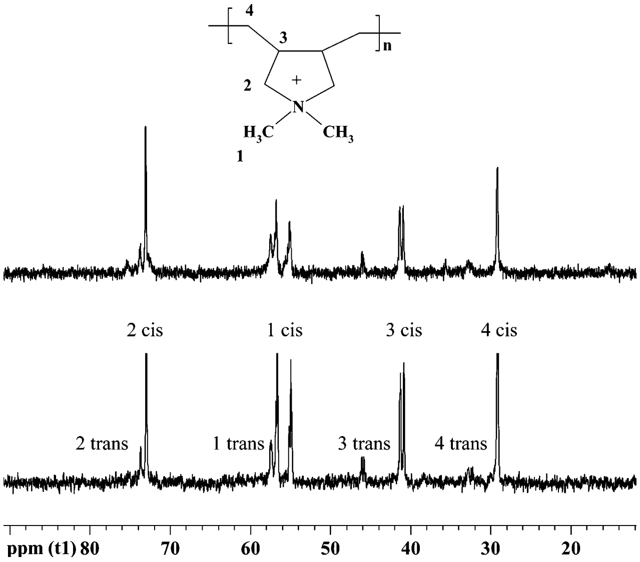


Figure 2. ^{13}C NMR spectra of poly(diallyldimethylammonium chloride) (PDADMAC) in D_2O: (top) commercial sample from Aldrich; (bottom) PDADMAC prepared via RAFT (run 6, Table 1).

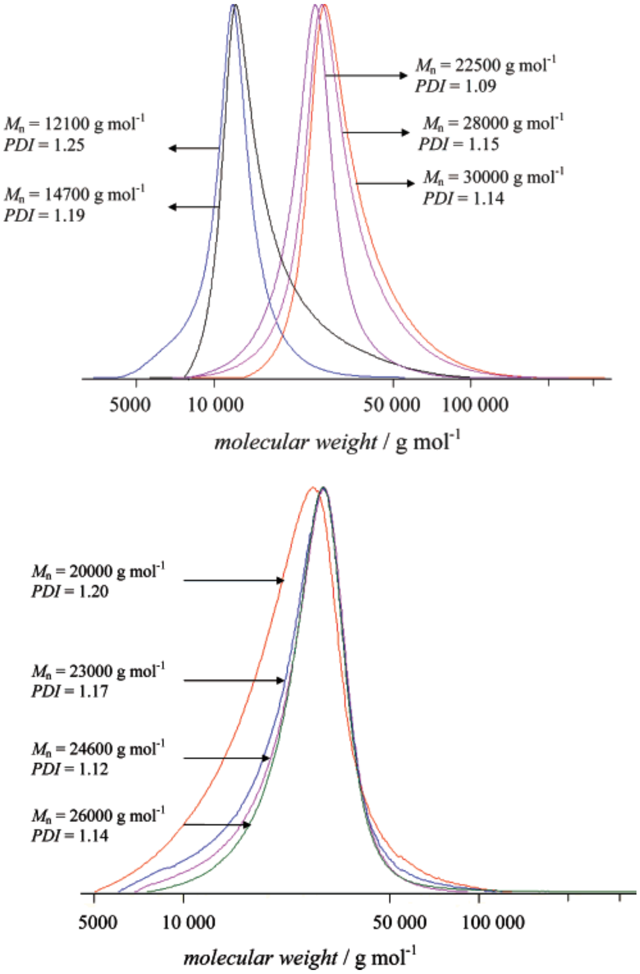


Figure 3. Molecular weight distributions of the poly(diallyldimethylammonium chloride) (PDADMAC) prepared via reversible addition fragmentation chain transfer (RAFT) at 60 °C for different time intervals: (top) trithiocarbonate RAFT agent (curves 1, 2, 3, 4, and 5 are entries 3, 4, 6, 8, and 10 in Table 1); (bottom) xanthate RAFT agent (curves 1, 2, 3, and 4 are the entries C1, C2, C3, and C4 in Table 2).

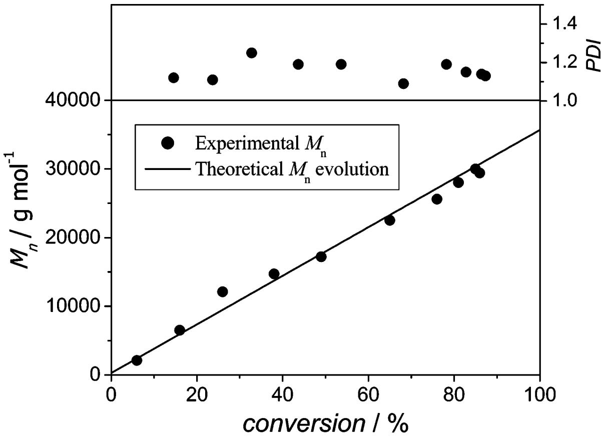


Figure 4. M_n (experimental and theoretical) and PDI as a function of conversion for the polymerization of poly(diallyldimethylammonium chloride) (DADMAC) at 60 °C, mediated by 3-benzyltrithiocarbonyl propionic acid (trithiocarbonate reversible addition fragmentation chain transfer (RAFT) agent). The polydispersities are seen to be low and there is excellent agreement between theoretical and experimental molecular weight.

Table 3. Effect of Temperature on Cyclopolymerization of Diallyldimethylammonium Chloride (DADMAC)[a]

run no.	temp (°C)	conversion (%)	$M_{n,GPC}$ (g mol^{-1})	M_{nth} (g mol^{-1})[b]	PDI
1	60	81	28000	29000	1.15
2	80	78	27700	27800	1.10
3	90	80	33000	28500	1.41

[a] Reaction run in H_2O using 2.1 mol L^{-1} monomer, 9.6 × 10^{-3} mol L^{-1} 3-benzyltrithiocarbonyl propionic acid reversible addition fragmentation chain transfer (RAFT) agent, 1.1 × 10^{-2} mol L^{-1} ammonium persulfate for 20 h. A loss of control is observed for the 90 °C polymerization, evidenced by a high PDI of 1.41.

groups produced using the trithiocarbonate RAFT agent; however, such an analysis was more difficult for the aromatic group lacking xanthate mediated polymer. Peaks due to end groups and polymer in the ^1H NMR spectrum are overlapping, and in the ^{13}C spectrum it was not possible to differentiate peaks from the noise in the region of interest and assign them to end groups.

The cyclopolymerization of DADMAC using concentrated monomer solution (4.2 mol L^{-1}, see run 11, Table 1) led to a reaction which reached 100% conversion after 20 h and a high polydispersitiy of 2.72. This may have been due to (a) a high viscosity causing propagating radicals to have difficulty in reacting with S=C bonds owing to a diffusion limitation but (b) may also have been influenced by other kinetic complications arising from a high concentration of the monomer,[35] for example $\pi-\pi$ associations of monomer molecules.

The effect of temperature on the trithiocarbonate RAFT mediated ring-closing polymerization was also studied. The polymerizations were conducted at 60, 80, and 90 °C, and the results appear in Table 3. Both 60 and 80 °C experiments gave low polydispersities with close agreement between theoretical and experimental molecular weights. The 90 °C experiment gave a higher PDI of 1.41, indicating some loss of control, and the experimental molecular weight differed significantly from the theoretical one. This behavior may reflect a competing conventional radical cyclopolymerization process.

The response of the system to RAFT agent concentration has also been evaluated (see Table 4). For the trithiocarbonate mediated system, the response of molecular weight to increasing the RAFT agent concentration is well described by theory, showing a decrease in molecular weight as the amount of RAFT agent is increased. The molecular weight in xanthate mediated systems also responds to RAFT agent concentration but as has

Table 4. Effect of Reversible Addition Fragmentation Chain Transfer (RAFT) Agent Concentration: An Increase in RAFT Agent Concentration Reduces the Molecular Weight[a]

run no.	RAFT (mol $L^{-1} \times 10^2$)	conversion (%)	$M_{n,GPC}$ (g mol^{-1})	M_{nth} (g mol^{-1})[b]	PDI
1	0.96	84	27000	29900	1.11
2	1.44	86	23000	20500	1.15
3	1.92	81	15400	14500	1.30
4	2.40	88	14200	12700	1.17

[a] Reaction run using 3-benzyltrithiocarbonyl propionic acid RAFT agent, 60 °C in H_2O:dimethylformamide (DMF) (1:1 V/V) using 2.1 mol L^{-1} monomer and 1.1×10^{-2} mol L^{-1} ammonium persulfate for 20 h).

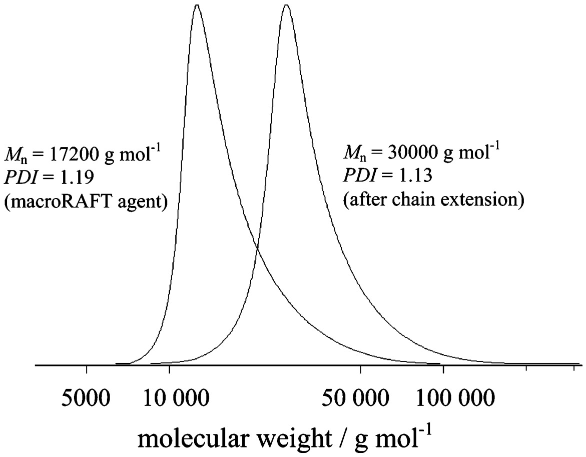


Figure 5. Molecular weight distributions of the macroreversible addition fragmentation chain transfer (RAFT) agent (run 5, Table 1) and its subsequent chain-extended product. The polymerization made use of the trithiocarbonate RAFT agent and was carried out at 60 °C for 20 h.

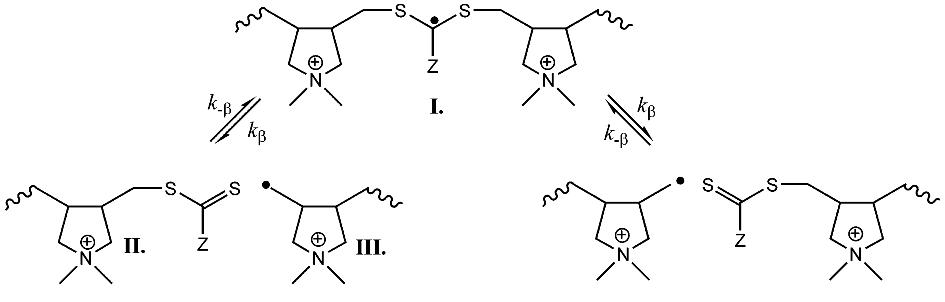
been seen earlier, close agreement with theoretical molecular weights is not observed. The living character of the polymer chains produced with the trithiocarbonate system has been further confirmed by chain extension using a second addition of the same monomer DADMAC. An amount of 0.25 g of PDADMAC (entry 5 in Table 1, 8 h, M_n = 17200 g mol^{-1}, PDI = 1.19) was employed as a macroRAFT agent for further chain extension. The M_n of the chain-extended polymer was increased to 30000 g mol^{-1} with a PDI of 1.13, indicating that the cyclopolymer is effectively functionalized with RAFT end groups. NMR analysis showed the polymer to have the same structure as the initial macroRAFT agent sample. The MWD of the macroRAFT agent and the chain extended product appear in Figure 5.

In general, absolute molecular weight analysis of polyelectrolytes with accuracy and certainty is difficult. For example, as shown by Laschewsky et al.,[31] the M_n for polymers of *N*-vinylbenzyl-*N*,*N*,*N*-trimethylammonium chloride, derived by three independent methods, namely multiangle laser light scattering (MALLS), end-group analysis, and GPC calibrated with P2VP standards, are not in agreement. For this system, the M_n values estimated from end-group analysis agree well with the theoretically expected ones, GPC calibration by P2VP standards provides much lower values, whereas evaluation by MALLS provides much higher values. In the current study, the excellent agreement obtained between the observed M_n from GPC (calibration with P2VP standards) and the M_{nth} for the polymers obtained from the trithiocarbonate RAFT agent in the present work is notable. It seems unlikely that such excellent agreement could occur by accident. This close correlation lends support to the notion that P2VP is an appropriate standard for GPC analysis of PDADMAC. However, despite the linear increase of molar mass, very low polydispersities, and successful chain-extension experiments, all of which clearly demonstrate a controlled process, a detailed study using absolute molecular weight determination methods is required to determine how well the molecular weights measured in the current study reflect the true molecular weights.

Rate of Polymerization. It must be noted at the outset that the two different systems, while being conducted at the same temperature, have both different RAFT agents and different initiators. Although the decomposition kinetics of 4,4′-azobis-(4-cyanovaleric acid) are those of first-order decay, the supply of radical from ammonium persulfate is a kinetically complex process, proceeding through both a redox reaction of the persulfate ion with the chloride ion and also through formation of a complex between monomer cations and the persulfate ion, which subsequently undergoes homolytic cleavage.[35] This explains the differences in rates of polymerization between the two RAFT systems.

From the established body of mechanistic and kinetic knowledge about the RAFT process, the equilibrium constant $K = k_{-\beta}/k_{\beta}$ (see Scheme 2) is known to affect the rate of polymerization.[32−34] In particular, if the stability of the RAFT adduct radical (P_n−S−C•(*Z*)−S−P_m, Scheme 2I) is far greater than that of the propagating radical (P_n•, Scheme 2III), the rate of the polymerization may be strongly retarded or experience an inhibition period because the propagating radical cannot effectively reform via the β-scission reaction (see Scheme 2). Propagating radicals produced when DADMAC forms five-membered rings via cyclopolymerization are always primary, and the molecules lack any other radical stabilizing features in their substrate. This is in contrast to the RAFT adduct radical which must have a higher stability because it is tertiary and experiences additional stabilization from the presence of three electron lone pair donors (three sulfur atoms in the case of the trithiocarbonate and two sulfurs and an oxygen atom in the case

Scheme 2. The Core Reversible Addition Fragmentation Chain Transfer (RAFT) Equilibrium in which the MacroRAFT Radical (I) Undergoes Reversible *β*-Scission to Yield MacroRAFT Agent (II) and Propagating Radicals (III)



Z = S-CH_2-CH_2-COOH or O-CH_2-CH_3

Table 5. Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization of Diallyldimethylammonium Chloride (DADMAC) in Saturated NaCl: A Reduction in the Rate of the NaCl Containing Systems is Observed when Compared to the Non-NaCl Containing Systems[a]

conditions	run no.	time (h)	conversion (%)	$M_{n,GPC}$ (g mol^{-1})	M_{nth} (g mol^{-1})[b]	PDI
A	1	2	14	8100	52000	1.36
A	2	8	31	14000	11200	1.18
A	3	20	53	22000	19000	1.13
A	4	24	54	23000	19300	1.17
B	1	2.8	7	22500	7100	1.33
B	2	4.7	10	29000	9500	1.17
B	3	6.6	11	29000	11000	1.38
B	5	7.8	13	34000	13000	1.10

[a] Condition A: 9.6 × 10^{-3} mol L^{-1} 3-benzyltrithiocarbonyl propionic acid, 1.1 × 10^{-2} mol L^{-1} ammonium persulfate, 2.1 mol L^{-1} monomer. Condition B: 4.6 × 10^{-3} mol L^{-1} ethylxanthogenacetic acid, 1.5 × 10^{-3} mol L^{-1} 4,4′-azobis(4-cyanovaleric acid), 2.7 mol L^{-1} monomer.

of the xanthate/MADIX agent). On the basis of radical stabilities alone, but in contrast to what is observed, it might be expected therefore that the DADMAC system should exhibit significant or total rate retardation/inhibition.

It is likely that there is a thermodynamic driving force, other than chemical radical stability, that causes β-scission to occur and that this might be the Coulombic repulsion experienced by the two polyelectrolyte chains that are held together in close proximity by a RAFT agent (see Scheme 2I). It is known from the theory of electrolytes that electric charges in solution can be screened from one another by the presence of counterions, and it is here postulated that a reduction in the fragmentation tendency of the RAFT adduct radical might be affected if the electrostatic repulsion between positively charged chains could be reduced. To probe this effect, saturated NaCl was introduced to the reaction medium to see if this led to a reduction in the rate of polymerization (Table 5).

As can be seen in Figure 6, a reduction in the rate (of similar magnitude) was indeed observed for both the trithiocarbonate and xanthate systems, indicating that an electrostatic interaction might be responsible for the lack of rate retardation/inhibition. As a control, a polymerization was performed using only monomer, water, initiator (4,4′-azobis(4-cyanovaleric acid) and saturated NaCl, data not depicted). In this experiment, no reduction in the rate was observed, excluding the possibility that the reduced rate was related to an initiator or chain-propagation phenomenon. On the contrary, it is known that an increase in the ionic strength should increase the rate of the propagation reaction because there is a reduced Coulombic repulsion between the polyelectrolyte radical and monomer species.[35]

It is interesting that propagation is clearly not prevented by the same electrostatic repulsions that induce fragmentation of the RAFT-adduct radical. This might be (a) because the fragmentation reaction creates two (large) polycations and propagation is a reaction between a polycation and a (small) monomer or (b) because it just so happens that, while strong enough to induce faster fragmentation, the electrostatic repulsions are not strong enough to prevent propagation.

Conclusions

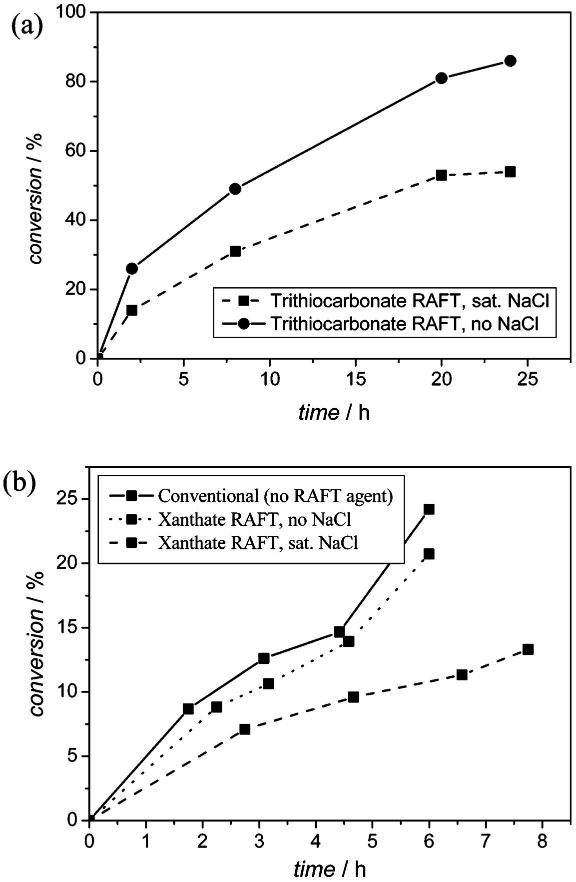


Figure 6. Conversion vs time plots for (a) 3-benzyltrithiocarbonyl propionic acid (trithiocarbonate reversible addition fragmentation chain transfer agent (RAFT) agent) and ammonium persulfate polymerizations and (b) ethylxanthogenacetic acid (xanthate RAFT agent) and 4,4′-azobis(4-cyanovaleric acid) polymerizations. Both contain data from experiments with and without saturated NaCl and demonstrate the difference in rate of polymerization between these systems. All polymerizations were carried out at 60 °C with water as solvent. NaCl was added such that a small amount remained, even at the reaction temperature, indicating saturation. This quantity was close to 2 mol L^{-1}.

Controlled/living cyclopolymerization of DADMAC in aqueous medium using reversible addition fragmentation chain transfer (RAFT) under mild temperature conditions is achieved. The two RAFT agents ethylxanthogenacetic acid and 3-benzyltrithiocarbonyl propionic acid were not equally suitable however: the former, while giving low polydispersities indicative of a controlled process, did not give the desirable linear evolution of molecular weight that was affected by the latter. The polymerization led to the formation of water-soluble linear polycations with very narrow polydispersity, with PDIs reaching ca. 1.10. Saturation of polymerizing systems with NaCl led to reductions in the rate (without loss of control), indicating that in this system, Coulombic interactions might be crucial in interpreting the chemical equilibrium in the RAFT process, a phenomenon not previously observed. This work demonstrates a highly effective method of achieving molecular weight control over cyclopolymerizations. We believe that controlled cyclopolymerization of DADMAC via RAFT will allow for tailored and complex macromolecular architectures which might find application in fields where PDADMAC is already of importance.

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