

Thermolysis of RAFT-Synthesized Poly(Methyl Methacrylate)

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Thermolysis provides a simple and efficient way of eliminating thiocarbonylthio groups from RAFT-synthesized polymers. The course of thermolysis of poly(methyl methacrylate) (PMMA) prepared with dithiobenzoate and trithiocarbonate RAFT agents was followed by thermogravimetric analysis (TGA), ¹H NMR spectroscopy, and gel permeation chromatography (GPC). The weight loss profile observed depends strongly on the RAFT agent used during polymer synthesis. PMMA with a methyl trithiocarbonate end group undergoes loss of that end group at ~180°C, at least in part, by a mechanism believed to involve homolysis of the C–CS₂SCH₃ bond and subsequent depropagation. In contrast, PMMA with a dithiobenzoate end appears more stable. Only the end group is lost at ~180°C and the dominant mechanism is proposed to be a concerted elimination process analogous to that involved in the Chugaev reaction.

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Introduction

Radical polymerization with thiocarbonylthio RAFT (reversible addition–fragmentation chain transfer) agents is arguably one of the most versatile processes for living free-radical polymerization in displaying superior flexibility with respect to monomers and reaction conditions.^[1–3] A key feature of RAFT polymerization is that the thiocarbonylthio group(s), present in the initial RAFT agent, is(are) retained in the polymeric product(s). The retention of these groups is responsible for the polymers' living character. However, the presence of the thiocarbonylthio groups also means that the polymers are usually coloured. The polymers may also, in some cases, be odorous or release an odor over time due to decomposition of the thiocarbonylthio groups and the evolution of volatile sulfur compounds. The presence of such colour and odor can be disadvantageous in some applications. Even though many of these issues are mitigated or overcome by appropriate selection of the initial RAFT agent, these issues have nonetheless provided an incentive for developing effective methods for treatment of RAFT-made polymers to cleave and remove the thiocarbonylthio groups in a post-polymerization process. Cleavage of polymer chains at the thiocarbonylthio groups can also be an aid in providing information on the mechanism of RAFT polymerization.^[4,5]

The chemistry of the thiocarbonylthio group is well known from small molecule chemistry^[6,7] and much of this knowledge has been shown to be applicable to transforming the thiocarbonylthio groups in RAFT-synthesized polymers.^[2] Thiocarbonylthio groups undergo reaction with nucleophiles and ionic reducing agents (e.g. amines,^[8–15]

hydroxide,^[16,17] borohydride^[18,19]) to provide thiols. They also react with various oxidizing agents (including NaOCl, H₂O₂, Bu^tOOH, peracids, ozone)^[2,20–22] and are sensitive to UV irradiation.^[23,24] However these processes, while they result in loss of the thiocarbonylthio group, leave reactive end group functionality and thus are not suitable in many circumstances. Thermolysis^[5,8,25,26] and various radical-induced reactions (reduction,^[5,8,27–29] termination^[5,30]) provide solutions to this dilemma and can provide desulfurization by complete end-group elimination/transfer.

It was recently reported that butyl trithiocarbonate groups were readily cleaved from RAFT-synthesized polystyrene^[5,8,25] and poly(butyl acrylate) (PBA)^[25,26] by heating at ~180°C under nitrogen. The dominant mechanism of end group loss was found to depend on the particular polymer, involving concerted elimination in the case of polystyrene (Scheme 1) and initial C–S bond homolysis followed by backbiting and β-scission in the case of PBA (Scheme 2). The thermolysis of xanthate-terminated polymers has also been reported.^[26,31] For the case of both *S*-polystyrene and *S*-poly(*t*-butyl acrylate) *O*-isobutyl xanthate, the reported mechanism involves selective elimination to provide 2-butene and a polymer with a thiol end group.^[31] In contrast, for the case of *O*-ethyl *S*-poly(vinyl acetate) xanthate,^[26] the observed products are consistent with involvement of the poly(vinyl acetate) (PVAc) propagating radical and suggest a mechanism involving initial C–S bond homolysis analogous to that shown in Scheme 2. The thermolysis of RAFT agents has also been studied; cumyl dithiobenzoate was reported to reversibly eliminate dithiobenzoic acid when heated at 120°C while phenylethyl

and benzyl dithiobenzoate are comparatively stable under these conditions.^[32]

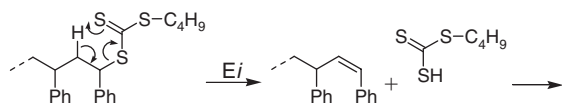
Thermogravimetric analysis (TGA) of poly(methyl methacrylate) (PMMA) with dithiobenzoate end groups has been reported by Lima et al.^[13] (telechelic PMMA \overline{M}_n 17000, TGA 40–500°C at 10° min⁻¹ under nitrogen), Patton et al.^[15] (telechelic PMMA \overline{M}_n 14000, TGA 20–550°C at 20° min⁻¹ under nitrogen), and Xu et al.^[33] (\overline{M}_n 3600, TGA 20–550°C at 20° min⁻¹ under nitrogen). The authors do not discuss the thermolysis mechanism in detail and, while all indicate some instability of the RAFT-synthesized polymer versus the similar polymer with the dithiobenzoate ends removed, they observe remarkably different thermolysis behaviour even after allowing for the obvious differences in thermolysis conditions. Patton et al.^[15] observe an onset of weight loss at about 200°C, attributed to the loss of the dithiobenzoate groups. Lima et al.^[13] show a thermogram that suggests an onset temperature for degradation of approximately 120°C and 20% weight loss below 200°C. Xu et al.^[33] report a very low onset temperature of 65°C and a complex decomposition mechanism. Possible explanations for this difference in behaviour are discussed below.

In this paper, we further explore the applicability of thermolysis as a method of end-group removal to a series of PMMA synthesized by high-conversion RAFT polymerization with either methyl trithiocarbonate or dithiobenzoate RAFT agents and report on the dependence of the thermolysis mechanism and product distribution on the RAFT agent-derived end groups.

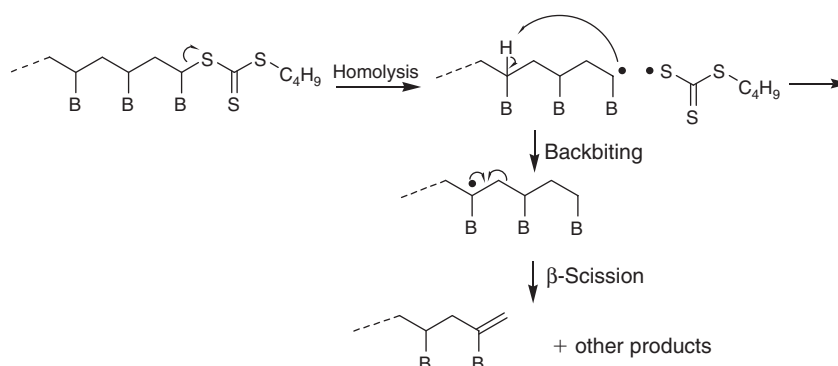
Experimental

General

Solvents used for column chromatography and polymerization were of AR grade and were distilled. MMA (Aldrich) was filtered through neutral alumina (70–230 mesh), fractionally distilled under reduced pressure, and redistilled under reduced pressure immediately before use. The RAFT agents, 2-cyanoprop-2-yl methyl trithiocarbonate **1**^[34] and



Scheme 1. *Ei* = intramolecular electrocyclic reaction.



Scheme 2. B = CO₂C₄H₉.

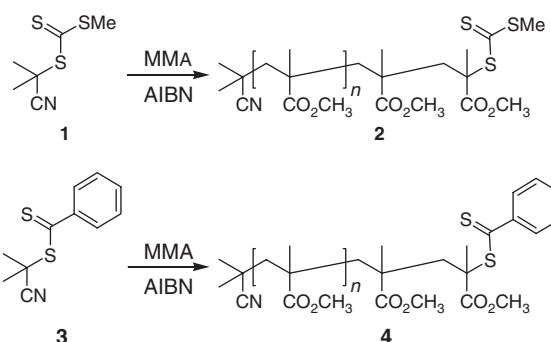
2-cyanoprop-2-yl dithiobenzoate **3**^[35,36] were synthesized as previously described.

Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker AC200 or a Bruker AV400 spectrometer. Chemical shifts are reported in ppm from external tetramethylsilane. Gel permeation chromatography (GPC) was performed on a Waters 515 HPLC pump and Waters 717 Plus Autosampler equipped with Waters 2414 refractive index detector and three Mixed C and one mixed E PLgel column (each 7.5 mm × 300 mm) from Polymer Laboratories. Tetrahydrofuran (flow rate 1.0 mL min⁻¹) was used as eluent at 22 ± 2°C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories). A third-order polynomial was used to fit the log₁₀ *M* versus time calibration curve which was almost linear across the molecular weight range 2 × 10²–2 × 10⁶ g mol⁻¹. Thermogravimetric analysis (TGA) was carried out with a Mettler TGA/SDTA521 thermobalance equipped with a sample robot. Experiments were performed under nitrogen (50 mL min⁻¹).

Poly(Methyl Methacrylate)

The following procedure is typical. A stock solution was prepared comprising MMA (11.25 mL), benzene (3.75 mL), and azobis(1-isobutyronitrile) (0.0155 g). Aliquots of this solution (2.5 mL) were transferred to a vial containing the RAFT agent **3** (0.0075 mg). The contents of the vial were transferred to an ampoule that was degassed through three freeze–evacuate–thaw cycles, sealed under nitrogen and heated in a constant temperature bath at 60°C for 16 h. The ampoule was then cooled, opened, diluted with benzene, and precipitated into methanol.

The monomer conversions (Table 1) were calculated by determining the residual monomer in the ¹H NMR spectrum of small samples of the polymerization mixtures. The molecular weights shown in Table 1 are for the precipitated samples. Some loss of low molecular weight material on precipitation probably accounts for the discrepancy between found and calculated molecular weights.



Scheme 3.

Table 1. Synthesis conditions^A and properties of poly(methyl methacrylate)
Refer to Scheme 3

RAFT agent	Polymer	RAFT agent conc. [M]	Conversion [%]	\bar{M}_n^B [g mol ⁻¹]	\bar{M}_n^C [g mol ⁻¹]	$\bar{M}_n^{\text{Calc D}}$ [g mol ⁻¹]	\bar{M}_w/\bar{M}_n
1	2a	0.060	97	12600	13800	11500	1.11
1	2b	0.022	99	29000	31800	31300	1.10
1	2c	0.0123	96	49500	54200	53500	1.13
3	4a	0.068	97	13200	14500	10200	1.19
3	4b	0.0136	96	55300	60500	48600	1.08
None ^E	5	0.000	90	53000	—	—	6.80

^A [MMA] = 7.01 M in benzene, [AIBN] = 6.7×10^{-4} M, 60°C, 16 h.

^B Number average molecular weight of precipitated samples in polystyrene equivalents.

^C Molecular weight obtained by applying the Mark–Houwink–Sakaruda relationship ($K_{\text{PMMA}} M_{\text{PMMA}}^{\alpha_{\text{PMMA}}+1} = K_{\text{PS}} M_{\text{PS}}^{\alpha_{\text{PS}}+1}$) with $K_{\text{PS}} = 11.4 \times 10^8$, $\alpha_{\text{PS}} = 0.716$ for polystyrene^[37] and $K_{\text{PMMA}} = 9.44 \times 10^8$, $\alpha_{\text{PMMA}} = 0.719$ for PMMA.^[38]

^D Calculated as $\bar{M}_n^{\text{Calc}} = [\text{MMA}] / \{ [\text{RAFT agent}]_0 + [\text{AIBN}]_0 \times df \times (1 - \exp k_d t) \times \text{Conv} \times m_{\text{MMA}} + m_{\text{RAFT}} \}$, where df is the number of initiator-derived polymer chains formed per molecule of initiator decomposed (the number of chains produced from radical–radical termination ($d \sim 1.67$ for MMA polymerization)), f is the initiator efficiency ($f \sim 0.7$ for AIBN at 60°C), k_d is the AIBN decomposition rate constant ($k_d = 9.7 \times 10^{-6} \text{ s}^{-1}$ for AIBN at 60°C), t is the reaction time, Conv is the monomer conversion, and m_{MMA} and m_{RAFT} are the molecular weights of MMA and the RAFT agent respectively.^[35]

^E [AIBN] = 8.35×10^{-4} M, bulk polymerization.

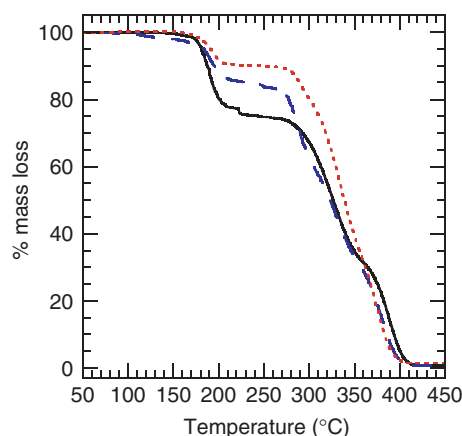


Fig. 1. Normalized mass loss curves for poly(methyl methacrylate) **2** with a methyl trithiocarbonate end group. Samples: **2a** (\bar{M}_n 12600 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.11, —), **2b** (\bar{M}_n 29000 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.10, ---), **2c** (\bar{M}_n 49500 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.13, -.-). Samples were heated from 50 to 450°C at 5°C min⁻¹ under nitrogen.

Thermolysis Procedure

Dynamic Thermolysis

Samples of PMMA (~5 mg) were placed in alumina crucibles and transferred to the carousel of the sample robot coupled to the thermogravimetric balance. The samples were heated at 5°C min⁻¹ under nitrogen from 50 to 600°C. Example thermograms are shown in Figs 1 and 2.

Isothermal Thermolysis

Small scale preparative thermolysis was also carried out using the thermogravimetric balance. Samples were heated from 50°C to the requisite temperature (140, 160, 180, 200, 220, or 240°C) at 5°C min⁻¹ then maintained at that temperature for 20 min. The entire process was carried out under a flow of nitrogen.

The following procedure is typical. A sample of pale yellow PMMA **2a** (18 mg, \bar{M}_n 12600 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.11) was weighed into a large (50 μ L alumina crucible) and placed in the sample furnace of the thermobalance. The sample was heated at 5°C min⁻¹ under nitrogen from

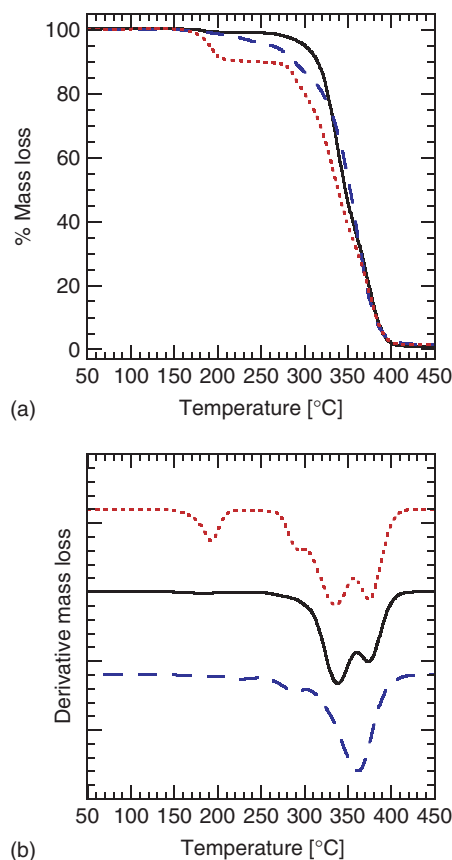


Fig. 2. (a) Percentage mass loss and (b) derivative of mass loss (arbitrary units, curves are offset) for poly(methyl methacrylate). Samples: **2c** (methyl trithiocarbonate end, \bar{M}_n 49500 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.13, ---), **4b** (dithiobenzoate end, \bar{M}_n 55300 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.08, —), **5** (prepared by conventional free radical polymerization, \bar{M}_n 53000, \bar{M}_w/\bar{M}_n 6.80, -.-). Samples were heated from 50 to 600°C at 5°C min⁻¹ under nitrogen.

50 to 240°C then isothermally under nitrogen at 240°C for 20 min to provide a colourless product that was dissolved in chloroform and analyzed directly by ¹H NMR and GPC (\bar{M}_n 11000 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.13). NMR data are shown in Figs 3 and 5.

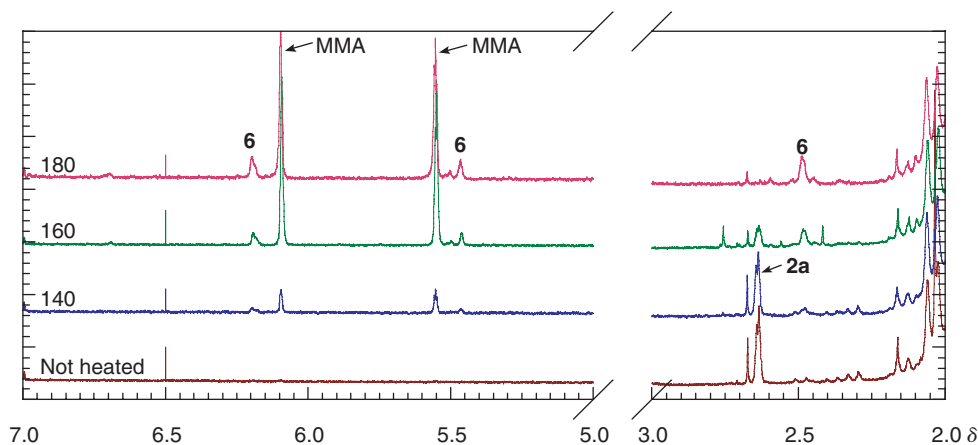
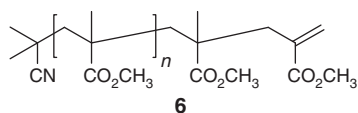


Fig. 3. Regions δ_{H} 7.0–5.0 and 3.0–2.0 of the ^1H NMR spectrum (400 MHz, CDCl_3) of poly(methyl methacrylate) **2a** (\bar{M}_n 12600 g mol^{-1} , \bar{M}_w/\bar{M}_n 1.11) (lower spectrum) and the thermolysis products at 140, 160, and 180°C. The samples were heated at 5°C min^{-1} under nitrogen in alumina crucibles then held at the indicated temperature for 20 min. Signals at δ_{H} 6.2, 5.5, and 2.5 are attributable to the olefinic hydrogens and the methylene adjacent to the double bond of **6**. Signal at δ_{H} 2.65 is attributable to the trithiocarbonate methyl of **2a**.



Scheme 4.

Results

Thermolysis of Poly(Methyl Methacrylate) with Methyl Trithiocarbonate End Groups

The TGA thermogram of PMMA **2** with a methyl trithiocarbonate end group displays two mass loss regions (Fig. 1), the first between 170 and 220°C and another beginning at 280°C that results in complete degradation of the polymer. The mass loss between 170 and 220°C is substantially greater than that expected on the basis of loss of the end group alone. For PMMA **2a** (\bar{M}_n 12600 g mol^{-1} , \bar{M}_w/\bar{M}_n 1.11) there is 26% mass loss in this interval, yet only 1.70% is expected for loss of $\text{C}_2\text{H}_3\text{S}_3$. For **2b** (\bar{M}_n 29000 g mol^{-1} , \bar{M}_w/\bar{M}_n 1.10) and **2c** (\bar{M}_n 49500 g mol^{-1} , \bar{M}_w/\bar{M}_n 1.13) the mass losses between 150 and 240°C are 18% (0.6% expected for $\text{C}_2\text{H}_3\text{S}_3$ loss) and 10% (0.3% expected for $\text{C}_2\text{H}_3\text{S}_3$ loss) respectively (Fig. 1). In similar experiments with PMMA with dithiobenzoate end groups (see below and Fig. 2) or polystyrene with butyl trithiocarbonate end groups, the size of the initial mass loss step (between 200 and 270°C in the case of polystyrene) is commensurate with elimination of the end group alone.^[5,25]

Isothermal thermolysis at 180°C of the pale yellow trithiocarbonate-terminated PMMA **2** (Scheme 1), provides a colourless product. The ^1H NMR spectrum of **2a** (Fig. 3) shows disappearance of the broad singlet for the trithiocarbonate methyl at δ_{H} 2.65 and the appearance of signals attributable to macromonomer chain end **6** (Scheme 4) at δ_{H} 6.2, 5.5, and 2.5. Signals for the olefinic hydrogens of entrapped MMA also appear at δ_{H} 6.1 and 5.6. The end group concentrations for **2a** and its thermolysis products obtained

at various temperatures were estimated by integrating the signals associated with the end groups versus that for the PMMA methoxy and are summarized in Table 2. Because of the small end group concentrations, the error in this data is large ($\sim \pm 20\%$) nonetheless it provides an indication of how the product distribution depends on thermolysis temperature. The concentration of macromonomer ends in the thermolysis product appears to be significantly less than the concentration of trithiocarbonate ends in the precursor **2a**.

GPC analysis of the thermolysis product from **2** at 240°C shows a small yet significant lowering of the number average molecular weight (Figs 4a–4c). This is most noticeable for the thermolysis of the lowest molecular weight sample (**2a**; \bar{M}_n 12600 g mol^{-1} , \bar{M}_w/\bar{M}_n 1.11) which produced a product with a molecular weight \bar{M}_n 11000 g mol^{-1} , \bar{M}_w/\bar{M}_n 1.13. Nonetheless, it is clear that the decrease in molecular weight is small with respect mass loss and there is only a small change in the molecular weight distribution. A slight broadening is observed for the lowest molecular weight sample. Thus, there is complete loss of fraction of chains rather than loss of a fraction of most chains. These observations are consistent with the chains degrading by end-initiated unzipping (rather than by random chain scission).

Thermolysis of Poly(Methyl Methacrylate) with Dithiobenzoate End Groups

The PMMA **4** synthesized with a dithiobenzoate RAFT agent displays thermolysis behaviour that is quite different to that of the PMMA with a methyl trithiocarbonate end (**2**). The thermogram (not shown) for the lower molecular weight sample **4a** (\bar{M}_n 13200 g mol^{-1} , \bar{M}_w/\bar{M}_n 1.19) an initial mass loss between 150 and 220°C is commensurate with loss of the end group; the mass loss corresponds to 0.9% mass loss (2.10% expected for $\text{C}_7\text{H}_5\text{S}_2$). For sample **4b** (\bar{M}_n 55300 g mol^{-1} , \bar{M}_w/\bar{M}_n 1.08; Fig. 2) the initial mass loss is 0.9% mass loss (0.42% expected for $\text{C}_7\text{H}_5\text{S}_2$).

Table 2. End group concentration in thermolyzed poly(methyl methacrylate)

Polymer	Thermolysis temperature	\bar{M}_n^A [g mol ⁻¹]	Total ends (calc) ^B	Total ends ^C	RAFT ends ^D	Macro ends ^E
2a	—	12600	0.0079	0.0081	0.0081	<0.0002
	140	—	—	0.0087	0.0075	0.0012
	160	—	—	0.0051	0.0026	0.0026
	180	—	—	0.0050	—	0.0050
	200	—	—	0.0055	—	0.0055
	220	—	—	0.0057	—	0.0057
	240	11000	0.0090	0.0049	—	0.0049
4a	—	13200	0.0076	0.0065	0.0065	<0.0002
	140	—	—	0.0064	0.0056	0.0008
	160	—	—	0.0050	0.0030	0.0020
	180	—	—	0.0048	—	0.0048
	200	—	—	0.0046	—	0.0046
	220	—	—	0.0048	—	0.0048
	240	13100	0.0076	0.0037	—	0.0037

^A Number average molecular weight in polystyrene equivalents after precipitation.

^B Thiocarbonylthio end groups per monomer unit approximated as $100.12/(\bar{M}_n - m_{\text{RAFT}})$.

^C Total RAFT chain ends (**2a** or **4a**) plus macromonomer chain ends (**6**).

^D RAFT chain ends from integration of signals at δ_{H} 2.6 (trithiocarbonate methyl of **2a**) or δ_{H} 7.8 and 8.0 (dithiobenzoate *ortho*-Ar-H of **4a**).

^E Macromonomer (**6**) chain ends from integration of olefinic signals at δ_{H} 6.2, 5.5, and 2.5.

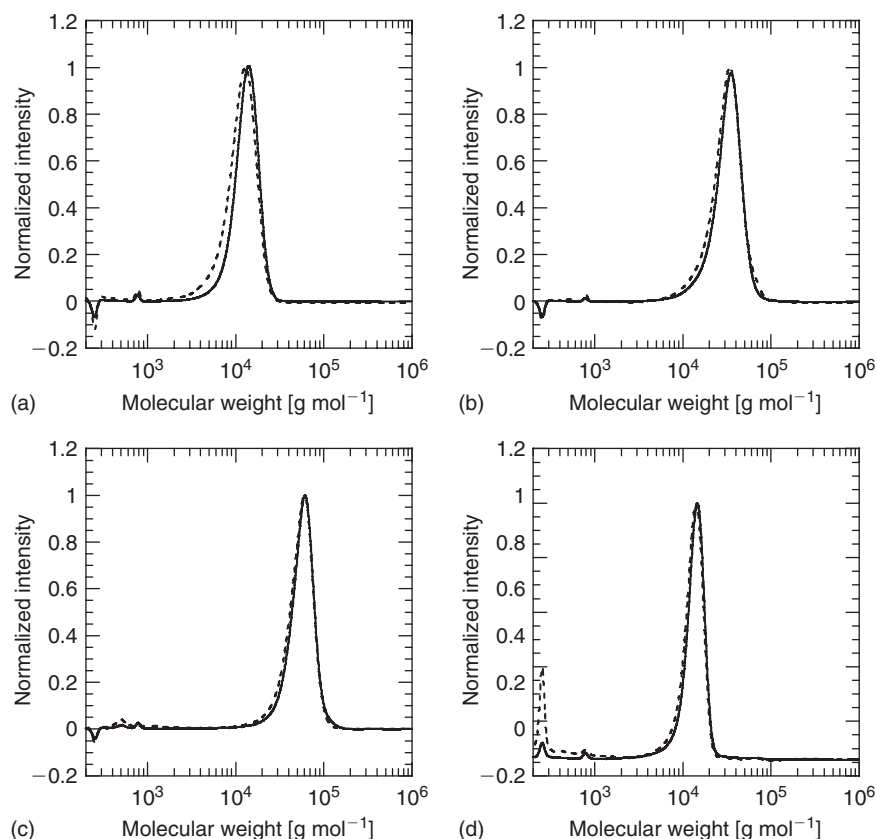


Fig. 4. GPC traces for precursor polymers (—) and product from thermolysis at 240°C for 20 min under nitrogen (- - -). (a) **2a** (\bar{M}_n 12600, \bar{M}_w/\bar{M}_n 1.11) and thermolysis product (\bar{M}_n 11000, \bar{M}_w/\bar{M}_n 1.13). (b) **2b** (\bar{M}_n 29000, \bar{M}_w/\bar{M}_n 1.10) and thermolysis product (\bar{M}_n 26900, \bar{M}_w/\bar{M}_n 1.19). (c) **2c** (\bar{M}_n 49500, \bar{M}_w/\bar{M}_n 1.13) and thermolysis product (\bar{M}_n 47000, \bar{M}_w/\bar{M}_n 1.14). (d) **4a** (\bar{M}_n 13200, \bar{M}_w/\bar{M}_n 1.19) and thermolysis product (\bar{M}_n 13100, \bar{M}_w/\bar{M}_n 1.06). Molecular weights are in polystyrene equivalents.

The PMMA **4a** was heated isothermally at 140, 160, 180, 200, 220, and 240°C for 20 min. The samples heated at 140 and 160 remained pink. The samples heated at 180 and 200°C became colourless. Those heated at higher temperatures showed some yellow discoloration.

The ¹H NMR spectrum of the unheated PMMA sample **4a** shows signals at δ_{H} 7.8 and 8.0 (ratio ~3:1) which are believed to correspond to the *ortho* aromatic hydrogens for the diastereomeric dithiobenzoate end groups (Fig. 5). The sample of **4a** heated at 140°C shows that the smaller of

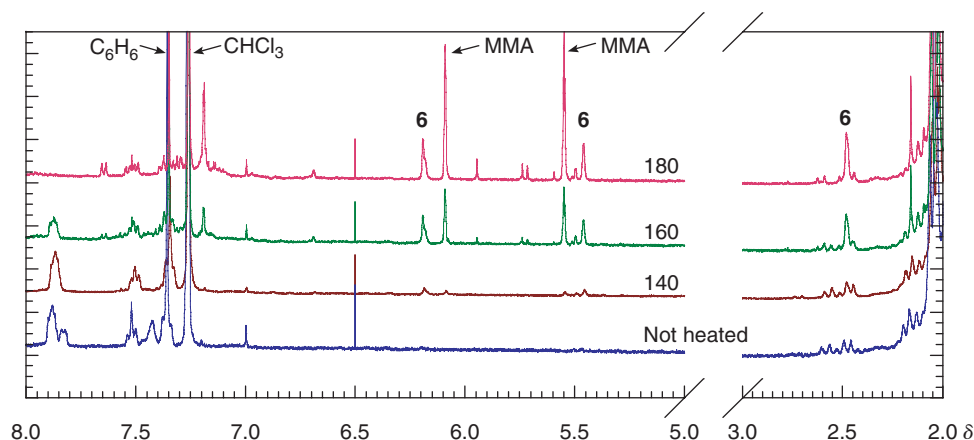
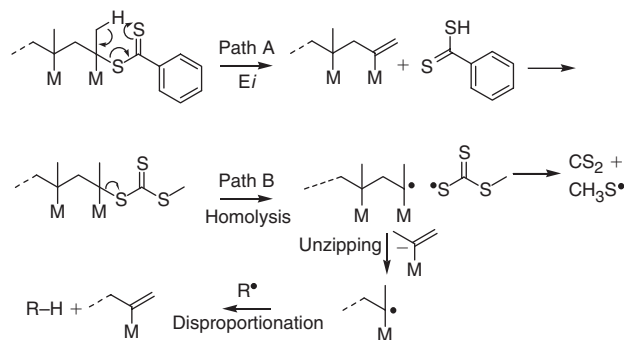


Fig. 5. Regions δ_{H} 8.0–5.0 and 3.0–2.0 of the ^1H NMR spectrum (400 MHz, CDCl_3) of poly(methyl methacrylate) **4a** (\overline{M}_n 13200 g mol^{-1} , $\overline{M}_w/\overline{M}_n$ 1.19) (lower spectrum) and the thermolysis products at 140, 160, and 180°C. The samples were heated at 5°C min^{-1} under nitrogen in alumina crucibles then held at the indicated temperature for 20 min. Signals at δ_{H} 6.2, 5.5, and 2.5 are attributable to the olefinic hydrogens and the methylene adjacent to the double bond of **6**.

these has disappeared and that signals at δ_{H} 6.3, 5.5, and 2.5, associated with the olefinic hydrogens and the methylene adjacent to the double bond of the PMMA **6**, have appeared. The difference in stability of the two diastereomers is likely to be steric in origin and related to the ease of adoption of the transition state for concerted elimination.^[39] The ^1H NMR spectrum of **4a** heated at 180°C shows the complete disappearance of the *ortho* hydrogen signals of the dithiobenzoate group and the appearance of peaks corresponding to macromonomer **6** and methyl methacrylate. The precise fate of the dithiobenzoate group is unknown and signals in the aromatic region remain. The ^1H NMR spectrum of the thermolysis product obtained at 200 or 220°C is similar to that obtained at 180°C. Signals due to entrapped MMA monomer are also seen in the thermolysis products. The GPC, even for the lowest molecular weight sample **4a** at 240°C, suggests little change in molecular weight (Fig. 4d).

Discussion

Analogous dithiobenzoate- and trithiocarbonate-terminated PMMA show quite different thermolysis behavior. PMMA is known to degrade by unzipping or depropagation which can be initiated at weak links or by random chain scission.^[40–48] Any structures that are less stable than the backbone or side chain bonds and which give rise to propagating radicals may constitute weak links. PMMA formed by conventional radical polymerization in the absence of transfer agents is known to contain weak links formed as a consequence of termination by combination or disproportionation.^[40] The appearance of thermograms of PMMA can depend strongly on such factors as sample size and heating rate^[42] but typically show two or three stages of degradation. The thermogram (Fig. 2) of PMMA **5** synthesized using bulk polymerization with AIBN initiator illustrates the three stages of degradation. The first stage with onset under our conditions at $\sim 160^\circ\text{C}$, is attributed to degradation initiated by scission of those chains containing head-to-head linkages formed



Scheme 5. M = CO_2CH_3 ; Ei = intramolecular electrocyclic reaction.

by termination by combination. The second stage of degradation, with onset $\sim 240^\circ\text{C}$ is associated with those chains possessing unsaturated end groups (analogous to **6**) formed by disproportionation undergoing radical-induced decomposition. A final stage of degradation is attributed to chains undergoing degradation initiated by random chain scission.

Two possible thermolysis mechanisms for RAFT-synthesized PMMA are shown in Scheme 5. It is proposed that the dithiobenzoate terminated PMMA degrades by Path A which involves concerted elimination of the end group possibly by a process analogous to that involved in the Chugaev reaction^[39,49] to form PMMA with an unsaturated chain end. The observation of MMA in the ^1H NMR (Fig. 5) may result from unzipping of propagating radicals formed by degradation of small amount of PMMA with unstable head to head linkages formed during polymer synthesis as a consequence of termination by combination.^[41] The extent of termination by radical–radical reaction and the combination disproportionation ratio in RAFT polymerization is expected to be similar to that for a conventional radical polymerization carried out under similar reaction conditions.

PMMA with a trithiocarbonate chain end is proposed to primarily degrade by Path B which involves homolysis of the C–S bond joining PMMA chain to the trithiocarbonate

end to generate propagating radicals which then unzip or depropagate to form MMA until terminated by transfer or radical-radical reaction.

There is no direct correlation between the mass loss through unzipping (region of 150–240°C) and the concentration of trithiocarbonate functionality. However, it is clear that the higher the concentration of trithiocarbonate groups, the greater number of radicals produced through homolysis of the C–S bond, the greater the percentage mass lost through unzipping, which is consistent with the proposed mechanism.

We are unable to reconcile our data for PMMA with dithiobenzoate ends with recent work of Xu et al.^[33] These authors reported that PMMA with dithiobenzoate ends degraded at substantially lower temperature than found in this work or in other recent studies.^[13,15] They used a higher heating rate, 20°C min⁻¹ versus 5°C min⁻¹. We briefly explored the effect of heating rate and sample size and found as expected that the onset temperature decomposition increased for higher temperatures for higher heating rate and for larger sample sizes. Xu et al.^[33] suggest in their paper that their lower degradation temperature with respect to other literature reports^[13,15] may be an effect of molecular weight. We have performed thermogravimetric analysis of a PMMA of similar molecular weight (\bar{M}_n 3670) to that used by Xu et al.^[33] (\bar{M}_n 3600), and find it to be no less stable with respect to weight loss or end group elimination than higher molecular weight PMMA (onset temperature for degradation ~190°C for 5°C min⁻¹ under nitrogen). Air contamination of the nitrogen purge gas is expected make PMMA appear more stable^[50] (oxygen traps PMMA propagating radicals interrupting the unzipping of chains) but would not prevent end group elimination. Factors which might lead to PMMA appearing less stable by TGA include the presence of residual initiator or metal contamination of the sample.

Notwithstanding these issues we concur with Xu et al.^[33] on the finding that thermolysis is a suitable method for cleanly removing dithiobenzoate chain ends of PMMA prepared by RAFT polymerization albeit that a somewhat higher temperature is required.

Conclusions

Thermolysis can be used to cleanly remove dithiobenzoate chain ends from PMMA resulting in a macromonomer product with molecular weight and polydispersity similar to that of the precursor polymer. Thermolysis is less suitable for removal of the trithiocarbonate end groups from PMMA since end group loss is accompanied by some polymer degradation and lowering of molecular weight.

The mechanism of the thiocarbonylthio end group cleavage from RAFT-synthesized polymers during thermolysis depends on both the polymer and the type of RAFT agent used in its synthesis. End group loss during thermolysis of PMMA, PBA^[25,26] synthesized with alkyl trithiocarbonate RAFT agents, and poly(vinyl acetate)^[26] synthesized with an *O*-ethyl xanthate RAFT agent follows a mechanism involving initial C–S bond homolysis (path B). Elimination of the end groups of PMMA synthesized with dithiobenzoate

RAFT agent and polystyrene synthesized with trithiocarbonate RAFT agent^[5,8,25] follows a concerted mechanism (path A).

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References

- [1] G. Moad, E. Rizzardo, S. H. Thang, *Aust. J. Chem.* **2005**, *58*, 379. doi:10.1071/CH05072
- [2] J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, *31*, 5559. doi:10.1021/MA9804951
- [3] G. Moad, E. Rizzardo, S. H. Thang, *Aust. J. Chem.* **2006**, *59*, 669. doi:10.1071/CH06250
- [4] S. Harrisson, K. L. Wooley, *Chem. Commun.* **2005**, 3259. doi:10.1039/B504313A
- [5] A. Postma, T. P. Davis, R. A. Evans, G. Li, G. Moad, M. O'Shea, *Macromolecules* **2006**, *39*, 5293. doi:10.1021/MA060245H
- [6] S. Kato, M. Ishida, *Sulfur Rep.* **1988**, *8*, 155.
- [7] R. Mayer, S. Scheithauer, in *Methoden der organischen Chemie* (Eds K. H. Buechel, J. Falbe, H. Hagemann, M. Hanack) **1985**, Vol. E5, pp. 891–930 (Thieme: Stuttgart).
- [8] G. Moad, Y. K. Chong, E. Rizzardo, A. Postma, S. H. Thang, *Polymer* **2005**, *46*, 8458. doi:10.1016/J.POLYMER.2004.12.061
- [9] R. T. A. Mayadunne, J. Jeffery, G. Moad, E. Rizzardo, *Macromolecules* **2003**, *36*, 1505. doi:10.1021/MA021219W
- [10] R. T. A. Mayadunne, E. Rizzardo, J. Chiefari, J. Krstina, G. Moad, A. Postma, S. H. Thang, *Macromolecules* **2000**, *33*, 243. doi:10.1021/MA991451A
- [11] Z. M. Wang, J. P. He, Y. F. Tao, L. Yang, H. J. Jiang, Y. L. Yang, *Macromolecules* **2003**, *36*, 7446. doi:10.1021/MA025673B
- [12] A. Favier, C. Ladaviere, M. T. Charreyre, C. Pichot, *Macromolecules* **2004**, *37*, 2026. doi:10.1021/MA030414N
- [13] V. Lima, X. L. Jiang, J. Brokken-Zijp, P. J. Schoenmakers, B. Klumperman, R. Van Der Linde, *J. Polym. Sci. Part A Polym. Chem.* **2005**, *43*, 959. doi:10.1002/POLA.20558
- [14] D. B. Thomas, A. J. Convertine, R. D. Hester, A. B. Lowe, C. L. McCormick, *Macromolecules* **2004**, *37*, 1735. doi:10.1021/MA035572T
- [15] D. L. Patton, M. Mullings, T. Fulghum, R. C. Advincula, *Macromolecules* **2005**, *38*, 8597. doi:10.1021/MA051035S
- [16] C. Schilli, M. G. Lanzendoerfer, A. H. E. Mueller, *Macromolecules* **2002**, *35*, 6819. doi:10.1021/MA0121159
- [17] M. F. Llauro, J. Loiseau, F. Boisson, F. Delolme, C. Ladaviere, J. Claverie, *J. Polym. Sci. Part A Polym. Chem.* **2004**, *42*, 5439. doi:10.1002/POLA.20408
- [18] C. L. McCormick, A. B. Lowe, *Acc. Chem. Res.* **2004**, *37*, 312. doi:10.1021/AR0302484
- [19] B. S. Sumerlin, A. B. Lowe, P. A. Stroud, P. Zhang, M. W. Urban, C. L. McCormick, *Langmuir* **2003**, *19*, 5559. doi:10.1021/LA034459T
- [20] P. Vana, L. Albertin, L. Barner, T. P. Davis, C. Barner-Kowollik, *J. Polym. Sci. Part A Polym. Chem.* **2002**, *40*, 4032. doi:10.1002/POLA.10500
- [21] F. Cerreta, A. M. Le Nocher, C. Leriverend, P. Metzner, T. N. Pham, *Bull. Soc. Chim. Fr.* **1995**, *132*, 67.
- [22] A. Ah Toy, P. Vana, T. P. Davis, C. Barner-Kowollik, *Macromolecules* **2004**, *37*, 744. doi:10.1021/MA035244T
- [23] H. de Brouwer, M. A. J. Schellekens, B. Klumperman, M. J. Monteiro, A. L. German, *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 3596. doi:10.1002/1099-0518(20001001)38:19<3596::AID-POLA150>3.0.CO;2-F

- [24] J. F. Quinn, L. Barner, C. Barner-Kowollik, E. Rizzardo, T. P. Davis, *Macromolecules* **2002**, *35*, 7620. doi:10.1021/MA0204296
- [25] A. Postma, T. P. Davis, G. Moad, M. S. O'Shea, *Macromolecules* **2005**, *38*, 5371. doi:10.1021/MA050402X
- [26] A. Postma, T. P. Davis, G. Li, G. Moad, M. O'Shea, *Macromolecules* **2006**, *39*, 5307. doi:10.1021/MA0604338
- [27] M. Chen, K. P. Ghiggino, T. A. Smith, S. H. Thang, G. J. Wilson, *Aust. J. Chem.* **2004**, *57*, 1175. doi:10.1071/CH04087
- [28] M. Chen, K. P. Ghiggino, S. H. Thang, J. White, G. J. Wilson, *J. Org. Chem.* **2005**, *70*, 1844. doi:10.1021/JO047899D
- [29] W. B. Farnham, M. Fryd, G. Moad, S. H. Thang, E. Rizzardo, *Int. Pat. WO2005113612A1* **2005** [*Chem. Abs.* **2005**, *144*, 23268].
- [30] S. Perrier, P. Takolpuckdee, C. A. Mars, *Macromolecules* **2005**, *38*, 2033. doi:10.1021/MA047611M
- [31] M. Destarac, C. Kalai, A. Wilczewska, G. Mignani, S. Z. Zard, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2005**, *46*(2), 213.
- [32] Y. Liu, J. P. He, J. T. Xu, D. Q. Fan, W. Tang, Y. L. Yang, *Macromolecules* **2005**, *38*, 10332. doi:10.1021/MA0513970
- [33] J. Xu, J. He, D. Fan, W. Tang, Y. Yang, *Macromolecules* **2006**, *39*, 3753. doi:10.1021/MA060184N
- [34] J. Chiefari, R. T. A. Mayadunne, C. L. Moad, G. Moad, E. Rizzardo, A. Postma, M. A. Skidmore, S. H. Thang, *Macromolecules* **2003**, *36*, 2273. doi:10.1021/MA020883+
- [35] Y. K. Chong, J. Krstina, T. P. T. Le, G. Moad, A. Postma, E. Rizzardo, S. H. Thang, *Macromolecules* **2003**, *36*, 2256. doi:10.1021/MA020882H
- [36] G. Moad, J. Chiefari, J. Krstina, A. Postma, R. T. A. Mayadunne, E. Rizzardo, S. H. Thang, *Polym. Int.* **2000**, *49*, 993. doi:10.1002/1097-0126(200009)49:9<993::AID-PI506>3.0.CO;2-6
- [37] R. A. Hutchinson, S. Beuermann, D. A. Paquet, Jr, J. H. McMinn, *Macromolecules* **1997**, *30*, 3490. doi:10.1021/MA970176U
- [38] R. A. Hutchinson, J. H. McMinn, D. A. Paquet, S. Beuermann, C. Jackson, *Ind. Eng. Chem. Res.* **1997**, *36*, 1103. doi:10.1021/IE9604031
- [39] C. H. DePuy, R. W. King, *Chem. Rev.* **1960**, *60*, 431. doi:10.1021/CR60207A001
- [40] T. Kashiwagi, A. Inaba, J. E. Brown, K. Hatada, T. Kitayama, E. Masuda, *Macromolecules* **1986**, *19*, 2160. doi:10.1021/MA00162A010
- [41] A. Meisters, G. Moad, E. Rizzardo, D. H. Solomon, *Polym. Bull.* **1988**, *20*, 499. doi:10.1007/BF01153444
- [42] L. E. Manring, *Macromolecules* **1988**, *21*, 528. doi:10.1021/MA00180A046
- [43] L. E. Manring, *Macromolecules* **1989**, *22*, 2673. doi:10.1021/MA00196A024
- [44] L. E. Manring, *Macromolecules* **1991**, *24*, 3304. doi:10.1021/MA00011A040
- [45] L. E. Manring, D. Y. Sogah, G. M. Cohen, *Macromolecules* **1989**, *22*, 4652. doi:10.1021/MA00202A048
- [46] B. J. Holland, J. N. Hay, *Polym. Degrad. Stabil.* **2002**, *77*, 435. doi:10.1016/S0141-3910(02)00100-3
- [47] B. J. Holland, J. N. Hay, *Thermochim. Acta* **2002**, *388*, 253. doi:10.1016/S0040-6031(02)00034-5
- [48] Y. H. Hu, C. Y. Chen, *Polym. Degrad. Stabil.* **2003**, *82*, 81. doi:10.1016/S0141-3910(03)00165-4
- [49] L. Chugaev, *Ber.* **1899**, *32*, 3332.
- [50] J. D. Peterson, S. Vyazovkin, C. A. Wight, *J. Phys. Chem. B* **1999**, *103*, 8087. doi:10.1021/JP991582D