RAFT Polymerization with Phthalimidomethyl Trithiocarbonates or Xanthates. On the Origin of Bimodal Molecular Weight Distributions in Living Radical Polymerization

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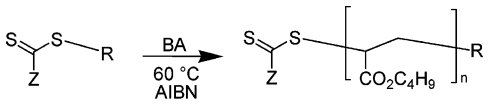
ABSTRACT: Phthalimidomethyl trithiocarbonate reversible addition−fragmentation chain transfer (RAFT) agents are effective in imparting living characteristics to radical polymerizations of butyl acrylate (BA) and *N*-isopropylacrylamide (NIPAM) and provide a route to end-functional polymers with predictable molecular weight and narrow molecular weight distributions (e.g., number-average molecular weight for PBA ($\bar{M}_n$) = 21 300 and polydispersity ($\bar{M}_w/\bar{M}_n$) = 1.1 at 96% conversion). End group determination suggests that bimodal molecular weight distributions and long chain branches in PBA arise by copolymerization of a PBA macromonomer formed by backbiting β-scission. The *S*-phthalimidomethyl xanthates provide good control over polymerizations of the less-activated monomers *N*-vinylpyrrolidone (NVP) and vinyl acetate (VAc). In the case of PBA with a trithiocarbonate end or PVAc with a xanthate end, the C−S bond to the thiocarbonylthio end group can be homolyzed by thermolysis at >180 °C leaving the phthalimidomethyl end group and the ester side groups intact providing macromonomers, with ω end group $-CH_2-C(CO_2C_4H_9)(=CH_2)$ or $-CH_2-C(O_2CCH_3)(=CH_2)$ respectively, as the main products.

Introduction

Polymerization with reversible addition fragmentation chain transfer (RAFT polymerization) with thiocarbonylthio compounds (dithioesters, trithiocarbonates, xanthates, dithiocarbamates) as RAFT agents **1** was first described in 1998.[1] The RAFT process has now emerged as one of the most versatile for conferring living characteristics on a radical polymerization.[2,3] The overall process involves insertion of monomer units into the C−S bond of an organic thiocarbonylthio compound as illustrated in Scheme 1. Both the "R" (α-) and "ZCS_2" (ω-) end groups are retained. The polymer product is itself a RAFT agent. This enables chain extension and block copolymer synthesis by addition of further monomer and renders the process eminently suited for the synthesis of end functional polymers.[4]

The main features that determine the activity of thiocarbonylthio RAFT agents are summarized in Scheme 2. They should possess a reactive C=S double bond. The activity of the double bond toward radical addition is determined by the substituents "Z" and "R" .[5−7] With appropriate choice of "R" , trithiocarbonates (Z = *S*-alkyl) are effective RAFT agents for polymerization of styrenic and acrylic monomers (acrylates, methacrylates, acrylamides).[2,8] Similarly, xanthates (Z = *O*-alkyl) are one of the RAFT agents of choice for vinyl monomers such as vinyl acetate (VAc) or *N*-vinylpyrrolidone (NVP).[2,9,10] The substituent "R" must be a good homolytic leaving group with respect to the propagating radical "P_n" and must be able to efficiently reinitiate polymerization. Higher transfer constants for the initial RAFT agent are favored if "R" is bulky, if "R" is electrophilic, and if "R" is a more stable radical.[5,11] The phthalimidomethyl radical is neither especially bulky nor stabilized but it does have electrophilic character.

Scheme 1. Overall RAFT Process



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In recent papers,[4,12] we have described the synthesis of polystyrene with amine chain ends by RAFT polymerization or atom transfer radical polymerization (ATRP).[13] In those works we made use of phthalimidomethyl trithiocarbonate[14] RAFT agents (e.g. **2**) or *N*-bromomethylphthalimide respectively to introduce latent primary amine groups as phthalimidomethyl residues. There are previous reports of phthalimido-functional RAFT agents in the patent literature.[15−17] In this paper, we report on the utility of **2** and the corresponding *S*-phthalimidomethyl xanthate **3** in RAFT polymerizations of butyl acrylate (BA), *N*-isopropylacrylamide (NIPAM), NVP and VAc. We also examine removal of the trithiocarbonate end group from the RAFT-synthesized poly(butyl acrylate) (PBA) by thermolysis.[18]

A further property of the RAFT agents **2** and **3** is that they possess a distinct UV chromophore in each of the "R" (i.e., the phthalimido group) and "ZCS_2" groups. This provides a means of estimating the relative number of each type of end group in derived polymers. We use this feature to elucidate the origin of bimodal distributions in acrylate polymers with otherwise narrow molecular weight distributions.

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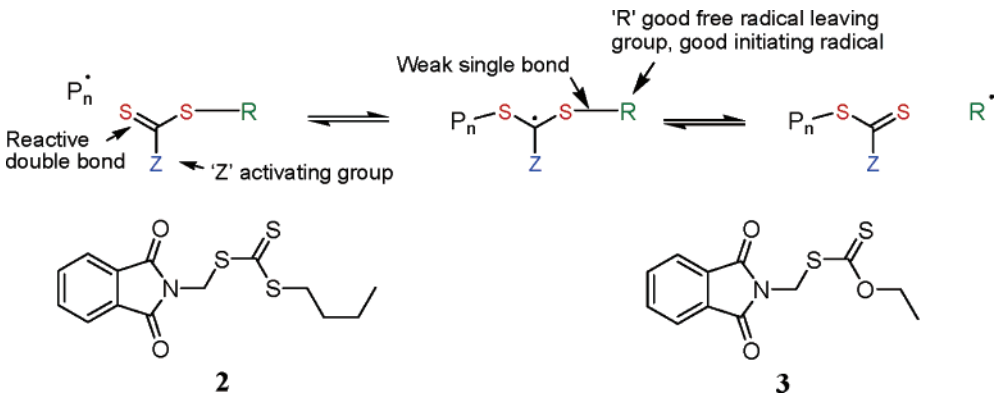
Scheme 2. Mechanism for Reversible Addition Fragmentation Chain Transfer (RAFT)



Experimental Section

General Data. Solvents were of AR grade and were distilled before use. *O*-Ethyl xanthic acid potassium salt (potassium ethyl xanthogenate) (>99%) was purchased from Aldrich. *N*-Bromomethylphthalimide (97%) was obtained from Aldrich. Azobis(isobutyronitrile) (AIBN) was obtained from DuPont and purified by crystallization from chloroform/methanol. Monomers were purified immediately prior to use. BA (Aldrich) was filtered through neutral alumina (70−230 mesh). VAc (Aldrich) and NVP (Aldrich) were flash distilled. NIPAM (Aldrich) was recrystallized twice from benzene/hexane 3:2 (v:v) and dried under vacuum. ^{1}H NMR spectra were obtained with a Bruker Advance DRX500, Bruker Av400 or a Bruker AC200 spectrometer on samples dissolved in deuteriochloroform, unless stated otherwise. Chemical shifts are reported in ppm from external tetramethylsilane. High-resolution electron impact (EI) mass spectra were obtained with a ThermoQuest MAT95XL mass spectrometer. Gel permeation chromatography (GPC) of PBA and PVAc was performed on a system comprising a Waters 515 HPLC pump, a Waters 717 Plus Autosampler and a Waters 2414 refractive index detector equipped with 3 × Mixed C (7.5 mm × 300 mm, 5μ particle size, linear molecular weight range 200−2000000) and 1 mixed E PLgel column (7.5 mm × 300 mm, 3μ particle size, linear molecular weight range up to 30000) from Polymer Laboratories. Tetrahydrofuran (THF, flow rate of 1.0 mL min^{-1}) was used as eluent at 22 ± 2 °C. GPC with UV detection was performed on a Waters 2695 Separations Module equipped with Waters 2414 refractive index detector and Waters 2996 photodiode array detector with similar columns/operating conditions. The GPC columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories) ranging from 200 to 7.5 × 10^6 g mol^{-1}. A third-order polynomial was used to fit the log M vs time calibration curve, which appeared to be linear across the molecular weight range 200 to 2 × 10^6. GPC analyses of PNIPAM and PNVP were performed with a Shimadzu modular system equipped with a SIL-10AD autoinjector and a RID-10A differential refractive index detector. The columns comprised four linear PL-gel columns (5 μm particle size, 10^5, 10^4, 10^3, and 500 Å, each 300 mm × 7.5 mm) and a guard column (50 mm × 7.5 mm) from Polymer Laboratories. The eluent was *N*,*N*-dimethylacetamide (containing 0.03% w/v LiBr and 0.05% w/v BHT) at 40 °C (flow rate: 1 mL min^{-1}). Gel permeation chromatography (GPC) of PNVP was also performed on a system comprising a Waters 590 HPLC pump and a Waters 410 refractive index detector equipped with three Waters Styragel columns (HT2, HT3, and HT4, each 300 mm × 7.8 mm, 5 μm particle size, providing an effective molecular weight range of 100−600000). The eluent was *N*,*N*-dimethylacetamide (containing 0.045% w/v LiBr) at 80 °C (flow rate: 1 mL min^{-1}). GPC calibration was performed with narrow polydispersity polystyrene standards ranging from 200 to 10^6 g mol^{-1}. Thin-layer chromatography was run on MERCK aluminum, silica gel 60 F_{254} plates with CH_2Cl_2 as the eluent. Thermogravimetric analysis (TGA) was carried out with a Mettler TGA/SDTA521 thermobalance equipped with a sample robot. Thermolyses were carried out under nitrogen (flow rate 50 mL min^{-1}).

Table 1. Evolution of Number-Average Molecular Weight ($\bar{M}_n$) and Polydispersity ($\bar{M}_w/\bar{M}_n$) with Time/Conversion for Poly(butyl acrylate) Formed During Polymerization of Butyl Acrylate (BA, 3.49 M in Benzene) in the Presence of Reversible Addition Fragmentation Chain Transfer (RAFT) agent 2 and with AIBN Initiator at 60 °C[a]

time (h)	$[Ba]_0/[2] \times 10^2$	convn[b] (%)	$\bar{M}_n^{Calc}$ [c,d] (g mol^{-1})	$\bar{M}_n$[c,e] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
1	1.51	33	6700	5910	1.29
2	1.51	58	11 500	12 100	1.11
4	1.51	77	15 200	16 700	1.09
8	1.51	91	17 800	19 600	1.10
16	1.51	96	18 600	21 300	1.10

[a] Azobis(isobutyronitrile) (AIBN) initiator 1.16 × 10^{-3} M. [b] Monomer conversion. [c] Values rounded to three significant figures. [d] $\bar{M}_n^{Calc}$ obtained using eq 1. [e] Polystyrene equivalents.

Table 2. Extent of Short Chain and/or Long Chain Branching in Poly(butyl acrylate) Prepared by Polymerization in the Presence of Reversible Addition Fragmentation Chain Transfer (RAFT) Agent 2 at 60 °C from ^{13}C NMR Analysis[19]

time (h)	convn (%)	total branches[b,c] (%)	total branches[b,d] (%)	long branches[e] (%)
1	33	0.40 ± 0.01	0.53 ± 0.01	0
2	58	0.60 ± 0.08	0.70 ± 0.02	0
4	77	0.74 ± 0.05	0.81 ± 0.01	0.05
8	91	1.06 ± 0.04	1.06 ± 0.02	0.04
16	96	1.15 ± 0.10	1.28 ± 0.01	0.03

[a] Polymerization conditions given in Table 1. [b] Error quoted is the standard deviation based on four determinations. [c] Total branch points (long + short) per hundred monomer units based on integration of the branch point quaternary carbon. [d] Total branch points (long + short) per hundred monomer units based on integration of the branch CH + CH_2 carbons. [e] Branch points (long only) per hundred monomer units formed by backbiting, β-scission and copolymerization based on analysis of GPC traces (Figure 1).

RAFT Agents. The synthesis of butyl phthalimidomethyl trithiocarbonate (**2**) is described in an another paper.[12]

Synthesis of *O*-Ethyl *S*-(Phthalimidylmethyl) Xanthate (3). *O*-Ethyl xanthic acid potassium salt (1.03 g, 0.0064 mol) was suspended in chloroform (20 mL) in a dry two-necked round-bottomed flask. *N*-(Bromomethyl)phthalimide (1.00 g, 0.0042 mol) in chloroform (20 mL) was added dropwise with stirring; the solution became paler yellow with the precipitation of white KBr as the reaction proceeded. The solution was stirred at room temperature for 18 h when complete reaction was confirmed by TLC (product R_f = 0.60). Additional chloroform (20 mL) was added prior to washing with deionized water (2 × 50 mL) and brine (1 × 50 mL). The solution was dried over anhydrous $MgSO_4$, filtered and the solvent removed from the filtrate by rotary evaporation to give a pale yellow solid (1.16 g, 98%), mp = 94−95 °C. ^{1}H NMR ($CDCl_3$) δ: 1.46 (tr, J = 7.1 Hz, 3H, C**H**$_3$CH$_2$−), 4.68 (q, J = 7.1, 2H, CH$_3$C**H**$_2$−O), 5.33 (s, 2H, N−C**H**$_2$−S), 7.75 (m, 2H, aromatic H), 7.85 (m, 2H, aromatic H). ^{13}C NMR ($CDCl_3$) δ: 13.7 (**C**H$_3$-CH$_2$−), 41.2 (N−**C**H$_2$−S), 70.5 (CH$_3$**C**H$_2$−),123.6 (2 × *o*-Ph, **C**H),

Table 3. Molecular Weights and Polydispersities for Poly(*N*-isopropylacrylamide) Obtained by Polymerization of *N*-Isopropylacrylamide (NIPAM, 1.78 M in dioxane) in the Presence of Reversible Addition Fragmentation Chain Transfer (RAFT) Agent 2 and AIBN Initiator at 60 °C[a]

time (h)	$[M]_0/[RAFT]_0 \times 10^2$	$\bar{M}_n^{Calc}$ [b,c] (g mol^{-1})	$\bar{M}_n$ [b] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	convn[d] (%)
16	0.50	5500	(2580)[e,f] 10 600[e,g] (6000)[h]	(1.38)[f] 1.07[g]	~80

[a] Azobis(isobutyronitrile) (AIBN) concentration 6.81×10^{-3}. [b] Values rounded to three significant figures. [c] $\bar{M}_n^{Calc} \sim [M]/[RAFT]_0 - convn \times 113+325$). [d] Monomer conversion based on yield of polymer isolated by precipitation. [e] Polystyrene equivalents. [f] Apparent $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ from GPC with THF eluent. [g] $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ from GPC with DMAc/LiBr eluent. [h] $\bar{M}_n$ based on ratio signal for phthalimide aromatics to polymer NH signal determined by integration of ^{1}H NMR spectrum obtained at 170 °C in DMSO-d_6.

Table 4. Molecular Weights and Polydispersities for Poly(*N*-vinylpyrrolidone) Obtained by Bulk Polymerization of *N*-Vinylpyrrolidone (NVP) in the Presence of RAFT Agent 2 and AIBN Initiator at 60 °C[a]

time (h)	$[M]_0/[RAFT] \times 10^2$	$\bar{M}_n^{Calc}$ [b,c] (g mol^{-1})	M_n[d] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$[d]	convn[e] (%)
1	1.51	2400	oligomer		<11
2	1.51	3090	oligomer		<14
4	1.51	3100	oligomer		<14
8	1.51	5130	22 600[e]	1.48	25
16	1.51	9540	26 700[e]	1.61	48

[a] Azobis(isobutyronitrile) (AIBN) concentration 3.08×10^{-3} M. [b] Values rounded to three significant figures. [c] $\bar{M}_n^{Calc} \sim [M]/[RAFT]_0 \times convn \times 111+325$. [d] GPC with DMAc/LiBr eluent in polystyrene equivalents. [e] Monomer conversion.

131.8 (2 × Ph, **C**), 134.4 (2 × *p*-Ph, **C**H), 166.6 (2 × **C**=O), 210.2 (O**C**S$_2$). MS (HREI, +VE, +LMR): *m/z* 281.0174 (M$^+$) ($C_{12}H_{11}NO_3S_2$ requires 281.0175).

RAFT Polymerization. The following procedure is typical. RAFT agent **3** (0.281 g, 9.98×10^{-4} mol), AIBN (101.9 mg, 6.21×10^{-5} mol), and VAc (9.34 g, 1.09×10^{-1} mol) were combined to form a stock solution. Aliquots of 2 mL were transferred to ampules, degassed with 4 freeze−pump−thaw cycles, and sealed under vacuum. The five ampules were heated at 60 °C for 1, 2, 4, 8, and 16 h when the polymerizations were quenched by rapid cooling in liquid nitrogen. Samples of the monomer/polymer mixture were diluted with THF or $CDCl_3$ (for GPC or NMR analysis respectively). Results of the analyses for this polymerization are summarized in Table 6.

Monomer conversions were calculated by determining the amount of residual monomer from the ^{1}H NMR (400 MHz) spectrum of a sample of the polymerization mixture diluted with $CDCl_3$.

For BA polymerization, the amount of residual monomer was obtained from the signals at δ 5.8 (d, BA trans −CH=CH**H**), 6.2 (dd, −C**H**=CHH) and 6.5 (d, cis −CH=C**H**H) and the amount of monomer plus polymer from the overlapping resonances at 4.2 (br t, PBA −OC**H**$_2$) and 4.4 (t, BA −OC**H**$_2$).

For NVP polymerization, the amount of residual monomer was obtained from the signal at δ 7.0 (dd, NVP −C**H**=CHH) and the amount of monomer plus polymer from the overlapping resonances at 2.9−4.0 (br m, PNVP C**H**$_2$NC**H**) and 3.4 (t, NVP C**H**$_2$N).

For VAc polymerization, the amount of residual monomer was obtained from the signals at δ 7.2 (dd, VAc −C**H**=CHH) and 4.5 (d, VAc trans −CH=C**H**H) and the amount of monomer plus polymer from the overlapping resonances at 4.9 (br m, PVAc −C**H**-**(**OAc)−) and 4.8 (d, VAc cis −CH=CH**H**).

For NIPAM polymerization, the monomer conversion was determined gravimetrically.

Determination of Branching in Poly(Butyl Acrylate). ^{13}C NMR spectra were obtained under conditions similar to those described by Ahmad et al.[19] The relevant portions of the NMR spectra are shown in Figure 4. Assignments for branch carbons and the calculations of total log + short chain % branching were also performed as described by Ahmad et al.[19] Each spectrum was processed four times to provide the results are shown in Table 2. The error is the standard deviation associated with performing the integration on the spectra shown. The main error is signal-to-noise and the error in the branching is estimated to be ±20% although the relative error should be smaller.

An estimate of long chain branching by the mechanism shown in Scheme 5 (Table 2) is based on integration of the "molecular weight distributions" shown in Figure 2c. These were obtained with UV detection at 305 nm where the trithiocarbonate end group absorbs. The *y*-axis was converted to a concentration axis by dividing by the molecular weight.

Thermolysis Experiments. Dynamic Thermolysis. Samples of PBA (**4**) (~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 2 °C min^{-1} under nitrogen from 50 to 600 °C. A thermogram for PBA $\bar{M}_n$ 6830 g mol^{-1} and

Table 5. Molecular Weights and Polydispersities for Poly(*N*-vinylpyrrolidone) Obtained by Polymerization of *N*-Vinylpyrrolidone (NVP 50% v/v in toluene) in the Presence of RAFT Agent 3 and AIBN Initiator at 60 °C[a]

time (h)	$[NVP]_0/[\mathbf{3}]_0 \times 10^2$	convn[e] (%)	convn **3** (%)	$\bar{M}_n^{Calc}$ [b,c] (g mol^{-1})	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
0.25	0.71	9	25	990	4460	1.16
0.5	0.71	14	41	1360	4450	1.18
1	0.71	23	60	2030	4670	1.17
2	0.71	36	80	2980	4760	1.27
9.13	0.71	75	99.7	5870	7290	1.20
24	0.71	98	100	7570	8590	1.15
32	0.71	99	100	7650	8850	1.16
1	0.92	12	35	3670	5100	1.22
2	0.92	19	55	3820	5340	1.20
8	0.92	59	96	6620	7660	1.22
24	0.92	90	100	9490	9230	1.18
1	5.17	4	11	15 900		
2	5.17	7	23	21 100	12 800	1.48
8	5.17	32	66	28 900	13 000	1.57
24	5.17	53	96	30 500	18 500	1.54

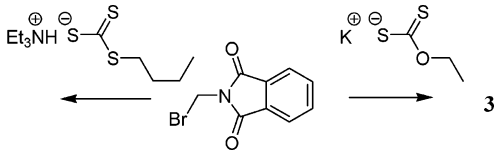
[a] Azobis(isobutyronitrile) (AIBN) concentration 1.28×10^{-2} for $[NVP]_0/[\mathbf{3}]_0 = 71$, 4.42×10^{-3} M for $[NVP]_0/[\mathbf{3}]_0 = 92$ and 8.82×10^{-4} for $[NVP]_0/[\mathbf{3}]_0 = 517$. [b] Values rounded to three significant figures. [c] $\bar{M}_n^{Calc} \sim [NVP] \times convn/[\mathbf{3}]_0 \times convn\ \mathbf{3} \times 111+281$. [d] GPC with DMF/LiBr eluent in polystyrene equivalents. [e] Monomer conversion.

Table 6. Molecular Weights and Polydispersities for Poly(vinyl acetate) obtained by Bulk Polymerization of Vinyl Acetate in the Presence of *O*-Ethyl *S*-Phthalimidomethyl Xanthate (3)[a]

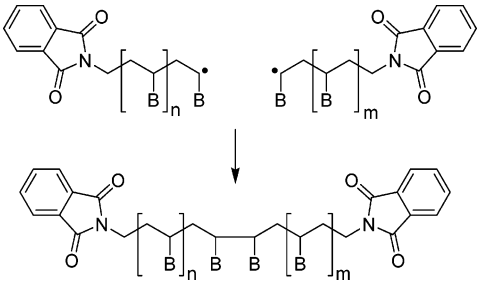
temp (°C)	time (h)	$[M]_0/[RAFT]_0 \times 10^2$	$\bar{M}_n^{Calc}$ [b,c] (g mol^{-1})	$\bar{M}_n$[b] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	convn[d] (%)
60	16	control		59 700	4.27	98
60	1	1.09	600	425	1.35	2.7
	2		1500	854	1.35	8.5
	4		3400	2300	1.24	23
	8		6600	5010	1.23	46
	16		10 900	8800	1.31	77
100	16	control		93 700	4.07	78
100	1	1.08	7700	5470	1.49	53
	2		10 800	8340	1.54	76
	4		11 500	9590	1.71	81
	8		11 600	10 200	1.70	81
	16		12 500	11 000	1.65	88

[a] Initiator was azobis(isobutyronitrile) (6.20×10^{-3} M) at 60 °C and azobis(cyclohexanenitrile) (8.42×10^{-4} M) at 100 °C. [b] Values rounded to three significant figures. [c] $\bar{M}_n^{Calc} = [M]/[\mathbf{3}]_0 \times (convn \times 86) + 281$. [d] Monomer conversion.

Scheme 3. Synthesis of Nonsymmetrical Trithiocarbonates or Xanthates



Scheme 4. Mechamism for Combination (B = $CO_2C_4H_9$)



$\bar{M}_w/\bar{M}_n$ 1.17 is shown in our preliminary communication[18] and it appears in a revised format as Figure 10.

Isothermal Thermolysis. Small scale preparative thermolysis was also carried out using the thermogravimetric balance. The following procedure is typical. A sample of pale yellow PBA (**4**) (26.5 mg, $\bar{M}_n$ 11500 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.11) was weighed into in large (50 μL alumina crucible) and placed in the sample furnace of the thermobalance The sample was heated isothermally under nitrogen at 240 °C for 3 h. to provide a colorless product ($\bar{M}_n$ 8300 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.58). The colorless residue was dissolved in chloroform and analyzed directly by ^{1}H NMR spectroscopy and GPC. The GPC chromatogram is shown as Figure 11b. There is negligible change in peak molecular weight but some broadening of the molecular weight distribution with formation of a high molecular weight shoulder and an oligomer tail.

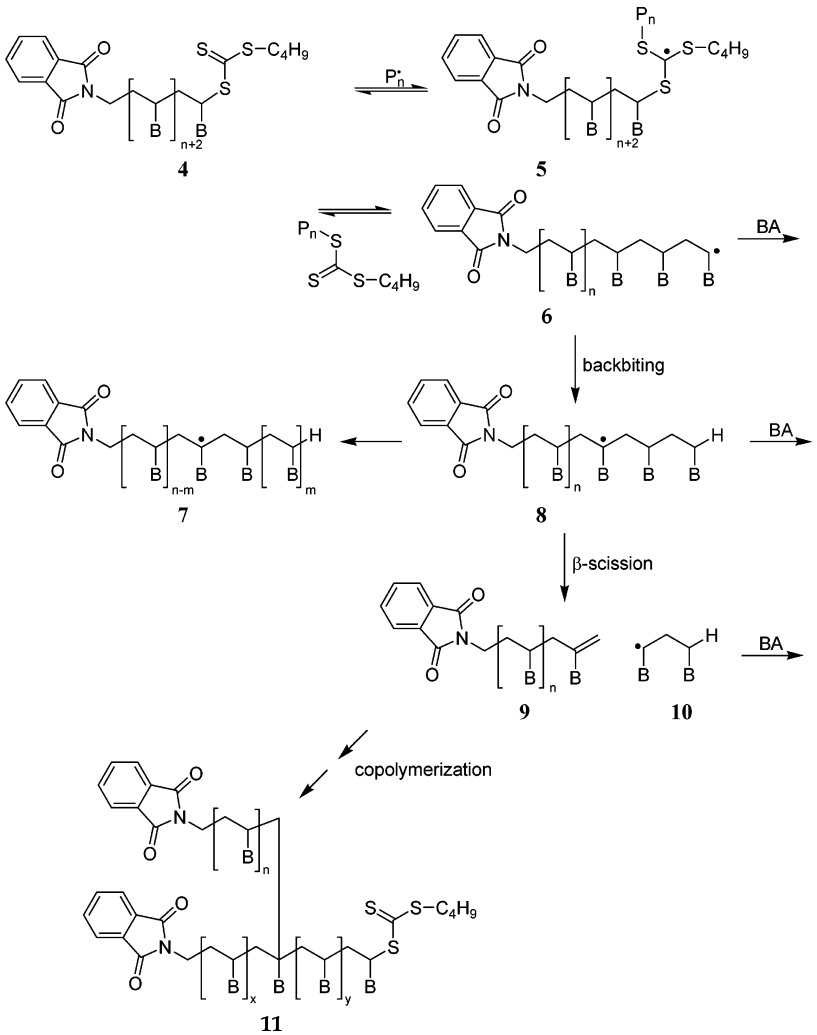
Results and Discussion

The RAFT agents **2**[12] and **3** were synthesized in high purity (>98%) and yield (>95%) by a simple "one pot" procedure involving alkylation of the appropriate salt with *N*-(bromomethyl)phthalimide as shown in Scheme 3. Issues associated with the synthesis of RAFT agent **2** are detailed in ref 12.

Butyl Acrylate Polymerization. Many papers have appeared on RAFT polymerization of acrylate esters.[2,20] The evolution of the molecular weight and polydispersity with conversion during BA polymerization in the presence of RAFT agent **2** at 60 °C is shown in Figure 1 and Table 1.

Residual RAFT agent is not detectable by ^{1}H NMR spectroscopy even at the first time/conversion point (1 h, 33%) and the polydispersity ($\bar{M}_w/\bar{M}_n$) narrows rapidly with conversion indicating that the phthalimidomethyl radical is a good homolytic leaving group relative to the PBA propagating radical ($P_n^\bullet$). Even though the polydispersity is low, examination of the GPC traces (Figure 2) shows the molecular weight distributions to be distinctly bimodal for conversions >77% with formation of a high molecular weight shoulder. Molecular weights at high conversions estimated using eqs 1 or 2 are slightly lower than those found. Correction of the molecular weights by use of the Mark−Houwink−Sakurada relationshipand Universal calibration lowers the found molecular weights by ca. 5% thus increasing the discrepancy.[21,22] It is also possible that the molecular weights appear low as a consequence

Scheme 5. Mechanism for Long Chain Branch Formation (B = $CO_2C_4H_9$)



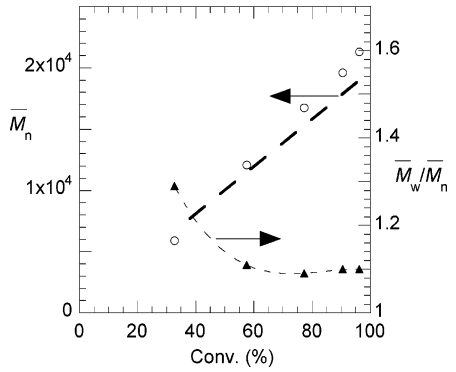


Figure 1. Evolution of number-average molecular weight ($\bar{M}_n$, in polystyrene equivalents) (○) and polydispersity ($\bar{M}_w/\bar{M}_n$, ▲) with conversion for poly(butyl acrylate) during polymerization of butyl acrylate (BA, 3.49 M in benzene) in the presence of reversible addition fragmentation chain transfer (RAFT) agent **2** and with azobis(isobutyronitrile) initiator at 60 °C. Also shown are the calculated molecular weight (− − −) and the line of best fit through the polydispersity data (- - -). For experimental details, see Table 1.

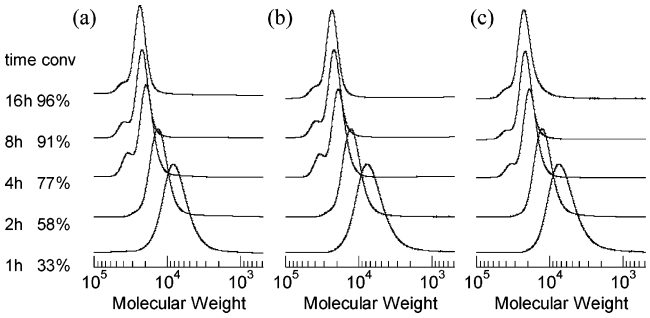


Figure 2. Normalized molecular weight distributions at various reaction times/conversions for polymerization of butyl acrylate at 60 °C with azobis(isobutyronitrile) initiator in the presence of reversible addition fragmentation chain transfer (RAFT) agent **2** with (a) RI detection, (b) UV detection at 220 nm, and (c) UV detection at 305 nm. Details of polymerization conditions are contained in Table 1.

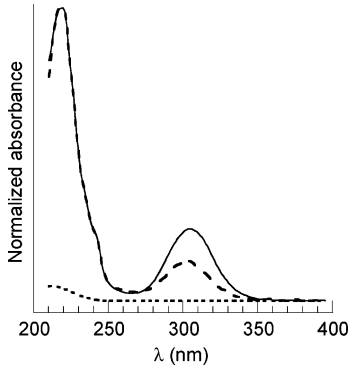


Figure 3. Normalized UV spectra of poly(butyl acrylate) (PBA) formed in the presence of trithiocarbonate **2** in tetrahydrofuran (extracted from the gel permeation chromatogram for sample 4 h, 77% conversion shown in Figure 2). The main peak (−−) and the high molecular weight shoulder (- - -) are compared to a conventional PBA (····). Trithiocarbonate absorption maximum is at 305 nm, phthalimide absorption maximum is at 220 nm, and a PBA maximum is at ∼200 nm.

of the PBA being branched.

$$\bar{M}_n^{Calc} = [M]/([RAFT]_o + [I]_0 * df * (1 - \exp(k_d t)) \times convn \times m_M + m_{RAFT} \quad (1)$$

for low initiator consumption this can be approximated as.

$$\bar{M}_n^{Calc} \sim [M]/([RAFT]_o \times convn \times m_M + m_{RAFT} \quad (2)$$

where [M], $[RAFT]_0$ and $[I]_0$ are the initial concentrations of monomer, RAFT agent and initiator respectively, *df* is the number of initiator derived polymer chains formed per mole of initiator decomposed ($d \sim 1.0$ for BA polymerization with termination by combination[23]), *f* is the initiator efficiency, k_d is the initiator decomposition rate constant ($k_d = 9.7 \times 10^{-6}$ s^{-1} and $f \sim 0.7$ for AIBN at 60 °C), *t* is the reaction time, convn is the monomer conversion and m_M and m_{RAFT} are the molecular weights of the monomer and the RAFT agent.

For polymers of sufficiently high molecular weight the end groups make no substantial contribution to the differential refractive index. Thus, in the GPC trace with refractive index (RI) detection where each monomer unit in the polymer chain contributes, the signal intensity should be proportional to the square of the molecular weight. With ultraviolet (UV) detection at the wavelengths chosen the absorbance of the monomer unit is negligible with respect to that of the end groups (phthalimide chromophore at 220 nm, Figure 2, trithiocarbonate chromophore at 305 nm). In the GPC traces with UV signal intensity should be directly proportional to molecular weight for a polymer chain with one chromophore per polymer chain. With detection at 305 nm the trithiocarbonate end group chromophore make the dominant contribution to the signal intensity. The reduced size of the high molecular weight shoulder in these traces with respect to that seen in the RI traces is consistent with there being one trithiocarbonate group per polymer chain, Even though the phthalimide chromophores should make the dominant contribution to the signal in the case of the GPC traces obtained with UV detection at 220 nm, they resemble the traces with RI detection. This suggests that the number of phthalimide chromophores per chain increases with the molecular weight of the chain and is consistent with ∼2 chromophores per chain for the high molecular weight shoulder and ∼1 chromophore per chain for the main peak.

Similar bimodal molecular weight distributions have been reported previously for RAFT polymerization of acrylates (e.g. MA, BA) using a range of RAFT agents suggesting this is a general phenomenon for polymerizations of acrylate esters.[5,24] That work showed that the shoulder became more pronounced with conversion and was most evident for higher molecular weight polymers. Our earlier work demonstrates that bimodal distributions of this form can only be reliably observed when $\bar{M}_w/\bar{M}_n$ is less than 1.2.[24] High efficiency GPC columns are also required, or the shoulder may be obscured by band broadening.

Radical−radical termination of propagating radicals can give rise to a shoulder peak of double molecular weight (e.g., Scheme 4). However, although termination reactions must undoubtedly occur during RAFT polymerization, we can reject the possibility that such processes involving either the PBA propagating radicals (**6**-**8**) or the RAFT intermediate (**5**) make a substantial contribution of the peak observed on two grounds:

(a) Such products should not contain the trithiocarbonate chromophore. Thus, the shoulder should be invisible with UV detection at 305 nm since PBA is transparent at this wavelength (Figure 3).

(b) The molar concentration of the termination products should not exceed the moles of radicals generated and will usually be less than this when termination is by combination.[23] The size of the shoulder peak is too large.

This situation can be contrasted with that for styrene polymerization where a higher molecular weight shoulder attributable to the occurrence of termination by coupling can sometimes be observed (both the above conditions being fulfilled).[7,24]

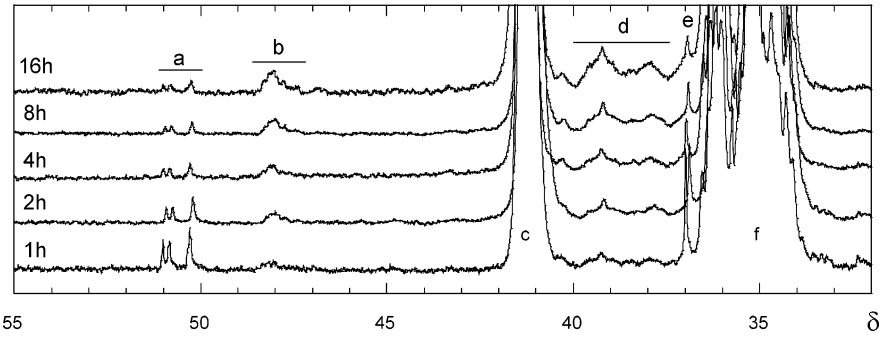


Figure 4. Region δ 32−55 of ^{13}C NMR spectra (125 MHz, $CDCl_3$) for poly(butyl acrylate) prepared at 60 °C with reversible addition fragmentation chain transfer (RAFT) agent **2** and azobis(isobutyronitrile) initiator for the reaction times indicated. Details of polymerization conditions for preparing the samples are given in Table 1. Signal assignments are as follows: a, end group $-\mathbf{C}H_2SC(=S)$; b, branch $\mathbf{C}_q$; c, backbone **C**H; d, branch **C**H + $\mathbf{C}H_2$; e, end group $-\mathbf{C}H_2N<$; f, backbone $\mathbf{C}H_2$. Signal intensity normalized vs peak c.

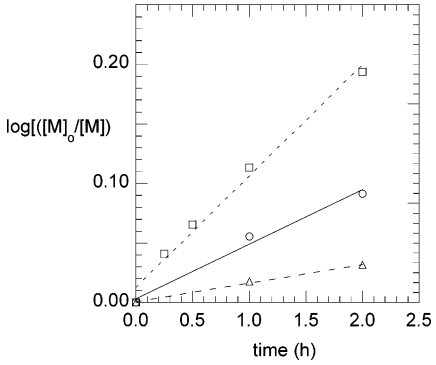


Figure 5. Plot of log of monomer concentration vs time to 2.5 h for polymerization of *N*-vinylpyrrolidone (∼50% v/v NVP in toluene) in the presence of reversible addition fragmentation chain transfer (RAFT) agent **3** and azobis(isobutyronitrile) initiator at 60 °C. Corresponds to experiments shown in Table 5 with [NVP]/[RAFT] = 71 (□, - - -); [NVP]/[RAFT] = 92 (○, −), [NVP]/[RAFT] = 151 (△, − − −).

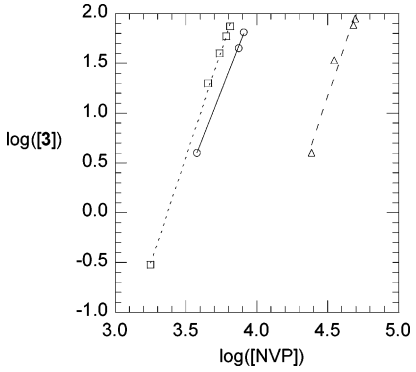


Figure 6. Log plot of monomer concentration vs reversible addition fragmentation chain transfer (RAFT) agent concentration for polymerization of *N*-vinylpyrrolidone (∼50% v/v NVP in toluene) the presence of RAFT agent **3** and azobis(isobutyronitrile) initiator at 60 °C. Corresponds to experiments shown in Table 5 with [NVP]/[RAFT] = 71 (□, - - -, slope 4.2); [NVP]/[RAFT] = 92 (○, −, slope 3.6), [NVP]/[RAFT] = 151 (△, − − −, slope 4.3).

The RAFT agent **2** has two chromophores, the trithiocarbonate ("ZC(=S)S") group with absorption at 305 nm and a phthalimido group as the "R" group with absorption at 220 nm. The same should be true of the polymer derived by RAFT polymerization (**4**). If it is assumed that within the main peak "R":"ZCS_2" are in the expected ∼1:1 ratio for a linear chain, then the high molecular weight shoulder has these groups in a ∼2:1 ratio (Figure 3). In a previous publication,[24] we proposed that this shoulder might arise by copolymerization of the macromonomer **9** which is formed by backbiting-β-scission (Scheme 5). The present data are consistent with this hypothesis

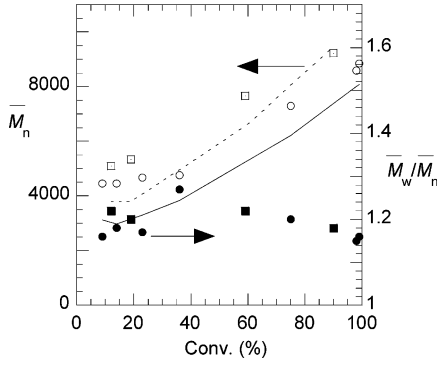


Figure 7. Evolution of number-average molecular weight ($\bar{M}_n$, polystyrene equivalents open symbols) and polydispersity ($\bar{M}_w/\bar{M}_n$, closed symbols) with conversion during polymerization of *N*-vinylpyrrolidone (∼50% v/v NVP in toluene) in the presence of *O*-ethyl *S*-phthalimidomethyl xanthate (**3**) and azobis(isobutyronitrile) initiator at 60 °C. Corresponds to experiments shown in Table 5 with [NVP]/[RAFT] = 71 (□, −); [NVP]/[RAFT] = 92 (○, - - -). Lines indicate calculated molecular weight.

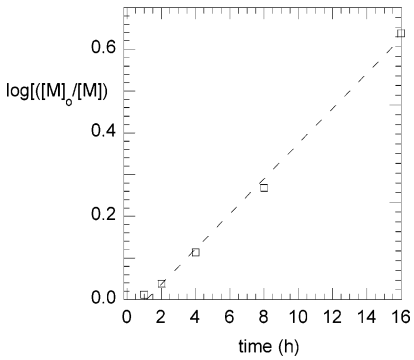


Figure 8. Plot of log of monomer concentration vs time for polymerization of vinyl acetate at 60 °C with azobis(isobutyronitrile) initiator in the presence of *O*-ethyl *S*-phthalimidomethyl xanthate (**3**). For experimental details, see Table 6.

and with the shoulder being due to polymer with the structure **11**.

PBA formed by conventional radical polymerization contains both short and long chain branches.[19,25] Ahmad et al.[19] showed that the total extent of branching could be determined by ^{13}C NMR spectroscopy. Regions of the ^{13}C NMR spectra for the PBA samples summarized in Table 1 are shown in Figure 4. The incidence of branching in our PBA samples (the total of long and short chain branches) determined applying their[19] signal assignments is shown in Table 2. The signals associated with both chain ends are also visible in the spectra. Long and short chain branches cannot be distinguished in the ^{13}C NMR spectra.

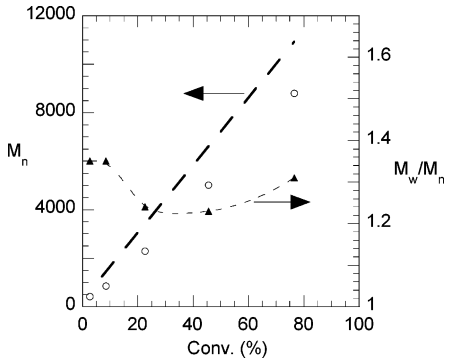


Figure 9. Evolution of number-average molecular weight ($\bar{M}_n$, polystyrene equivalents) and polydispersity ($\bar{M}_w/\bar{M}_n$) (▲ and ○) with conversion for polymerization of vinyl acetate at 60 °C with azobis(isobutyronitrile) initiator in the presence of *O*-ethyl *S*-phthalimidomethyl xanthate (**3**). Also shown are the calculated molecular weight (− − −) and the line of best fit through the polydispersity data (- - -). For experimental details, see Table 6.

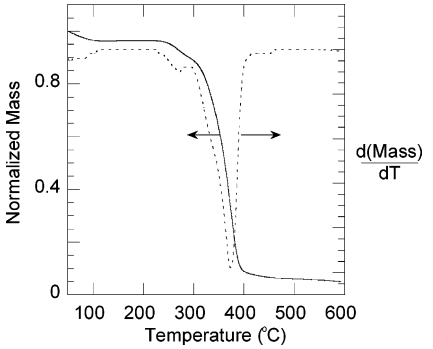


Figure 10. Normalized mass loss (−) and first derivative of mass loss (- - -, arbitrary units) vs temperature for poly(butyl acrylate) with number-average molecular weight ($\bar{M}_w/\bar{M}_n$) 6830 g mol^{-1} and polydispersity ($\bar{M}_n$) 1.17 heated from 50 to 600 °C at 10 °C min^{-1} under nitrogen.

Ahmad et al.[19] proposed that short chain branches were formed by backbiting and that long chain branches arose by intermolecular chain transfer. They also showed that short chain branches were dominant. Our results (Table 2) are not inconsistent with this finding.

We propose that long chain branches may also arise by β-scission of the midchain radical (**8**) formed by backbiting and subsequent copolymerization of the macromonomer so formed (**9**). This backbiting β-scission process is well-known at high temperatures.[26−30] While the incidence of midchain radical β-scission is lower for lower reaction temperatures,[31] it has been demonstrated to occur (e.g., 80 °C[27]) under conditions of higher monomer dilution. Since both backbiting and β-scis sion compete with propagation, their incidence is expected to increase with monomer conversion. Thus, the extent of macromonomer formation and macromonomer copolymerization should be more significant at higher monomer conversions. The number of branches/molecule (and the relative size of the high molecular weight shoulder on the molecular weight distribution) will therefore be greater for higher molecular weight polymers.

Previous work has demonstrated that, in β-scission following backbiting, there is a strong preference for forming a high molecular weight macromonomer (**9**) and a "dimer" radical (**10**) rather than a high molecular weight propagating radical and a low molecular weight macromonomer.[26−28] In this circumstance, we would also anticipate observing low molecular weight "living" chains stemming from propagation the "dimer" radical

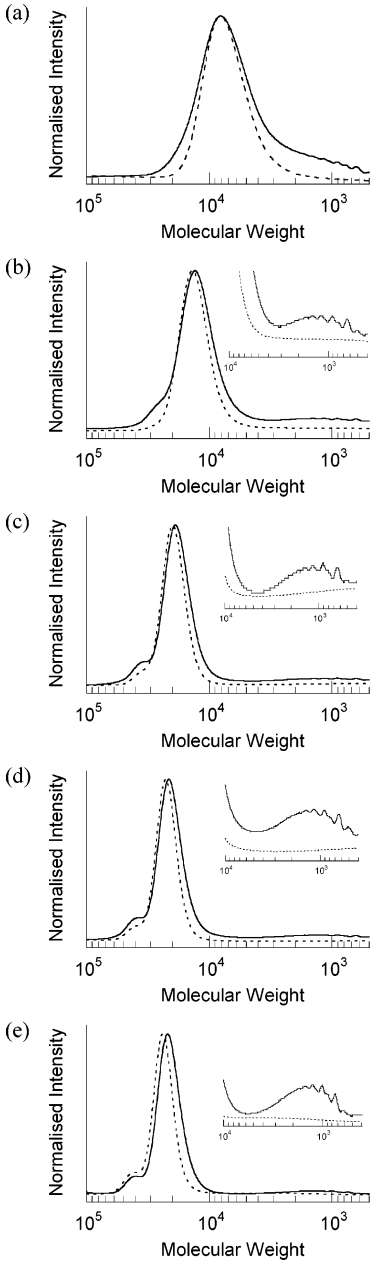
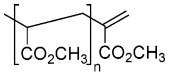


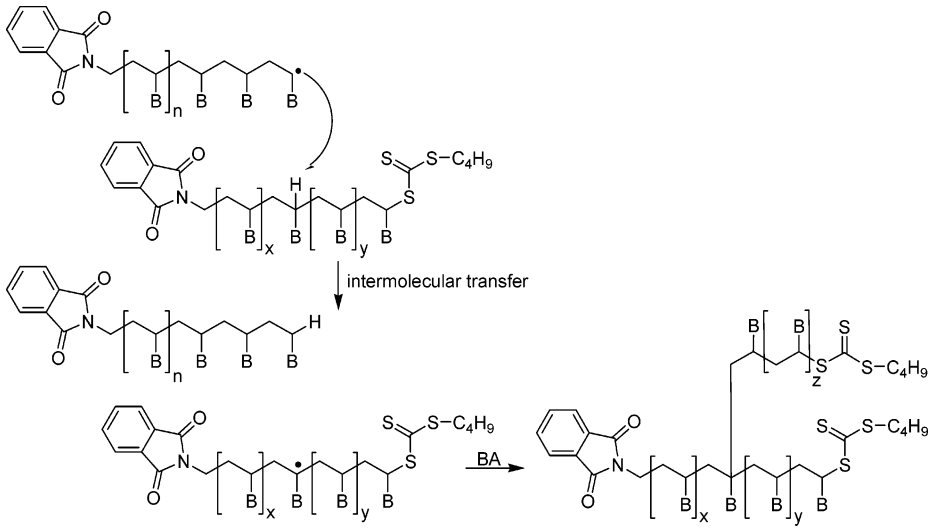
Figure 11. Molecular weight distributions for the precursor poly(butyl acrylate) (- - -) and the thermolysis product (−) which arises by heating at 210 °C under nitrogen for 3 h (the *y*-axis is normalized signal intensity observed in gel permeation chromatogram. The samples (a−e) are those described in Table 1. The insets show a ∼10-fold expansion of the *y*-axis. For details, see the Experimental Section.

(**10**). Although not immediately evident in Figure 2, closer examination of the GPC traces reveals the presence of some oligomeric product. The low molecular weight polymer is suppressed in conventional GPC distributions obtained withrefractive index detection because the *y*-axis (intensity) is proportional to the molecular weight squared and the distributionis smeared by the log dependence of the *x*-axis (molecular weight).



12a n=1
b n=2
c n=3

Scheme 6. Mechanism for Long Chain Branch Formation (B = $CO_2C_4H_9$)



One argument against the proposed mechanism is the absence of detectable amounts of macromonomer in the polymerization mixtures where the shoulder on the molecular weight distribution is prominent. Yamada and co-workers have examined the reactivity of methyl acrylate "dimer" **12a**,[32] "trimer" **12b**,[33,34] and "tetramer" **12c**[35] in copolymerization, and on this basis the macromonomer **9** might be anticipated to have a reasonably high reactivity in copolymerization with BA. For example, the reactivity ratios of the methyl acrylate "dimer" **12a** (M_2) and BA (M_1) in copolymerization at 60 °C are reported[32] as $r_1 = 0.52$ and $r_2 = 1.26$, indicating that the macromonomer is approximately twice as reactive as BA toward the PBA propagating radical. However, it nonetheless seems unlikely that macromonomer when formed should be quantitatively reincorporated into the polymer. On the basis of the level of incorporated macromonomer observed (Table 2), free macromonomer may not be visible in the NMR spectra.

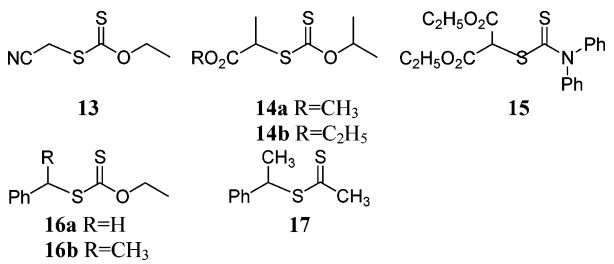
Intermolecular chain transfer can also provide a "three-armed star" as shown in Scheme 6. However, this material is expected to have the "R" and "ZCS_2" groups in a 1:2 ratio (Scheme 6) rather than the 2:1 ratio observed within the high molecular weight shoulder. The process would also produce a dead polymer chain with an "R" end (Scheme 6). While we do not suggest that intermolecular chain transfer does not occur, we exclude this from being a major mechanism contributing to the formation of the high molecular weight shoulder on the molecular weight distribution.

The mechanism proposed (Scheme 5) is not dependent on the RAFT process and should therefore be observed generally during radical polymerization of acrylates. It will only manifest as a bimodal molecular weight distribution during living polymerization when narrow molecular weight distributions are formed. Our search of the literature revealed few examples of living radical polymerization that produced very narrow polydispersities at high conversion for acrylate monomers (i.e., with $\bar{M}_w/\bar{M}_n$ less than 1.2 at high conversion and where GPC traces are shown).[36,37] Bimodal molecular weight distributions similar in appearance to those observed here have been reported for ATRP of methyl acrylate[36] and butyl acrylate[37] at high conversion. However, the bimodal distributions were attributed to the occurrence of termination by coupling.

***N*-Isopropylacrylamide Polymerization.** Several papers have appeared on RAFT polymerization of NIPAM.[24] RAFT agents used include dithioesters[38,39] and dithiocarbamates[40] and trithiocarbonates.[41,42] NIPAM was polymerized in the presence of RAFT agent **2** under conditions similar to those used previously.[40] Like BA polymerization, NIPAM polymerization appeared to be well controlled providing a polymer with a very narrow molecular weight distribution (Table 3).

Analysis of the polymer by conventional GPC (THF eluent) was problematic. The problems were resolved through the use of more appropriate analysis conditions (GPC with DMAc/LiBr eluent). High-resolution NMR spectra of the PNIPAM were obtained at 170 °C in DMSO-d_6 (to determine molecular weight). Some decolorization of the polymer solution was observed during the NMR experiment suggesting a loss of trithiocarbonate end groups.

***N*-Vinylpyrrolidone Polymerization.** Until recently little has been published on living radical polymerization of NVP. In their review, Moad et al.[2] mention RAFT polymerization of NVP in methanol with xanthate **13** at 60 °C to provide $\bar{M}_n$ of 17000 and $\bar{M}_w/\bar{M}_n$ of 1.35 for $M_0/[RAFT]_0 = 50$ and 53% conversion. Devasia et al. have recently described RAFT polymerization of NVP in dioxane with xanthate **14a**[43] or dithiocarbamate **15**[44] at 80 °C. For **14a** they report $\bar{M}_n$ of 8000 and $\bar{M}_w/\bar{M}_n$ of 1.3 for $M_0/[RAFT]_0 = 100$ and 80% conversion. Poor control ($\bar{M}_w/\bar{M}_n > 1.5$) was obtained using higher $M_0/[RAFT]_0$. Wan et al.[45] report that the dithioacetate **17** inhibited NVP polymerization while xanthates **16a** and **b** gave good control following inhibition periods of 6 and 1 h, respectively. The inhibition period seen with **16a/b** might be attributed tobenzylic radicals having poor reinitiating ability in NVP polymerization.



13 **14a** R=CH_3 **14b** R=C_2H_5 **15** **16a** R=H **16b** R=CH_3 **17**

Polymerizations of NVP in the presence of the trithiocarbonate RAFT agent **2** were characterized by an inhibition period

during which the polymerization medium was decolorized (Table 4). This suggests that the RAFT agent is being consumed during this time. The polymerization then commenced to form a high molecular weight polymer. Similar behavior has been observed during VAc polymerization[9] where the inhibition was attributed to the relative stability of the RAFT intermediate. In that case the problem was solved with the use of RAFT agents (xanthates, dithiocarbamates) where the "Z" substituent provides less stabilization for the intermediate radical.

Polymerization of NVP in the presence of the xanthate RAFT agent **3** appears to provide good control (Table 5). No inhibition period is discernible (Figure 5). The apparent transfer constant, estimated from the level of residual **3** detected in the polymerization mixtures, appears constant over a wide range of RAFT agent concentrations (~4 for [M]/[RAFT] = 71−517; Figure 6). The slope of a plot of $\log(R_p)$ vs log [AIBN] suggests that the rate of polymerization (R_p) is 0.67 ($R = 0.9999$) order with respect to initiator concentration (0.5 order expected in conventional radical polymerization with AIBN initiator). These data shows that the phthalimidomethyl radical is efficient in reinitiating polymerization of NVP and is consistent with expulsion of phthalimidomethyl radical from the RAFT intermediate being irreversible under the polymerization conditions.

For higher RAFT agent concentrations, the relatively narrow molecular weight distributions that are produced even at low conversions (Figure 7) seem inconsistent with the rate of utilization of the RAFT agent and its apparent transfer constant. Also for higher RAFT agent concentrations, the trend in molecular weight with conversion is consistent with calculations based on the rate of utilization of the RAFT agent. For lower RAFT agent concentration molecular weights are substantially lower than expected and polydispersities appear broad (Table 5). It is likely that GPC columns/conditions are inappropriate for PNVP.

Vinyl Acetate Polymerization. Poly(vinyl acetate) (PVAc) and its derivative, poly(vinyl alcohol) (PVA), are extremely important industrially for the production of adhesives and paints and have recently been investigated for various biomedical applications.[46,47] Living radical polymerization of VAc is often problematic and techniques such as atom transfer radical polymerization (ATRP) and nitroxide mediated polymerization (NMP) are not generally effective. Recently cobalt-mediated living radical polymerization of VAc has been reported.[48] Polymerization with reversible chain transfer to certain RAFT agents (see below), iodo-compounds[49] or organostibine derivitives[50] provide some control over VAc polymerization allowing PVAc with narrow molecular weight distribution to be prepared. RAFT polymerization with dithioester and trithiocarbonate RAFT agents are strongly retarded showing behavior analogous to that seen with NVP (above).[2,9] However, early work showed that RAFT polymerization with certain xanthate[9,10] and dithiocarbamate RAFT agents[9,51] can be successful and a significant number of papers on the use of these reagents have now appeared.[52−56] RAFT polymerization with xanthates is sometimes called MADIX (macromolecular design by interchange of xanthate).[2,10]

For polymerization of VAc with xanthate RAFT agents, the choice of the *O*-alkyl substituent is important.[57] For example, control (predicted $\bar{M}_n$, low $\bar{M}_w/\bar{M}_n$) can be obtained in RAFT polymerization with *O*-methyl, *O*-ethyl, *O*-isopropyl, and *O*-aryl xanthates[2] but not with *O*-*tert*-butyl xanthates.[52] The alkyl on oxygen needs to be a very poor homolytic leaving group with respect to the alkyl group on sulfur for cleavage of the "S−R" bond to be favored over cleavage of the "*O*-alkyl" bond.[57] Electron withdrawing substituents on oxygen enhance the transfer constant of xanthates.[6] The choice of the "R" group is also extremely important. It is necessary to choose "R" such that the radical R• is able to efficiently reinitiate VAc polymerization. For example, benzyl radical is slow to add to VAc and is a poor "R" group.

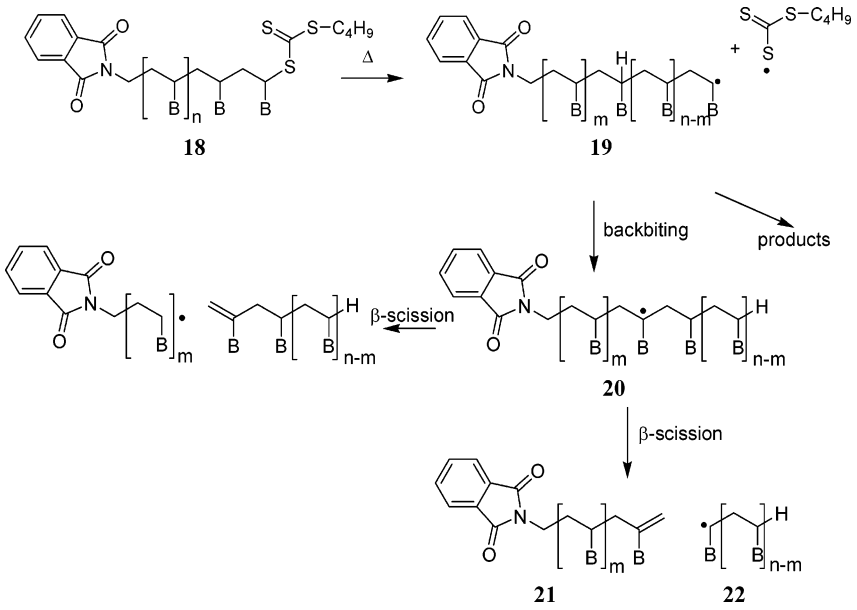
RAFT polymerization of VAc with the *S*-phthalimidomethyl xanthate **3** gave better control at 60 °C than at 100 °C (Table 6). This contrasts with the earlier finding[9] with dithiocarbamates and other xanthates that better control was obtained at higher temperatures and may be associated with the high rate of polymerization achieved at 100 °C with the initiator concentration employed. The polydispersities obtained at 60 °C ($\bar{M}_w/\bar{M}_n$ = 1.2−1.35) are comparable with those obtained in the earlier work.[9] Conversions after 16 h were lower than obtained in the control (no **3**). An inhibition period of ca. 1 h is evident (Figure 8) after which the rate of polymerization appears constant with time. For the polymerization at 60 °C, residual **3** in the polymerization mixtures was only evident in the ^{1}H NMR spectrum at the first conversion point (reduced ~5-fold to 0.0027 M at 2.7% monomer conversion). On the basis of this rate of consumption, the apparent transfer coefficient of **3** in VAc polymerization at 60 °C can be estimated[5,12] as ~7.

Thus, the *S*-phthalimidomethyl xanthate **3** appears to be an effective RAFT agent in VAc polymerization to yield phthalimido functional PVAc with a narrow molecular weight distribution.

Trithiocarbonate Group Elimination from Poly(butyl acrylate). The trithiocarbonate group of PBA (**4**) synthesized with RAFT agent **2** can be cleaved from the polymer by thermolysis. Preliminary details of these experiments including some details of product characterization have been provided in recent communications.[18,58] Thermogravimetric analysis in which a sample of PBA $\bar{M}_n$ (6830 g mol^{-1} and $\bar{M}_w/\bar{M}_n$ 1.17) was heated to 600 °C at 10 °C min $^{-1}$ showed (Figure 10) a mass loss of ~6% between 220 and 300 °C that was significantly greater than that expected for loss of the trithiocarbonate group (2.4% expected for $C_5H_{10}S_3$). Isothermal thermolysis carried out at 240 °C provided a colorless product that was characterized by NMR spectroscopy and GPC. The ^{1}H NMR spectrum of the material showed resonances at δ 5.55 and 6.1, which are characteristic of a methacrylate end group.[18] Corresponding ^{13}C NMR signals appeared at δ 127 and 138. Two-dimensional NMR experiments (HMBC, HSQC) proved the connectivity. The product is similar to that of the macromonomer that is formed by backbiting β-scission during high-temperature polymerization of butyl acrylate[26,27] or by copolymerization of butyl acrylate in the presence of a methacrylate and a catalytic chain transfer agent[59,60] The ratio unsaturated chain ends to phthalimide chain ends was estimated by integration of the ^{1}H NMR as ~6:10.

The GPC traces for a low molecular weight sample (6830 g mol^{-1} and $\bar{M}_w/\bar{M}_n$ 1.17) indicates some broadening of the molecular weight distribution to both higher and lower molecular weight and the formation of oligomeric products (Figure 11a). Thermolysis of a higher molecular weight PBA sample ($\bar{M}_n$ 23900 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.07) gave little change in overall molecular weight yet oligomer formation and development of a high molecular weight shoulder was clearly evident (overall $\bar{M}_n$ 20890 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.09, with the major component $\bar{M}_n$ 20900 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.08 and oligomer component $\bar{M}_n$ 1320 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.20) (Figure 11e). The intermediate samples (Figure 11b−d) show the same trend. A comparison of the peak molecular weight of the PBA before and after thermolysis is

Scheme 7. Thermolysis Mechanism



shown in Figure 12. The molecular weight distribution of the oligomer fraction appeared to be independent of the starting molecular weight of the PBA (Figure 11).

The behavior is clearly different from that observed for analogous polystyrene samples that are proposed to eliminate the trithiocarbonate group by a Chugaev mechanism.[4,12,18] The mechanism proposed for PBA thermolysis is shown in Scheme 7. The C−S bond of the PBA **18** undergoes homolysis to give a PBA propagating radical **19** and a byproduct which is likely to decompose to carbon disulfide and butanethiol under the thermolysis conditions. The propagating radical **19** then decays by intramolecular transfer and β-scission. This mechanism is analogous to that proposed for thermal degradation of PBA and other acrylate esters made by conventional radical polymerization at higher temperatures (304−370 °C).[61,62] Under those conditions, the propagating radical once formed unzips by a process thought to involve sequential backbiting and β-scission.[61,62] A process involving backbiting-β-scission has also been developed as a means of macromonomer synthesis.[26,27] In both thermal degradation and polymerization intramolecular backbiting appears to be strongly favored over intermolecular abstraction. It seems reasonable to expect the intramolecular process will also dominate under our thermolysis conditions. In polymerization, β-scission following backbiting strongly favors formation of the polymeric macromonomer (**21**) and a "dimer" radical (**22**, $m - n = 1$).[26,27] If β-scission from **19** ($n - m = 1$) takes the alternate pathway, the polymeric product will be a new PBA propagating radical with chain length shortened by three units (**20**) which can then decay by the same set of reactions and a "trimer" (**21**). Oligomers may result as a consequence of consecutive backbiting events (i.e., $n - m > 1$) followed by scission or oligomerization of the initially formed products. The high molecular weight shoulder may arise by coupling of the PBA propagating radicals formed by homolysis.

On the basis of this mechanism, we predict good end group purity. Analysis by ^{1}H NMR indicates between 65 and 90%. Thermolysis of RAFT-synthesized PBA may provide a route to relatively narrow polydispersity macromonomers **21**.

Xanthate Group Elimination from Poly(vinyl acetate). Thermolysis was also effective in cleaving the xanthate chain end from RAFT-synthesized PVAc ($\bar{M}_n$ 2300 g mol^{-1} and $\bar{M}_w/\bar{M}_n$ 1.24). However, after the sample was heated at 220 °C for 3 h, significant sample discoloration (sample turned brown) was observed. The GPC of the thermolysis product showed a substantial increase in molecular weight. The product had $\bar{M}_n$ 4250 g mol^{-1} and $\bar{M}_w/\bar{M}_n$ 1.70. The ^{1}H NMR spectrum showed the reduction of all signals associated with the xanthate end group to a level below detection (e.g. the signals "b" and "f" in Figure 13), a substantial increase in the signal attributed the methine of the head-to-head linkage [−C**H**(OCOCH$_3$)−C**H**(OCOCH$_3$)][63] and the appearance of a peak assigned to a macromonomer methylene [−C(OCOCH$_3$)(=C**H**$_2$)].[64,65] This is consistent with the thermolysis of PVAc, and loss of the xanthate end group, proceeding via a mechanism similar to that proposed for PBA and loss of the trithiocarbonate end group. Thus, it is proposed that the end group is lost by homolysis of the C−S bond to generate PVAc propagating radicals which may couple or decay by backbiting followed by β-scission.

Conclusion

RAFT polymerization with phthalimidomethyl trithiocarbonates provides a route to end-functional polymers of styrene,[12] BA, and NIPAM with narrow molecular weight distributions and predictable molecular weights. Use of the corresponding *S*-phthalimidomethyl xanthates as RAFT agents provides good control over polymerizations of both NVP and VAc. Thus, with

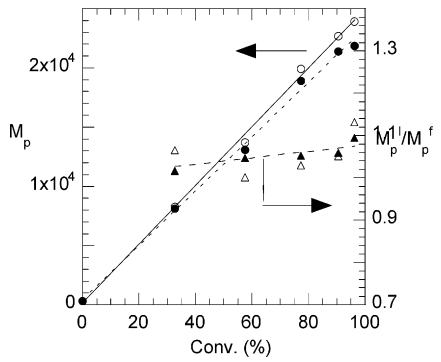


Figure 12. Comparison of peak molecular weights of poly(butyl acrylate) (**4**) synthesized in the presence of reversible addition fragmentation chain transfer (RAFT) agent **2**, before ($\bar{M}_p^i$) (○, —) and after ($\bar{M}_p^f$) (●, - - -) thermolysis and molecular weight ratios $\bar{M}_p^i/\bar{M}_p^f$ (▲, — — —) and $\bar{M}_w^i/\bar{M}_w^f$ (△).

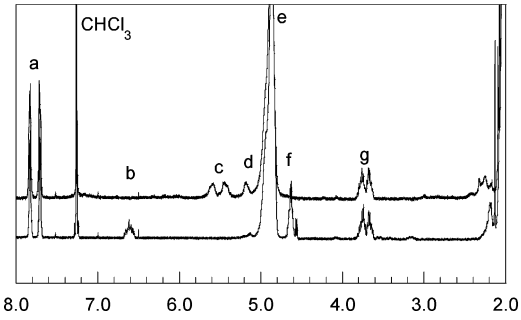


Figure 13. Region δ 2−8 of ^{1}H NMR spectra (400 MHz, $CDCl_3$) for VAc prepared at 60 °C with reversible addition fragmentation chain transfer (RAFT) agent **3** and azobis(isobutyronitrile) initiator and the thermolysis product (220 °C, 3 h, nitrogen). Signal assignments are as follows: a, phthalimide Ar−**H**; b, end group −C**H**SC(═S); c, −C(OCOCH$_3$)(═C**H**$_2$); d, head to head linkage −C**H**(OCOCH$_3$)−C**H**(OCOCH$_3$)−; e, backbone C**H**; f, xanthate −C(═S)OC**H**$_2$CH$_3$; g, end group −C**H**$_2$N<.

its ability to be a good homolytic leaving group and reinitiate a wide variety of polymerizations, the phthalimidomethyl radical performs as a universal "R" group in RAFT agents for use with monosubstituted monomers.

In the case of alkyl PBA trithiocarbonates, the C−S bond to the end group can be homolyzed by thermolysis at >200 °C leaving the phthalimidomethyl end group and the ester side groups intact providing a PBA macromonomer with ω end group −CH$_2$−C(CO$_2$C$_4$H$_9$)(═CH$_2$) as the major product. A similar mechanism appears to be operative in ethyl PVAc xanthate thermolysis. The observation of byproducts from radical−radical termination provides further support for the involvement of free radicals in the mechanism.

Determination of end group concentrations as a function of molecular weight for high conversion PBA prepared with RAFT agent **2** has provided evidence of the origin of bimodal molecular weight distributions. The data support the hypothesis that a high molecular weight shoulder on the molecular weight distribution arises by copolymerization of a PBA macromonomer formed during polymerization by a backbiting β-scission mechanism.

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