Aminolysis of Polymers with Thiocarbonylthio Termini Prepared by RAFT Polymerization: The Difference between Polystyrene and Polymethacrylates

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ABSTRACT: Aminolysis of polystyrene and poly(methyl methacrylate) (PMMA) prepared by reversible addition−fragmentation chain transfer (RAFT) polymerization was investigated. The product of the former contains predominantly double molecular weight species by the formation of disulfide bond, whereas the latter formed coupled species which consequently cleaved to unimolecular weight species. MALDI−TOF MS (matrix-assisted laser desorption ionization time-of-flight mass spectrometry), elemental analysis and ^{1}H NMR indicated that thiolactone terminus was formed after aminolysis of PMMA. We propose that the thiol end groups generated during the aminolysis of PMMA tend to cyclize through "backbiting" to form thiolactone structure. A similar reaction was observed in the case of poly(*N*, *N*-dimethylaminoethyl methacrylate) and poly(laury methacrylate). Despite this, the preparation of thiol-end functionalized PMMA was achieved by introducing a short block of polystyrene after the RAFT polymerization of MMA.

Introduction

Controlled radical polymerization mediated by thiocarbonylthio compounds through reversible addition−fragmentation chain transfer (RAFT) process[1] has been used to synthesize a variety of polymers with well-defined structures. An important characteristic of the RAFT polymerization is that the leaving group and the activating group of the thiocarbonylthio compound are retained at the ends of the resulting polymers. The retention of these groups affords the preparation of polymers with specific functional end groups by the choice of appropriate RAFT agents[2−5] or further transformation[6−8] of these groups through chemical reactions.

Polymers with thiol terminus or disulfide bond are of great interests in areas ranging from microelectronics to biotechnology[9−11] due to the reactivity of thiol or disulfide to, for example, gold substrate.[12,13] Thus, it is highly desired that such kind of polymers can be obtained in high yield from posttreatment of the product of RAFT polymerization. This was indeed achieved by aminolysis,[14−18] hydrolysis[19−21] and metal hydrides reduction[12,13,22,23] of the products such as polystyrene (PS), poly(acrylic acid) and poly(*N*-isopropylacrylamide). However, for poly(methyl methacrylate) (PMMA), remarkably low yield of thiol end was reported in hexylamine treatment of PMMA prepared by RAFT polymerization.[5] The same phenomenon was also observed in our and other laboratories,[24] implying different mechanisms of the reactions for PS and PMMA. The purpose of the present work is to investigate the mechanism of the transformation reaction, and to try to find an alternative scenario for the PMMA issue.

Experimental Section

Materials. Methyl methacrylate (MMA, Shanghai Fourth Factory of Chemicals, 98%), *N,N*-dimethylaminoethyl methacrylate (DMAEMA, Acros, 98%), laury methacrylate (LMA, Acros, 98%) and styrene (Yonghua Special Chemicals, 99%) were passed through Al_2O_3 and silica gel columns, respectively, distilled at reduced pressure and stored under argon. Benzene (Shanghai Fourth Factory of Chemicals, 99.5%) and tetrahydrofuran (THF, Shanghai Feida, 99.5%) were refluxed over sodium and distilled. Cyclohexylamine was distilled at reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN, Shanghai Fourth Factory of Chemicals, 99%) was recrystallized from methanol. Carbon disulfide (CS_2, Shanghai Fourth Factory of Chemicals, 99%) was purified by vigorously shaking with $KMnO_4$ (0.4 wt % based on CS_2) followed by filtration and distillation to collect a colorless fraction. Bromobenzene (Wulian Chemicals, 99.5%) was dried over $CaCl_2$ and distilled before use. Dimethyl sulfoxide (DMSO, Aldrich, 98%), ethyl α-bromoisobutyrate (Aldrich, 98%) and α-cyano-4-hydroxycinnamic acid (Aldrich, 99%) were used as received.

Measurement. Gel permeation chromatography (GPC) was performed on a Waters 410 GPC system equipped with Waters Styragel columns (pore size: 10^2, 10^3, 10^4 Å) using THF as eluent at a flow rate of 1 mL/min at 40 °C. The elution of the sample was detected by a Waters 410 RI detector. The system was calibrated by narrow poly(methyl methacrylate) standards (MW range: $700-3 \times 10^4$ g/mol) and narrow polystyrene standards (MW range: $200-3 \times 10^6$ g/mol). The ultraviolet absorption of cumyl dithiobenzoate in THF was recorded by a Perkin-Elmer Lambda35 UV−vis spectroscope at 25 ± 0.1 °C with wavelength from 190 to 650 nm. High-performance liquid chromatography (HPLC) was performed on an instrument composed of a Waters 515 pump, a C-18 column (SymmetryShield RP-18, 5.0 μm, 4.6×250 mm), and a UV detector with the wavelength settled at 254 nm. Acetonitrile/water (85/15, v/v) was used as eluent (1.0 mL/min) at 40 °C. Fourier transform infrared spectroscopy (FT-IR) was performed on a Magna-550 instrument (potassium bromide pellet). Gas chromatography−mass spectroscopy (GC−MS) was performed on a Finnigan Voyager instrument in electrospray ionization mode (70 eV), through a HP-5MS capillary column (0.25 μm, 0.25×30 mm) using helium as carrier gas at a flow rate of 1.0 mL/min. The initial temperature was kept at 100 °C for 2 min, then to 300 °C at a rate of 20 °C/min. Compounds was identified, if accessible, using the NIST Mass Spectral Search Program (NIST, Washington, DC). Elemental analysis was determined by oxygen flask combustion.

High-resolution liquid NMR spectroscopy was carried out on a Bruker DMX500 instrument operating at 500.13 MHz for ^{1}H and 125.77 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane

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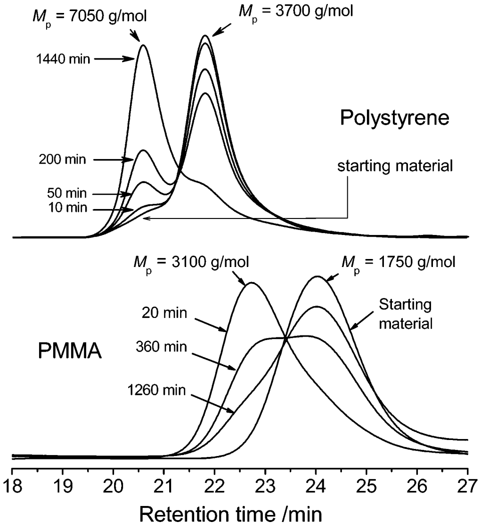


Figure 1. Gel permeation chromatograms of aminolysis of polystyrene (PS, $M_{n,\ GPC} = 3000$ g/mol, $M_w/M_n = 1.19$) (upper) and poly(methyl methacrylate) (PMMA, $M_n = 1500$ g/mol, $M_w/M_n = 1.16$) (lower) with cyclohexylamine at room temperature for different times indicated in the figure. PS system: 0.034 mol/L of PS, 1.76 mol/L of amine; PMMA system: 0.067 mol/L of PMMA, 3.41 mol/L of amine; Room temperature, tetrahydrofuran as the solvent.

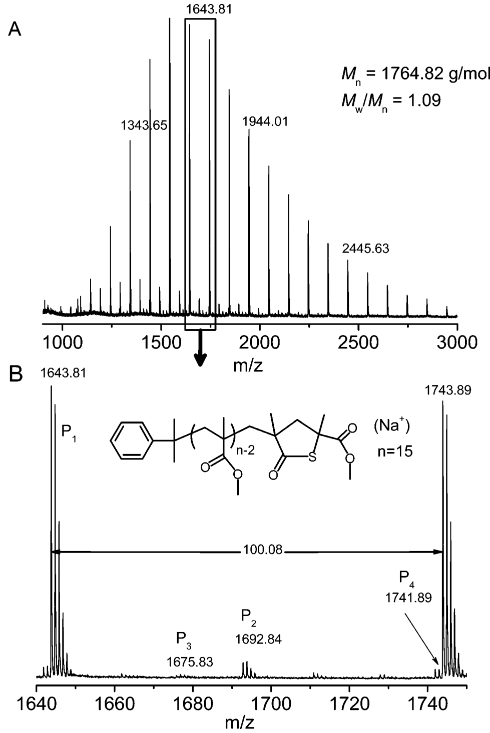


Figure 2. Matrix-assisted laser desorption ionization time-of-flight mass spectrum of aminolysis product of poly(methyl methacrylate) (PMMA,$M_n = 1500$ g/mol, $M_w/M_n = 1.16$). (A: full view, B: Partial enlargement.). Aminolysis conditions are identical with those in Figure 1.

as reference. 1D spectra were obtained with a 5 mm QNP probehead at 297 K. For 2D spectra, a broad-band probehead was used with heteronuclear single-quantum coherence (HSQC) for ^{1}H$-^{13}$C correlation. Distortionless enhancement by polarization transfer (DEPT, $\theta = 135°$), H, H$-$COSY and HSQC experiments were performed according to standard Bruker software.

Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI$-$TOF MS) analysis were performed on a Voyager-DE STR (Applied Biosystems, Framingham, MA) equipped with a nitrogen laser emitting at 337 nm with a 3 ns pulse duration. The instrument was calibrated with Angiotensin and Insulin and operated in the reflector mode. The accelerating potential is 20 kV. Spectra were the sum of 200 shots. The matrix used for all experiments was α-cyano-4-hydroxycinnamic acid (CHCA). Samples were prepared by mixing the solution of polymer (5 μL, 10 mg/mL in THF), the matrix (45 μL, 10 mg/mL in THF (for PMMA) or in DMSO (for PDMAEMA)), and sodium trifluoroacetate (STFA, cationizing agent, 5μL, 10 mg/mL in THF). For PDMAEMA, no cationizing agent was used according to literature.[25] An aliquot of 1 μL of the resulting mixture was spotted on the gold plate and air-dried.

Synthesis of Cumyl Dithiobenzoate (CDB). CDB was synthesized according to the literature procedure.[26] To obtain product of high purity, recrystallization was performed twice from petroleum ether. Purple-red crystals: yield 19% (based on dithiobenzoic acid); purity 99.1% by HPLC. FT-IR: υ/cm^{-1} = 1224 and 1046 (vs $C{=}S$). UV$-$vis max (CCl$_4$): 303 and 531 nm. ^{1}H NMR: δ (ppm) = 2.0 (s, 6H, C**H**$_3$), 7.21 (t, 1H, Ar**H**), 7.30 (m, 4H, Ar**H**), 7.43 (t, 1H, Ar**H**), 7.54 (d, 2H, Ar**H**), 7.84 (d, 2H, Ar**H**). MS: $m/e = 272$. Anal. Calcd for $C_{16}H_{16}S_2$: C: 70.49, H: 5.88, S: 23.63. Found: C: 70.83, H: 6.00, S: 23.39.

Synthesis of 2-(Ethoxycarbonyl)prop-2-yl Dithiobenzoate (ECPDB). ECPDB was synthesized using a modified Grignard process according to the literature.[8,26] The Grignard reagent, phenylmagnesium bromide, was prepared from bromobenzene (6.28 g, 0.04 mol) and magnesium powder (1.00 g) in dry THF (30 mL). The solution was warmed to 50 °C, and CS$_2$ (3.05 g, 0.04 mol) was added over 15 min while maintaining the reaction temperature at 50 °C. Ethyl α-bromoisobutyrate (7.00 g, 0.036 mol) was added to the resultant dark brown solution. The reaction temperature was raised to 80 °C and maintained for 60 h. Then, ice water (50 mL) was added, and the organic layer was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the crude product was purified by silica gel column chromatography, using *n*-hexane/diethyl ether (9:1) as eluent. Red oil: 1.48 g, yield 10.8%, purity = 96% by HPLC. ^{1}H NMR: δ (ppm) = 1.24 (t, 3H, CH$_2$C**H**$_3$), 1.76 (s, 6H, 2 × C**H**$_3$), 4.17 (q, 2H, OC**H**$_2$CH$_3$), 7.35 (dd, 2H, *meta* Ar**H**), 7.52 (dd, 1H, *para* Ar**H**), 7.95 (d, 2H, *ortho* Ar**H**).

Synthesis of Polystyrene (PS) with Dithiobenzoate Terminus. Styrene (5.37 g, 0.045 mol), CDB (0.129 g, 0.45 mmol), and AIBN (0.026 g, 0.15 mmol) were dissolved in benzene (3 mL) in a 25 mL flask, and the solution was degassed with three cycles of freezing$-$pump$-$thawing. The reaction mixture was heated under argon at 60 °C for 20 h before quenched into liquid nitrogen to stop the polymerization. The resulting PS was obtained as a pink powder by dissolving in THF and precipitating from 20-fold methanol for three times. The product was analyzed by GPC and ^{1}H NMR. Number-average molecular weight, $M_n = 3000$ g/mol, polydispersity index, $M_w/M_n = 1.19$.

Synthesis of Poly(methyl methacrylate) (PMMA) with Dithiobenzoate Terminus. MMA (1.91 g, 0.019 mol), CDB (1.29 g, 4.71 mmol), and AIBN (0.31 g, 1.91 mmol) were dissolved in benzene (3 mL) in a 10 mL flask and the solution was degassed with three cycles of freezing$-$pump$-$thawing. The reaction mixture was heated under argon at 60 °C for 5 h before quenched into liquid nitrogen to stop the polymerization. The resulting PMMA was obtained as a pink powder by dissolving in THF and precipitating from 20-fold petroleum ether three times. The product was analyzed by GPC and ^{1}H NMR. Number-average molecular weight: $M_n = 1500$ g/mol. Polydispersity index: $M_w/M_n = 1.16$.

Synthesis of Poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA) with Dithiobenzoate Terminus. DMAEMA (5.03 g, 0.032 mol), CDB (0.27 g, 0.97 mmol), and AIBN (0.053 g, 0.32 mmol) were dissolved in benzene (4 mL) in a 25 mL flask and the solution was degassed with three cycles of freezing$-$pump$-$thawing. The reaction mixture was heated under argon at 60 °C for 3 h before quenched into liquid nitrogen to stop the polymerization. The resulting PDMAEMA was obtained by dissolving in THF and precipitating from 20-fold cold hexane for three times.

Scheme 1

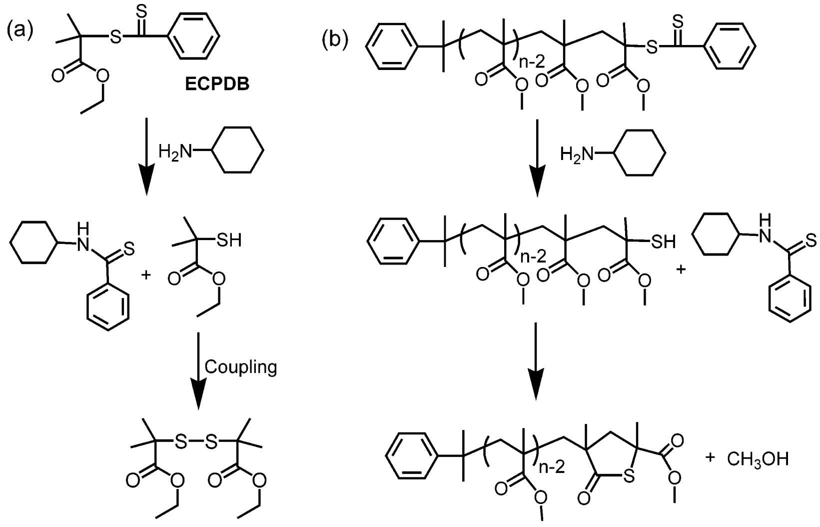
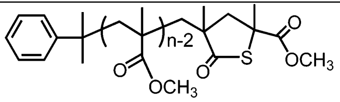
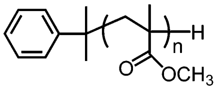
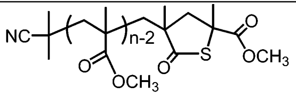
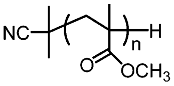
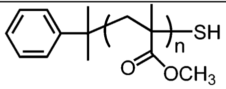
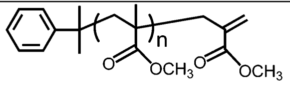


Table 1. Assignment of Matrix-assisted Laser Desorption Ionization Time-of-flight Mass Spectrum of Poly(methyl methacrylate) after Aminolysis

Peak	Monoisotopic Mass		Structure	Ion	Degree of Polymerization (n)
	Exp.	Theo.[a]			
P_1	1643.81	1643.82		Na	15
		1643.87		Na	15
P_2	1692.84	1692.82		Na	16
		1692.87		Na	16
P_3	1675.83	1675.84		Na	15
P_4	1741.89	1741.91		Na	15

[a] calculated by the isotope calculator in the Voyager-DE STR software.

The product was analyzed by GPC. Number-average molecular weight: $M_n = 4000$ g/mol. Polydispersity index: $M_w/M_n = 1.28$.

Synthesis of Poly(laury methacrylate) (PLMA) with Dithiobenzoate Terminus. LMA (7.20 g, 0.028 mol), CDB (0.38 g, 1.41 mmol), and AIBN (0.049 g, 0.30 mmol) were dissolved in benzene (4 mL) in a 25 mL flask, and the solution was degassed with three cycles of freezing-pump-thawing. The reaction mixture was heated under argon at 60 °C for 36 h before being quenched into liquid nitrogen to stop the polymerization. The resulting PLMA was obtained by dissolving in THF and precipitating from 20-fold methanol for three times. The product was analyzed by GPC. Number-average molecular weight: $M_n = 5100$ g/mol. Polydispersity index: $M_w/M_n = 1.15$.

Synthesis of Poly(methyl methacrylate)-*b*-polystyrene (PMMA-*b*-PS) Diblock Copolymer. PMMA macro-RAFT agent ($M_n = 3660$ g/mol, $M_w/M_n = 1.08$) was synthesized by RAFT polymerization as follows: MMA (6.20 g, 0.062 mol), CDB (0.57 g, 2.1 mmol), and AIBN (0.16 g, 0.97 mmol) were dissolved in benzene (16 mL) in a 50 mL flask and the solution was degassed with three cycles of freezing−pump−thawing. The reaction mixture was heated under argon at 60 °C for 8 h before quenched into liquid nitrogen to stop the polymerization. The resulting PMMA was obtained as a pink powder by dissolving in THF and precipitating from 20-fold petroleum ether for three times.

PMMA-*b*-PS was prepared by RAFT using above PMMA as macro-RAFT agent: Styrene (1.03 g, 0.01 mol), PMMA macro-

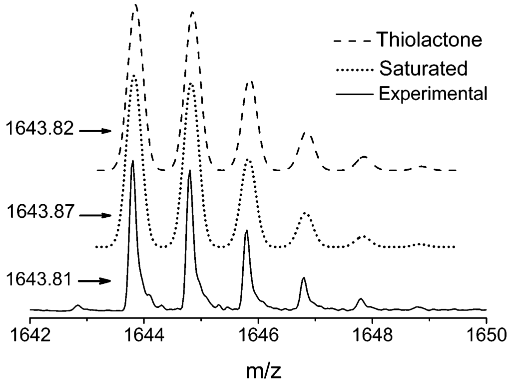


Figure 3. Calculated isotopic mass spectrum patterns of poly(methyl methacrylate) aminolysis product.

RAFT agent (1.54 g, 0.42 mmol) and AIBN (0.026 g, 0.15 mmol) were dissolved in benzene (5 mL) in a 25 mL flask and the solution was degassed with three cycles of freezing−pump−thawing. The reaction mixture was heated under argon at 60 °C for 24 h before quenched into liquid nitrogen to stop the polymerization. The resulting polymer was obtained by dissolving in THF and precipitating from 20-fold methanol for three times. The product was analyzed by GPC. Number-average molecular weight: $M_n = 4750$ g/mol. Polydispersity index: $M_w/M_n = 1.17$.

Aminolysis of Polymers with Cyclohexylamine. The THF solution of polymer was degassed from three freezing−pump−thawing cycles and sealed with rubber septum. Cyclohexylamine (50-folds in excess) was added into the solution with syringe after degassed from three freezing−pump−thawing cycles. For example, PMMA (1.01 g, 0.67 mmol) was dissolved in THF (10 mL) in a 25 mL flask and degassed. Cyclohexylamine (3.37 g, 0.034 mol) was degassed and added into the polymer solution with syringe. At predetermined periods, an aliquot of mixed solution was taken out and analyzed by GPC. The reaction mixture was precipitated from hexane for three times and resulting aminolysis product was dried under vacuum. The similar procedures were also applied to PS, PDMAEMA, PLMA, and PMMA-*b*-PS.

Aminolysis of ECPDB with Cyclohexylamine. ECPDB (0.105 g, 0.39 mmol) was dissolved in THF (1.5 mL) in a 10 mL flask and degassed. Cyclohexylamine (1.59 g, 0.017 mol) was degassed and added into the polymer solution with syringe. After 24 h, an aliquot of mixed solution was taken out and analyzed by GC−MS.

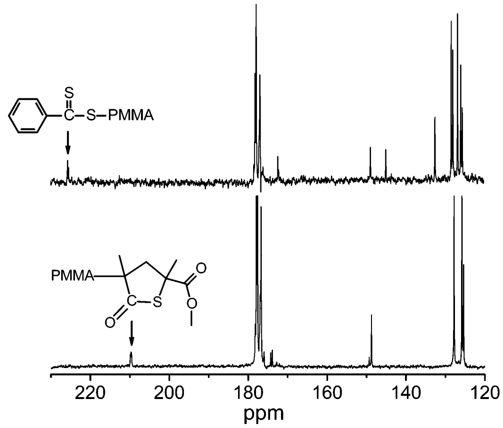


Figure 5. Partial ^{13}C NMR spectra (CDCl$_3$) of poly(methyl methacrylate) (PMMA, $M_n = 1500$ g/mol, $M_w/M_n = 1.16$) before (upper) and after (lower) aminolysis. Aminolysis conditions are identical with those in Figure 1.

Results and Discussion

We first compare the aminolysis of PS ($M_n = 3000$ g/mol, $M_w/M_n = 1.19$) and PMMA ($M_n = 1500$ g/mol, $M_w/M_n = 1.16$) which were prepared by RAFT polymerization mediated by cumyl dithiobenzoate (CDB). These pink products were stirred with cyclohexylamine (50-folds in excess) in tetrahydrofuran (THF) at room temperature for 24 h. For both of the reaction systems, the pink color of the solutions faded within about 30 min, indicating the reaction of thiocarbonylthio moieties. At predetermined period an aliquot of the reaction mixture was taken and analyzed by gel permeation chromatography (GPC). As shown in Figure 1, for PS, a new peak appeared at double molecular weight with increasing intensity, which was attributed

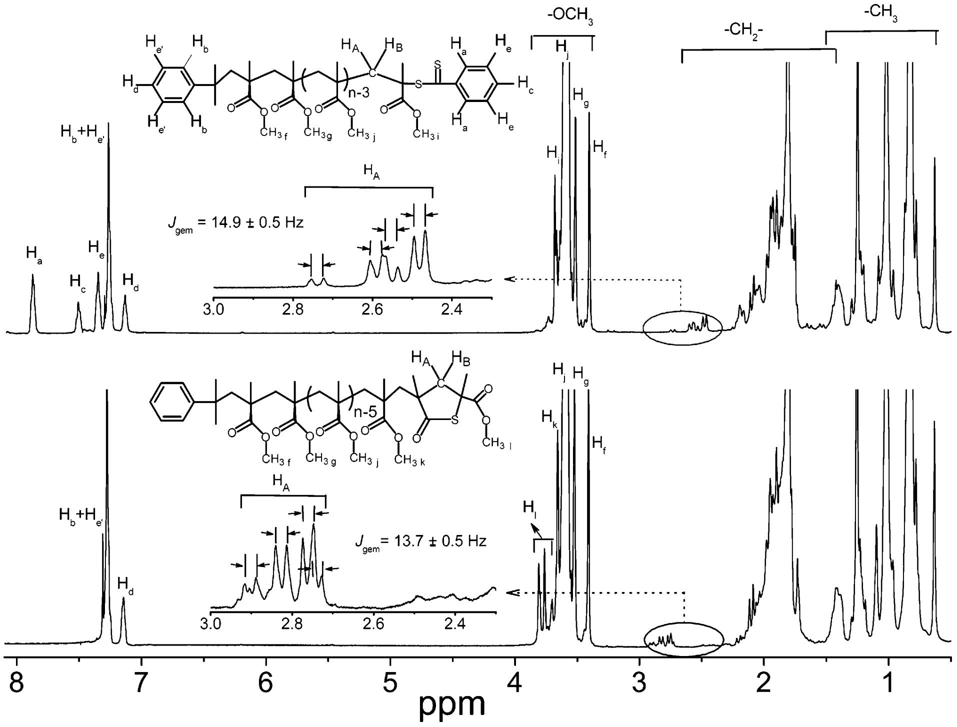


Figure 4. ^{1}H NMR spectra (500 MHz, CDCl$_3$) of poly(methyl methacrylate) (PMMA, $M_n = 1500$ g/mol, $M_w/M_n = 1.16$) before (upper) and after (lower) aminolysis. Inset shows expansion of region $\delta = 2.3-3.0$ ppm. Aminolysis conditions are identical with those in Figure 1.

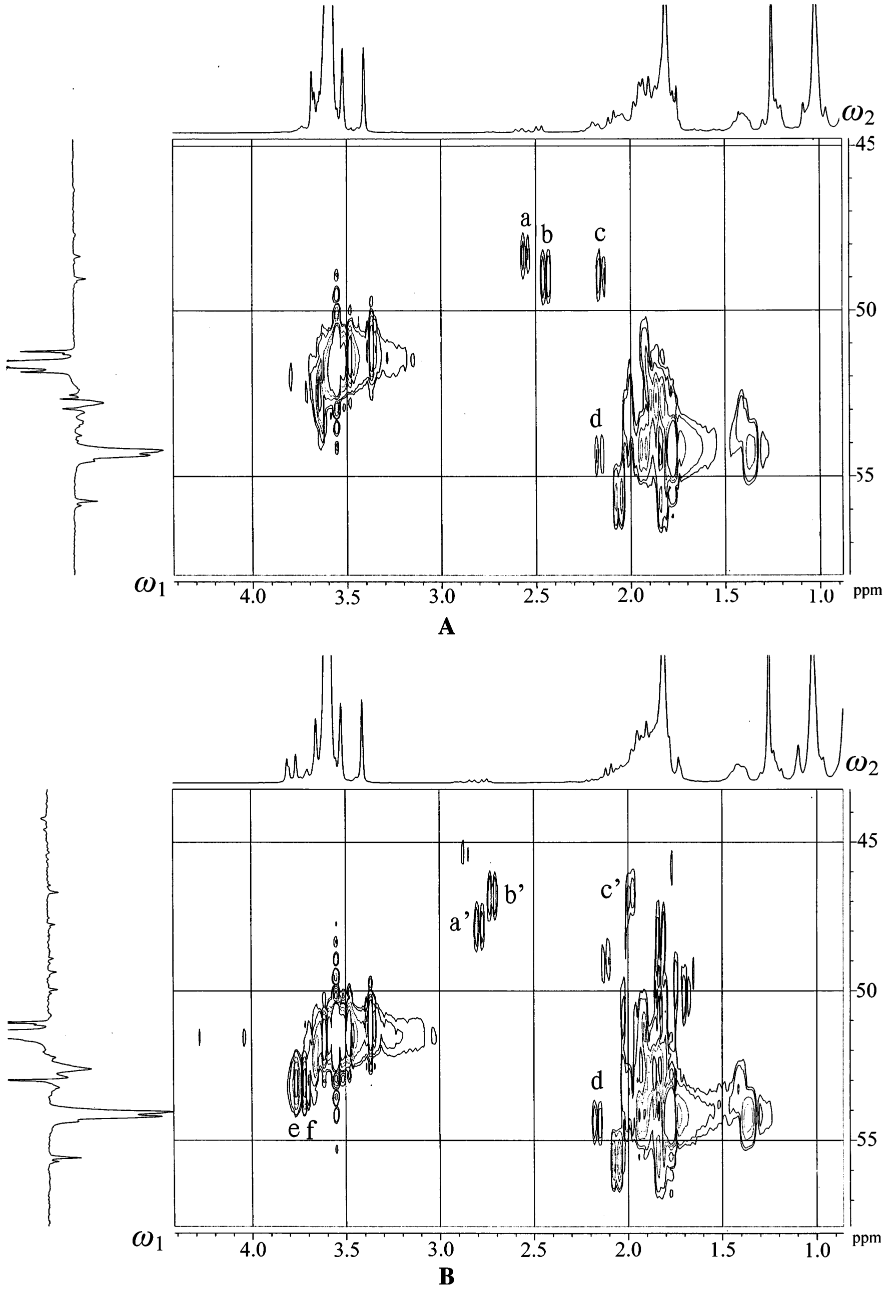


Figure 6. HSQC spectra of poly(methyl methacrylate) (PMMA, M_n = 1500 g/mol, M_w/M_n = 1.16) before (upper) and after (lower) aminolysis. Aminolysis conditions are identical with those in Figure 1.

to the coupling of the resulting thiol end groups to form disulfide.[16] After 24 h, a product of predominant coupled species was obtained. For PMMA, the trend seems to be reverse. At early 20 min a product with peak molecular weight 3100 g/mol, approximately double that of the starting material, was obtained. However, the intensity of the double molecular weight peak decreased remarkably. After 21 h, the reaction mixture contained mainly a product with nearly the same molecular weight as the starting material.

Therefore, PS and PMMA with thiocarbonylthio termini underwent different pathways in aminolysis. This could be due to the following: (1) the aminolysis of PMMA did not yield a thiol end group and/or (2) the resulting thiol group of PMMA could not couple to form disulfide bond. To test this idea, we used 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate, ECPDB (Scheme 1), as a small molecular model compound of PMMA to perform the aminolysis reaction under identical conditions except that the molar concentration of ECPDB was a little higher than that of PMMA. Within 30 min, the red color faded with the appearance of yellow precipitate due to the formation of thioamide that was insoluble in THF.[27] After 24 h, the reaction mixture was analyzed by gas chromatography−mass spectroscopy (GC−MS) (Supporting Information) and quite high amount of coupled species was observed in the GC−MS spectrum (peak e in Supporting Information). Thus, the model compound indeed underwent aminolysis and coupling as shown in reaction a, Scheme 1.

The aminolysis product of PMMA was further analyzed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF MS). As shown in Figure 2, the main series of the peaks exhibits an interval of 100.08 mass units, which corresponds to the MMA repeat unit. The number-average molecular weight and the polydispersity index are M_n = 1764.82 g/mol and M_w/M_n = 1.09, respectively. The main peak, for example m/z = 1643.81, can be attributed to the species with degree of polymerization 15 and two possible end

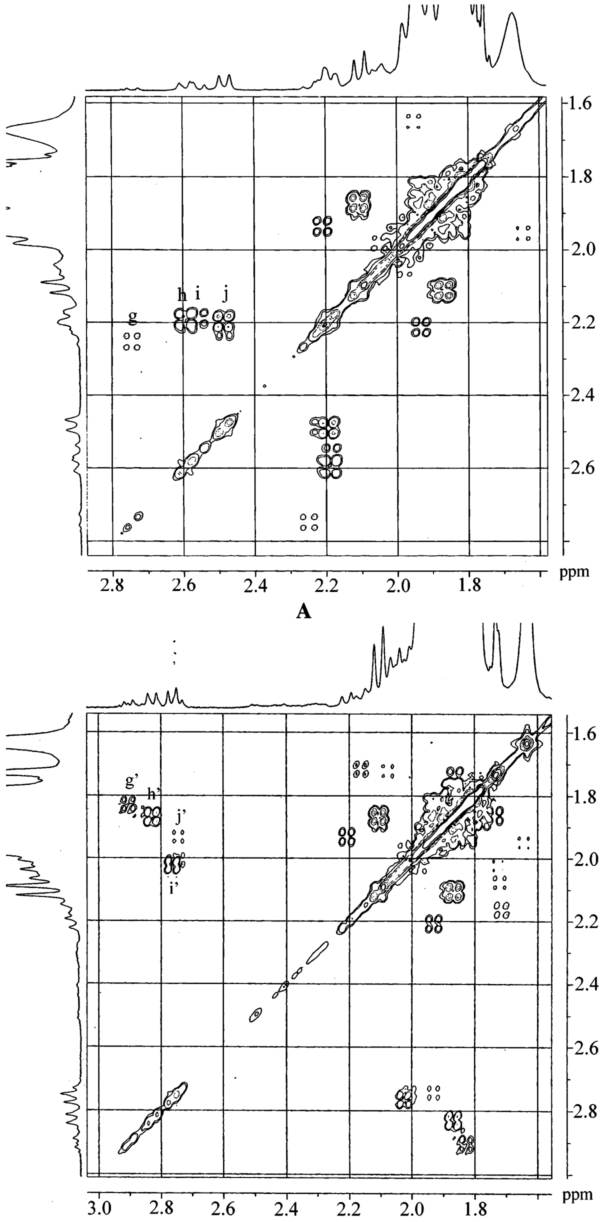


Figure 7. H, H−COSY spectra of poly(methyl methacrylate) (PMMA, M_n = 1500 g/mol, M_w/M_n = 1.16) before (upper) and after (lower) aminolysis. Aminolysis conditions are identical with those in Figure 1.

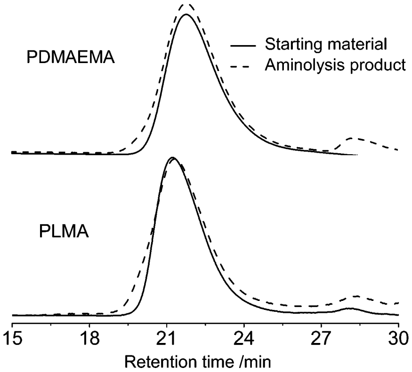


Figure 8. Gel permeation chromatograms of poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA, M_n = 4000 g/mol, M_w/M_n = 1.28) (upper) and poly(laury methacrylate) (PLMA, M_n = 5100 g/mol, M_w/M_n = 1.15) (lower) before (solid line) and after (dashed line) aminolysis. PDMAEMA system: 0.023 mol/L of PDMAEMA, 1.13 mol/L of cyclohexylamine. PLMA system: 0.018 mol/L of PLMA, 0.88 mol/L of cyclohexylamine. Room temperature; tetrahydrofuran as the solvent.

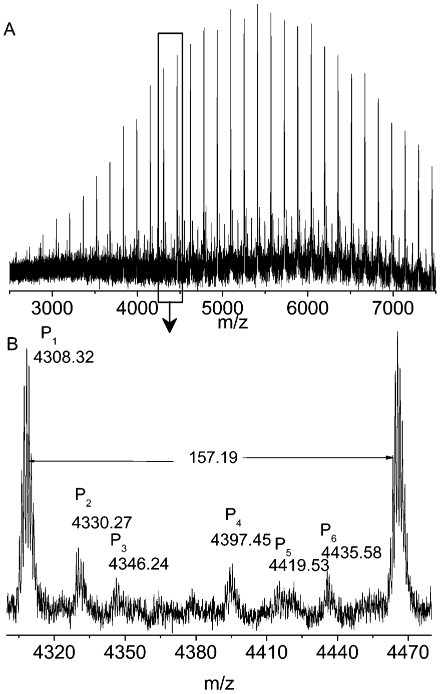


Figure 9. Matrix-assisted laser desorption ionization time-of-flight mass spectrum of aminolysis products of poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA, M_n = 4000 g/mol, M_w/M_n = 1.28). (A, full view; B, partial enlargement). Aminolysis conditions are identical with those in Figure 8.

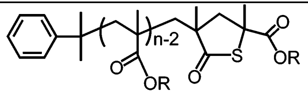
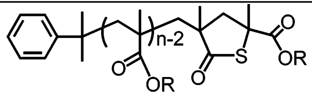
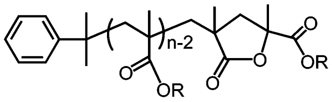
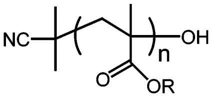
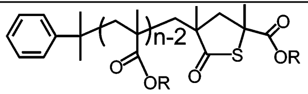
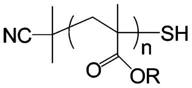
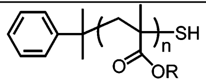
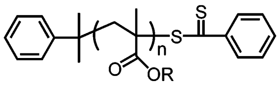
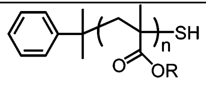
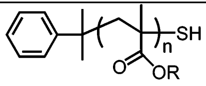
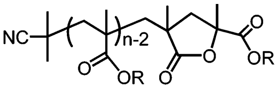
groups, i.e., saturated or thiolactone termini, cationized by Na^+ (Table 1). These two possible structures have equal molar mass and cannot be discriminated even with the aid of calculated isotopic patterns (Figure 3). The enlargement within the *m*/*z* range of 1640 and 1750 is shown in part B of Figure 2. It is interesting to note that initiator (2,2′-azobis(isobutyronitrile)) derived chains appear as a series (P_2, 1692.84) at low molecular weight due to the continuous initiation. In addition, trace amount of chains with thiol and unsaturated end groups, P_3 and P_4, respectively, are also observed (Figure 2B and Table 1).

To determine which structure, e.g., saturated or thiolactone terminus, is responsible for the main series of MALDI−TOF MS spectrum, elemental analysis was performed on the same sample. The result shows a sulfur content of about 1.61%, which is close to the theoretical value, 1.66%, calculated according to thiolactone terminus with the weight-average molecular weight determined by MALDI−TOF MS (M_w = 1921.26 g/mol). The measured sulfur content, together with the result of MALDI−TOF MS, indicates that the main product of aminolysis is that with thiolactone functionality.

The thiolactone terminus was formed by the "backbiting" of the thiol group toward the penultimate unit (reaction b in Scheme 1) due to the stability of five-membered ring. This explains why the model compound, ECPDB, results in merely coupled species due to the lack of penultimate unit. Similar results were also obtained by Ladavière and Claverie in the neutralization of poly(acrylic acid) (PAA) using aqueous NaOH.[21] In another paper, lactone end group was observed by MALDI−TOF MS of PMMA prepared by RAFT polymerization.[28] However, in these studies, the species with thiolactone and lactone terminus composed only small fractions of the samples.

The MALDI−TOF MS spectrum of PMMA prior to aminolysis is quite different from that after aminolysis. In the

Table 2. Assignment of Matrix-assisted Laser Desorption Ionization Time-of-flight Mass Spectrum of Poly(*N*,*N*-dimethylaminoethyl Methacrylate) after Aminolysis[a]

Peak	Monoisotopic Mass		Structure*	Cationization	Degree of Polymerization (n)
	Exp.	Theo.			
P_1	4308.32	4307.98		H	27
P_2	4330.27	4329.96		Na	27
		4329.96		K	27
		4330.09		H	27
P_3	4346.24	4345.94		K	27
		4346.07		H	27
P_4	4397.45	4397.07		H	27
		4397.82		K	26
P_5	4419.53	4419.05		Na	27
P_6	4435.58	4435.03		K	27
		4436.12		K	28

[a] The asterisk denotes R = $-CH_2CH_2N(CH_3)_2$.

former, the major series is assigned to the chains with unsaturated termini cationized by Na^+ (Figure S2 and Table S1 in Supporting Information). Although peaks were observed for chains with saturated and/or thiolactone termini (P_2 in Figure S2B), their intensities are quite low in relative to P_1 since these peaks are overlapped with isotopic peaks of P_1.

The terminal elimination and cyclization were also investigated by 1D and 2D NMR. In Figure 4, the ^1H NMR spectra of PMMA before and after aminolysis clearly show the disappearance of the aromatic protons of dithiobenzoic moiety (H_a, H_c, and H_e). The signals for the PMMA main chain are assigned according to the interpretation by Bovey and Tiers.[29] The methyl protons and methylene protons are resolved to pentad and tetrad (assignment not shown in Figure),[30] respectively, but complexed with the effect of end groups due to the low degree of polymerization (DP ≈ 15). For samples before aminolysis, the final methylene is adjacent to two chiral carbons at both sides, and is a AB system that should exhibit a total of 16 signals due to the different configuration sequences, *RS*, *RR*, *SR*, and *SS*, of the two chiral centers. However, only eight of these signals were observed in the range of $\delta = 2.4-2.8$ ppm (inset in Figure 4) with geminal coupling constant $J_{gem} = -14.9$ Hz, which are attributable to H_A of the AB system. The different intensities of these signals may be due to different contents of the

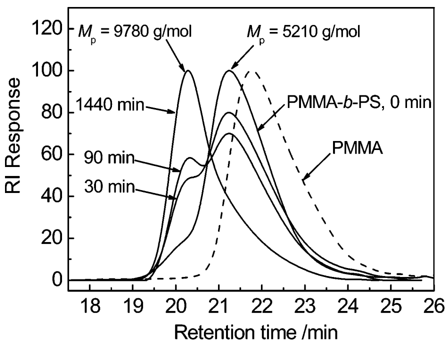


Figure 10. Gel permeation chromatograms of poly(methyl methacrylate) (PMMA,$M_n = 3660$ g/mol, $M_w/M_n = 1.08$) homopolymer (dotted line) and aminolysis of poly(methyl methacrylate)-*b*-polystyrene (PMMA-*b*-PS, $M_n = 4750$ g/mol, $M_w/M_n = 1.17$) diblock copolymer (solid lines) with thiocarbonylthio termini. Aminolysis conditions: 0.019 mol/L of PMMA-*b*-PS, 0.95 mol/L of cyclohexylamine, tetrahydrofuran as the solvent, and room temperature.

corresponding diastereomers and/or conformers. We suppose that the signals of H_B are overlapped with those of main chain methylene (in the range of 1.6−2.3 ppm), as indicated by 2D NMR (vide infra). After aminolysis, the final methylene became a AB system in thiolactone, and showed predominantly four doublets in the range of $\delta = 2.7-3.0$ ppm (inset in Figure 4) with $J_{gem} = -13.7$ Hz. In addition, the protons of axial and equatorial $-COOCH_3$ on the thiolactone can be clearly seen at 3.81 and 3.76 ppm (H_l in Figure 4).

In Figure 5, ^{13}C NMR showed the disappearance of $-\mathbf{C}(=S)S-$ (225 ppm) in the spectrum of the aminolyzed sample, and appearance of a new signal at 210 ppm which is assigned to carbonyl carbon of the thiolactone ring. This value of chemical shift is quite close to that reported by Engel and coworkers.[31] Therefore, both the results of ^1H and ^{13}C NMR support the mechanism of the formation of thiolactone ring.

2D NMR, namely HSQC, was recorded on the basis of ^{13}C NMR determined by DEPT experiment (The full spectra and the assignment of the ^{13}C NMR and DPET are given in Supporting Information Figure S1). As shown in Figure 6A, cross-peaks (a and b) are observed between proton signals (ω_1) at 2.45 and 2.55 ppm and ^{13}C signals (ω_2) at 48.3 and 49.1 ppm, which are assigned to terminal $-CH_2-$ of PMMA adjacent to dithioester moiety. The two peaks of ^{13}C should be due to different stereoisomers of the adjacent chiral centers, although it is difficult to make precise correlation between chemical shift and the isomers. The cross-peaks c and d in Figure 6A indicate overlapping of H_B signals of terminal AB system and main chain methylene groups. In the spectrum of the aminolyzed sample (Figure 6B), the chemical shifts of ^{13}C in terminal methylene group exhibit slight drifts, yet cross-peaks (a′, b′, c′, and d) with protons in the same group are clearly observed. In addition, the methoxy on the thiolactone ring shows two cross-peaks at $\omega_1 = 3.76-3.81$ and $\omega_2 = 53.2$ ppm (e and f in Figure 6B) due to the axial and equatorial positions. We noted more down peaks of methylene in the range of $\omega_2 = 48-50$ ppm for aminolyzed sample. These peaks are not correlated to methylene of thiolactone but may be assigned to that adjacent to the ring. However, exact correlation to the structure is very difficult, if not impossible, due to the complexity of the spectrum.

The correlations between H_A andH_B of the AB system in the samples before and after aminolysis are more clearly observed by H, H−COSY. As shown in Figure 7, the sample before aminolysis displays symmetric peaks (g, h, i, and j) at both sides of the diagonal. Thus, the signals of H_B are located within the range of 2.1−2.3 ppm. After aminolysis, these signals show slight shift to higher field to the range of 1.8−2.1 ppm. All these results agree very well with HSQC.

We also carried out aminolysis of poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA, $M_n = 4000$ g/mol, $M_w/M_n = 1.28$), poly(laury methacrylate) (PLMA, $M_n = 5100$ g/mol, $M_w/M_n = 1.15$), and poly(methyl acrylate) (PMA, $M_n = 1100$ g/mol, $M_w/M_n = 1.12$) prepared by CDB mediated RAFT polymerization. GPC curves of aminolysis of PDMAEMA and PLMA (Figure 8) indicated the same trend as that of PMMA. MALDI−TOF MS spectrum (Figure 9) of aminolyzed PDMAEMA shows predominantly product with thiolactone termini. For instance, a main peak, $m/z = 4308.32$, correlates to the mass of chains with degree of polymerization 27 and thiolactone end group, cationized by H^+ (Table 2).[25] The species with mercapto terminus appeared as a small peak at $m/z = 4397.45$ (Table 2).

The cyclization makes it difficult to prepare thiol-end functionalized polymethacrylates. Nevertheless, this can be overcome by introducing a short segment of polystyrene after the RAFT polymerization of methacrylates. The obtained polymethacrylate-*b*-polystyrene will undergo aminolysis according to the mechanism of polystyrene with thiocarbonylthio terminus. Figure 10 shows the results of preparation (by sequential RAFT polymerization) and aminolysis of a block copolymer, PMMA-*b*-PS. High content of coupled species was obtained. The disulfide bond in the coupled species can be cleaved by reduction with Zn/acetic acid[16] or dithiothreitol (DTT)[11] to prepare polymer with a thiol end group.

Conclusion

Although aminolysis of both polystyrene and poly(methyl methacrylate) prepared by the RAFT polymerization yield polymers with thiol termini, the former product couples through the formation of disulfide bond, whereas the latter cyclizes to form thiolactone end group. The cyclization is undesired in the sense of preparation of thiol-end functionalized polymers. Nevertheless, this can be achieved by introducing a short block of polystyrene after the RAFT polymerization of methacrylates.

On the other hand, GPC and MALDI−TOF MS results showed that the thiolactone functionalized product was abundant in the aminolysis product. Thus, it is in perspective that the product may be used as building blocks for further macromolecular engineering by the application of lactone chemistry, for example, as macromonomers in ring-opening polymerization of (thio)lactones.

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Supporting Information Available: Figures showing GC−MS, ^{13}C NMR, and DEPT data and a table of MALDI−TOF MS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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