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RAFT Polymerization: Adding to the Picture

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SUMMARY: Factors affecting the choice of RAFT agent [RSC(Z) = S] for a given polymerization are discussed. For polymerization of methyl methacrylate (MMA), tertiary cyanoalkyl trithiocarbonates provide very good control over molecular weight and distribution and polymerizations show little retardation. The secondary trithiocarbonate RAFT agents with R = CHPh(CN) also gives good control but an inhibition period attributed to slow reinitiation is manifest. Radical induced reduction with hypophosphite salts provides a clean and convenient process for removal of thiocarbonylthio end groups of RAFT-synthesized polymers. Two methods providing simultaneous control over stereochemistry and molecular weight distribution of chains formed by radical polymerization are reported. Polymerization of MMA in the presence of scandium triflate provides a more isotactic PMMA. A similar RAFT polymerization with trithiocarbonate RAFT agents also provides control and avoids issues of RAFT agent instability seen with dithiobenzoate RAFT agents in the presence of Lewis acids. RAFT polymerization of tetramethylammonium methacrylate at 45 °C provides a more syndiotactic PMMA of controlled molecular weight and distribution (after methylation; *mm:mr:rr* 2:21:77 compared to 3:35:62 when formed by bulk polymerization of MMA).

Keywords: molecular weight; radical polymerization; RAFT agents; facticity

Introduction

Control of radical polymerization with the addition of thiocarbonylthio compounds that serve as reversible addition fragmentation chain transfer (RAFT) agents was first reported in 1998.[1,2] Since that time much research carried out in these laboratories and elsewhere has demonstrated that RAFT polymerization is an extremely versatile process.[3–5] It can be applied to form narrow polydispersity polymers or copolymers from most monomers amenable to radical polymerization. It is possible to take RAFT polymerizations to high conversion and achieve commercially acceptable polymerization rates. Polymerizations can be successfully carried out in heterogeneous media (emulsion, miniemulsion, suspension). There is compatibility with a wide range of functionality in monomers, solvents and initiators. Stars, blocks, microgel and hyperbranched structures, supramolecular assemblies and other complex architectures are accessible and can have high purity.

In this paper we add to the picture by describing how to choose RAFT agents for controlling methyl methacrylate polymerization, how to remove the thiocarbonylthio functionality from RAFT-synthesized polymers and how to use RAFT polymerization to achieve simultaneous control over molecular weight, molecular weight distribution and tacticity.

Choice of RAFT Agents

RAFT polymerization comprises the sequence of addition-fragmentation equilibria shown in Scheme 1.[1] Initiation and radical-radical termination occur as in conventional radical polymerization. In the early

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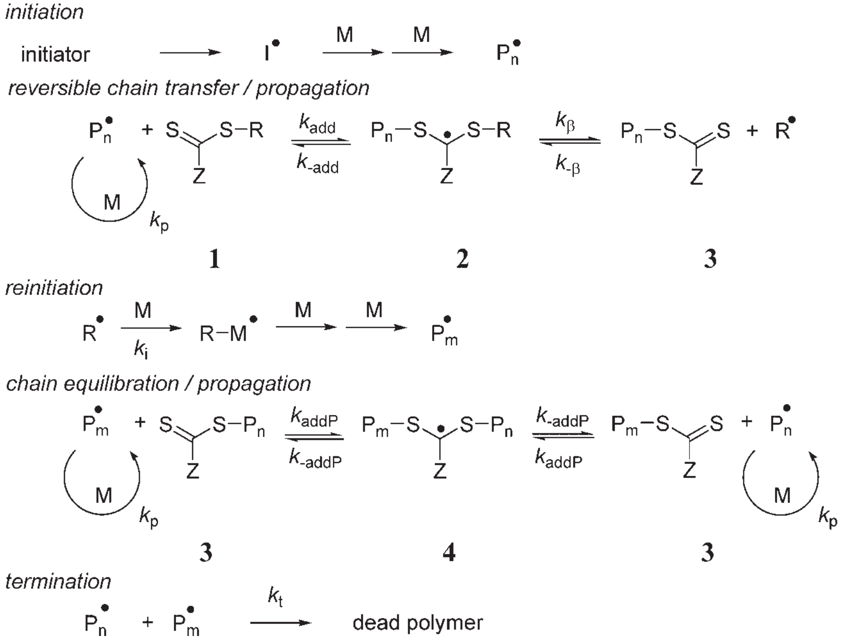


Scheme 1.
Mechanism of RAFT polymerization.

stages of the polymerization, addition of a propagating radical ($P_n^\bullet$) to the thiocarbonylthio compound [RSC(Z) = S (**1**)] followed by fragmentation of the intermediate radical provides a polymeric thiocarbonylthio compound [$P_nS(Z)C=S$ (**3**)] and a new radical (R●). Reaction of this radical (R●) with monomer forms a new propagating radical ($P_m^\bullet$). Rapid equilibrium between the active propagating radicals ($P_n^\bullet$ and $P_m^\bullet$) and the dormant polymeric thiocarbonylthio compounds (**3**) provides equal probability for all chains to grow and allows for the production of narrow polydispersity polymers. When the polymerization is complete (or stopped), the vast majority of chains retain the thiocarbonylthio end group and can be isolated as stable materials. The reactions associated with RAFT equilibria shown in Scheme 1 are in addition to those (*i.e.* initiation, propagation and termination) that occur during conventional radical polymerization. In an ideal RAFT process, the RAFT agent should behave as an ideal transfer agent. Thus, as with radical polymerization with conventional chain transfer, the kinetics of polymerization should not be directly influenced beyond those affects attributable to the differing molecular weights of the reacting species. Radical-radical termination is not directly suppressed by the RAFT process. Living characteristics are imparted when the molecular weight of the polymer formed is substantially lower than that which might be formed in the absence of a RAFT agent and the number of polymer molecules with RAFT agent-derived ends far exceeds the number formed as a consequence of termination.

A wide variety of thiocarbonylthio RAFT agents (ZC(=S)SR, **1**) have now been reported. A broad summary of these and the factors which influence choice of RAFT agent for a particular polymerization is presented in recent reviews.[3,6] The effectiveness of the RAFT agent depends on the monomer being polymerized and is determined by the properties of the free radical leaving group R and the group Z which can be chosen to activate or deactivate the thiocarbonyl double bond of the

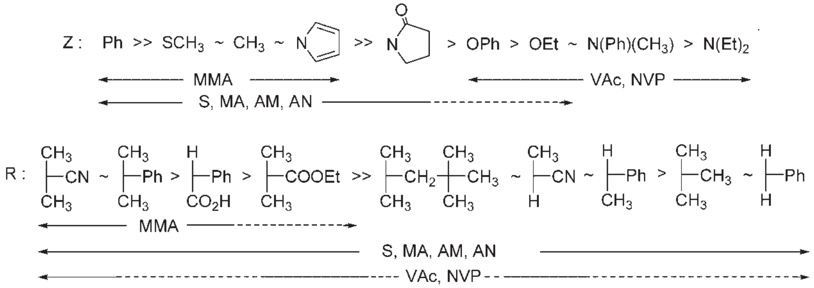


Figure 1.
Guidelines for selection of RAFT agents for various polymerizations.[3] For Z, addition rates decrease and fragmentation rates increase from left to right. For R, fragmentation rates decrease from left to right. Dashed line indicates partial control (*i.e.* control of molecular weight but poor polydispersity or substantial retardation in the case of VAc).

RAFT agent (**1**) and modify the stability of the intermediate radicals (**2**) and (**4**).

Figure 1, taken from our recent review,[3] provides a general summary of how to select the appropriate RAFT agent for particular monomers. Note should be made of the dashed lines in the chart. Although some control might be achieved with these monomer RAFT agent combinations, the molecular weight distribution may be broad or there may be substantial retardation or prolonged inhibition.

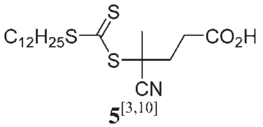
Trithiocarbonate RAFT Agents

The utility of trithiocarbonate RAFT agents was disclosed in the first RAFT patent[2] and many papers now describe their application.[3,7–12] Some of the desirable structural features of non-symmetrical trithiocarbonate RAFT agents are summarized below with reference to RAFT agent **5**.

Unsymmetrical primary and secondary trithiocarbonate RAFT agents are readily synthesized from a thiolate anion, carbon disulfide and an alkyl halide.[3]

Radical-induced decomposition of a bis (thioacyl) disulfide (e.g. Scheme 3).[10,13–16] is probably the most used method for the synthesis of RAFT agents requiring tertiary R groups. It is also possible to use this chemistry to generate a RAFT agent *in situ* during polymerization.[13]

Ideally, to avoid odor issues with the RAFT agent and polymer the 'Z', and preferably the 'R(S)' groups, should be based on non-volatile thiols (*e.g.* dodecanethiol for Z in **5**). RAFT agents of this type already described in the literature include



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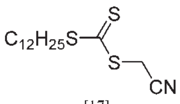

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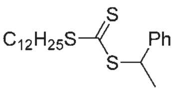
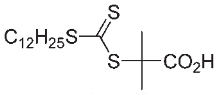
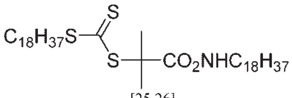


7[11,18,19]



8 [9,20-24]



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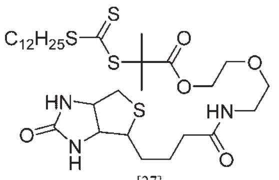

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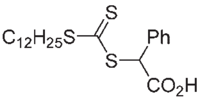

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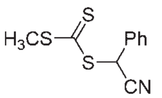

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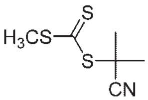

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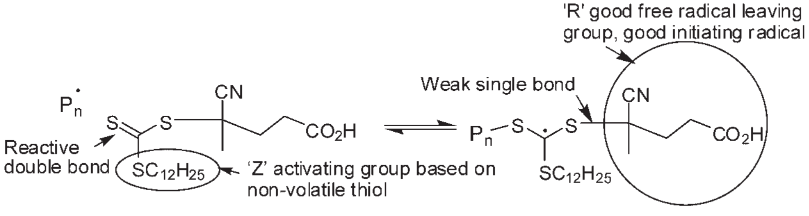

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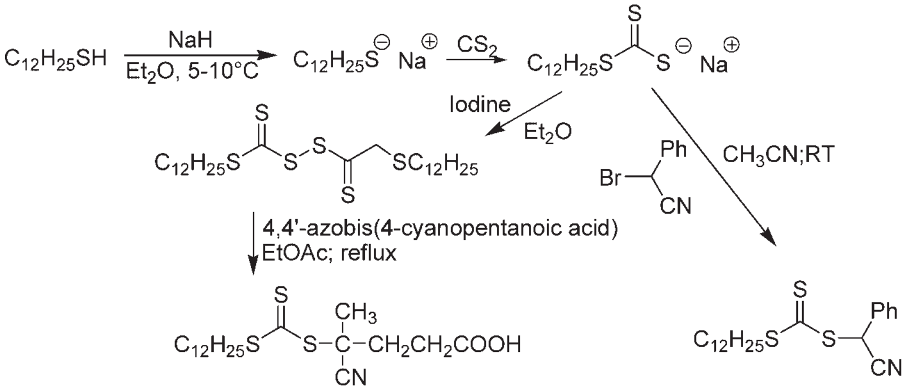
Scheme 2.

(**5**–**10**). RAFT agents based on volatile thiols (e.g. **12**, **13**) can be odorous.

Previous work[3] has shown that tertiary (cumyl, cyanoalkyl) dithiobenzoates and trithiocarbonates provide PMMA and other methacrylic polymers with narrow molecular weight distributions. Primary and secondary trithiocarbonates are more readily synthesized but while they may be used to control copolymerization of methacrylic monomers they are not effective in providing living characteristics to their homopolymerization. Recently, secondary aromatic dithioesters with R = –CHPh(CN)[28] or –CHPh(CO_2alkyl)[29,30] have been reported as RAFT agents for polymerization of methacrylate esters. We have observed that trithiocarbonates with R = –CHPh(CO_2H) (**11**) or –CHPh(CN) (**12**,[4]**14**) have utility in controlling polymerization of methacrylates. Results of MMA polymerizations at 90 °C with dithiobenzoate (**16**) and dodecyl trithiocarbonates (**5**), (**11**) and (**16**) are compared in Table 1 and Figure 2. The tertiary cyanoalkyl trithiocarbonate (**5**) appears almost as effective as cyanoisopropyl dithiobenzoate (**16**). Trithiocarbonate (**14**) also provides narrow molecular weight distributions (Table 1). However, an inhibition period is observed which is attributed to slow reinitiation by the CHPh(CN) radical. An inhibition period was also reported for with the corresponding dithiobenzoate (**15**) which has the same 'R' group.[28] The Trithiocarbonate (**11**) with secondary R [–CHPh(CO_2H)] provides a degree of control and no retardation or inhibition period is evident (Table 1). Higher than predicted molecular weights for low monomer



5 **14**

Scheme 3.[3]

Table 1.
Results for RAFT polymerizations of MMA at 90 °C[a]

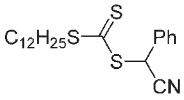
Time (h)	RAFT Agent											
	16[32]			**5**[10]			**11**			**14**		
	Conv (%)	$\overline{M}_n$[b] g mol^{-1}	$\overline{M}_w/\overline{M}_n$	Conv (%)	$\overline{M}_n$[b] g mol^{-1}	$\overline{M}_w/\overline{M}_n$	Conv (%)	$\overline{M}_n$[b] g mol^{-1}	$\overline{M}_w/\overline{M}_n$	Conv (%)	$\overline{M}_n$[b] g mol^{-1}	$\overline{M}_w/\overline{M}_n$
1	18	9400	1.28	16	9400	1.42	21	34000	1.70	3	1600	1.44
2	28	15900	1.15	27	12800	1.24	32	35100	1.65	7	3500	1.44
4	47	24200	1.11	48	25300	1.13	53	38100	1.56	23	11000	1.20
16	98	52500	1.09	100	50300	1.09	100	52900	1.33	90[c]	44300	1.06

[a] RAFT polymerizations of MMA (6.55 M in benzene) at 90 °C with RAFT agent (0.011 M) and azobis(cyclohexanenitrile) (0.0018 M) as initiator. Reaction mixtures degassed by three freeze-evacuation-thaw cycles. Polymer isolated by evaporation on monomer.

[b] GPC Molecular weights in polystyrene equivalents.

[c] 8 h polymerization time.

conversions is indicative of incomplete usage of RAFT agent and therefore of a low transfer constant.



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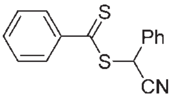

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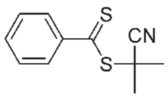


16[1,16,31]

End Group Removal by Radical-Induced Reduction

A key feature of the RAFT process is that the thiocarbonylthio groups, present in the initial RAFT agent, are retained in the polymeric product(s). This makes the process eminently suitable for synthesizing block copolymers and end functional polymers. It means that the polymeric products are themselves RAFT agents. However, in some circumstances, it is also necessary or desirable to deactivate thiocarbonylthio groups because of their reactivity or to

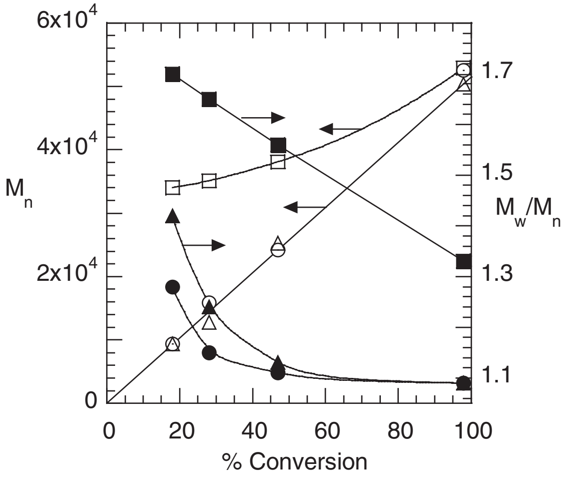
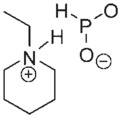


Figure 2.
Evolution of number average molecular weight ($\overline{M}_n$) (open symbols) and polydispersity ($\overline{M}_w/\overline{M}_n$) (closed symbols) with conversion for polymerization of methyl methacrylate (6.55 M in benzene) at 90 °C in the presence of dithiobenzoate **16** (●,—), trithiocarbonate **5** (▲,—), and trithiocarbonate **11** (■,—) with RAFT agent (0.011 M) and azobis(cyclohexanenitrile) (0.0018 M). Lines are lines of best fit through data points.

transform them for use in subsequent processing.

Thermolysis[10–12,33–35] and radical-induced reactions (such as reduction[10,11,36,37] or termination[11,38]) offer a solution and can provide complete desulfurization. Radical-induced reduction of low molecular weight thiocarbonylthio compounds is well known.[39] Radical-induced reduction of xanthates is the basis of the Barton- McCombie reaction for deoxygenation of secondary alcohols.[40–42] Stannanes are the most efficient reagents for use in this process but are toxic and residual reagent and the devived reaction bydroducts can be difficult to remove. Hypophosphite salts,[43–45] including *N*-ethylpiperidine hypophosphite (**17**),[45] have been recommended as an alternative to stannanes in the radical induced reductions.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Radical-induced reduction has also been shown to be applicable to end group removal for RAFT-synthesized polymers.[10,11,36,37] Successful radical-induced reductions with tributylstannane of poly(acenaphthalene)[36,37] or polystyrene[10,11] prepared with dithiobenzoate or trithiocarbonate RAFT agents respectively have been reported. However, residual stannane and derived byproducts can be difficult to remove and the process is unlikely to be industrially acceptable because of the toxicity of tin compounds. The use of less active H-atom donors (*e.g.* isopropanol,[46] silanes[11]) has been reported but these reagents are not always appropriate since coupling of propagating radicals and other side reactions may then compete with H-atom transfer. There is also reference in the patent literature to end group modification by radical-induced processes.[47–49]

We have found that thiocarbonylthio groups of polymers made by RAFT polymerization can be replaced by hydrogen by radical-induced reduction with hypophosphite salts, in particular, *N*-ethylpiperidine hypophosphite.[17,49] Hypophosphite salts are substantially more effective than H-donor solvents such as toluene or isopropanol. The outstanding feature of the hypophosphite salts is that they, and the bydroducts formed in the process, are water soluble and can be removed from the polymer by a simple water wash. GPC traces for poly(butyl acrylate), PMMA and polystyrene prepared with dodecyl trithiocarbonate end groups before/after reduction are shown in Figure 3.

The efficiency of radical induced reduction with the H-donors studied[17] increases in the series toluene $\ll$ isopropanol $<$ triethylsilane $<$ triphenylsilane $\ll$ tris(trimethylsilyl)silane $\sim$*N*-ethylpiperidine hypophosphite $<$ tributylstannane. The end groups of the (meth)acrylic polymers are more readily reduced than those of polystyrene which is in accordance with their known activity in other contexts.[39] Slightly longer reaction times or higher reaction temperatures were required for complete end group removal. The GPC of polystyrene post reduction shows a small high molecular weight shoulder which is attributed to coupling of polystyrene propagating radicals (Figure 3).

RAFT Polymerization in the Presence of Lewis Acids

Simultaneous control of stereosequence and molecular weight distribution has long been one of the 'holy grails' in the field of radical polymerization. Nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and RAFT all offer control over molecular weight distribution. However, polymers produced by these methods show similar tacticity to those obtained by the conventional process. Recently there have been reports of tacticity control of homopolymers[50–53] (which enables the synthesis of stereoblock copolymers[54]) and control of the alternating tendency for copolymerizations[55,56] in ATRP or RAFT polymerization through the use of Lewis acids as additives.

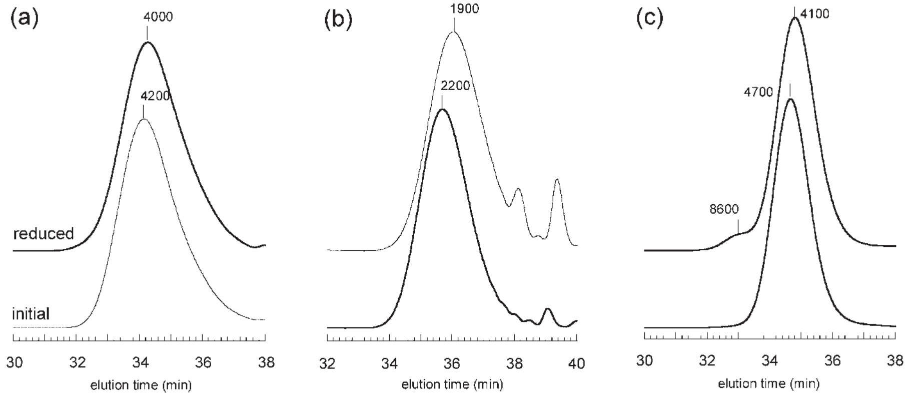
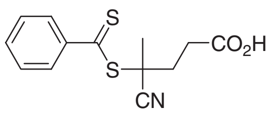


Figure 3.
GPC chromatograms for (a) poly(methyl methacrylate) (PMMA), (b) poly(butyl acrylate) (PBA) and (c) polystyrene (PS) prepared with dodecyl trithiocarbonate end groups and the products of their reduction with *N*-ethylpiperidine hypophosphite (**17**) and azobis(cyclohexanenitrile) (ACHN). Peak molecular weights are indicated on the chromatograms.[17] Conditions: (a) [PMMA] 0.05 M, [**17**] 0.25 M, [ACHN] 0.016 M degassed, heated 100 °C/2h; (b) [PBA] 0.05 M, [**17**] 0.42 M, [ACHN] 0.021 M, degassed, heated 100 °C/2h; (c) [PS] 0.05 M, [**17**] 1.0 M, [ACHN] 0.02 M, degassed, heated 110 °C/4h.

However, efforts in this area, particularly those directed towards MMA polymerization, have met with mixed success.

For MMA polymerization, the addition of a Lewis acid, specifically scandium triflate [$Sc(OTf)_3$], is known to increase the fraction of isotactic triads and enhance the rate of polymerization. Similar stereocontrol was observed for RAFT polymerization with cumyl dithiobenzoate and $Sc(OTf)_3$.[57] However, these RAFT polymerizations gave only poor control over molecular weight and polydispersity.[51] Our NMR analyses confirm that the poor results might be attributed to the Lewis acid catalyzed degradation of the dithiobenzoate RAFT agents.[3] It is known from other work that dithiobenzoates are more prone to hydrolysis than, for example, trithiocarbonates or aliphatic dithioesters.[58–60] We have found that trithiocarbonate RAFT agents are also substantially more stable than dithiobenzoates in the presence of Lewis acids. Thus, polymerizations with the trithiocarbonate RAFT agent (**13**) provided polymer with a relatively narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n <$ 1.3 at >95% conversion) as well as the expected enhancement in the fraction of isotactic triads and the rate of polymerization (Table 2). Molecular weights are slightly higher than calculated, the discrepancy increasing at higher $Sc(OTf)_3$ concentrations.



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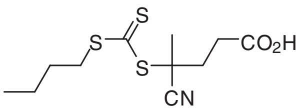

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RAFT Polymerization of Methacrylate Salts

It has been reported that low temperature photopolymerization of tetraalkylammonium methacrylate salts in water provides a highly syndiotactic polymer.[61]

Table 2.
Effect of scandium triflate [Sc(OTf)$_3$] concentration on RAFT polymerization of MMA with methyl cyanoisopropyl trithiocarbonate (**13**) and azobis(isobutyronitrile) initiator at 60 °C.[a]

[MMA]: [Sc(OTf)$_3$][b]	time (h)[c]	conv %	$\overline{M}_n$[d](g mol^{-1})	$\overline{M}_n$ (theor.) (g mol^{-1})	$\overline{M}_w/\overline{M}_n$	*mm*	*mr*	*rr*	*m*
Control[e]	8	50	33900	33914	1.17	4	33	63	21
Control[e]	16	98	61000	66471	1.08	4	33	63	21
34:1	4	44	32000	29844	1.26	5	36	59	23
34:1	8	94	63600	63758	1.12	6	39	55	26
16:1	2	43	35000	29166	1.35	7	39	54	27
16:1	6	86	69000	58332	1.22	7	38	55	26
8.5:1	1	26	32300	17635	1.61	7	38	55	26
8.5:1	4	87	78900	59010	1.31	12	44	44	34

[a] [**13**] = 0.106 M, [AIBN] 0.0061 M.
[b] Mole ratio.
[c] Reactions times were chosen to provide ~50 and >90% conversion.
[d] Molecular weight are in polystyrene equivalents.
[e] Control experiment without scandium triflate.

Polymerization of tetramethylammonium methacrylate was carried out in water at 45 °C in the presence of the water soluble dithiobenzoate RAFT agent **18** and with 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (Wako VA-044) initiator. Methylation of the resultant poly(tetramethylammonium methacrylate) with excess methyl iodide provided PMMA with $\overline{M}_n$ 8200, $\overline{M}_w/\overline{M}_n$ 1.17 and *mm:mr:rr* 2:21:77 compared to poly(methacrylic acid) under similar conditions with *mm:mr:rr* 3:34:63 (this is similar to PMMA obtained by bulk polymerization for which *mm:mr:rr* 3:35:62). Polymerization of salts (Na, K, Cs) methacrylic acid with inorganic counterions also gave a more syndiotactic polymer though the effect appears smaller (Table 3). The enhanced syndiotacticity has been attributed to the mutual repulsion between carboxylate groups favoring alternation in configuration (Figure 5).[61]

Conclusions

RAFT agents have been compared for their ability to control MMA polymerization. Tertiary cyanoalkyl trithiocarbonates provide very good control over molecular weight and distribution and there is little retardation. The secondary trithiocarbonate RAFT agent with R = –CHPh(CN) also provides good control but a prolonged inhibition period attributed to slow reinitiation is manifest. The trithiocarbonate

Table 3.
Molecular weight and tacticity of poly(methyl methacrylate) formed by RAFT polymerization of methacrylic acid and salts.

Base	RAFT agent	[RAFT]:[MAA]	Conv %	$\overline{M}_n$[a] g mol^{-1}	$\overline{M}_w/\overline{M}_n$	*mm*	*mr*	*rr*	*m*
$(CH_3)_4NOH$[b),c)]	**19**	0.0050	97	20000	1.11	1	25	74	14
NaOH[b),c)]	**19**	0.0050	99	21200	1.11	2	24	75	14
KOH[b),c)]	**19**	0.0050	99	20000	1.09	3	27	69	16
CsOH[b),c)]	**19**	0.0050	98	20400	1.09	2	26	72	15
none[b]	**19**	0.0050	99	20600	1.07	3	34	63	19
none[b]	none	–	100	745000	2.24	4	33	64	20
$(CH_3)_4NOH$[d]	**18**	0.00724[d]	58	8200	1.17	2	21	77	13

[a] Molecular weight are in polystyrene equivalents.
[b] Polymerization of methacrylic acid or salt (33% w/w) in water at 45 °C for 16 h with 2,2′-azobis[2-(2-imidazolin-2-yl)propane] initiator (0.00063% w/w).
[c] The salt was formed in situ by neutralization with one molar equivalent of the indicated base (Experimental Part - procedure b).
[d] Polymerization of preprepared tetramethylammonium methacrylate (~25% w/v) in water at 45 °C for 16 h (Experimental Part - procedure a).

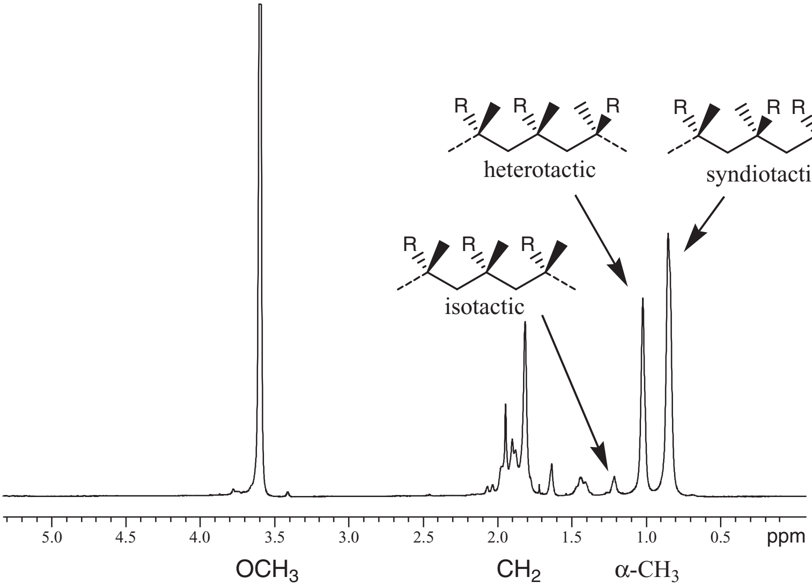

Figure 4.
400 MHz ^{1}H NMR spectrum of poly(methyl methacrylate) indicating triad assignments for resonances attributable to the hydrogens of the α-methyl group ($R = CO_2CH_3$).

RAFT agents with $R = –CHPh(CO_2H)$ give poor control and no inhibition period.

Radical induced reduction with hypophosphite salts provides a clean and convenient process for removal of thiocarbonylthio end groups of RAFT-synthesized polymers.

Two methods offering simultaneous control over both molecular weight and polymer chain stereochemistry are reported. RAFT polymerization of MMA with trithiocarbonate RAFT agents and added scandium triflate provides a more isotactic PMMA. RAFT polymerization of tetramethylammonium methacrylate at 45 °C provides a more syndiotactic PMMA.

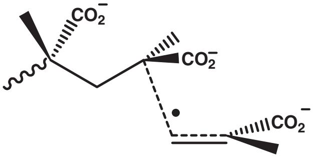

Figure 5.
Schematic representation of the transition state for poly(tetramethylammonium methacrylate) propagating radical adding to tetramethylammonium methacrylate leading to a syndiotactic chain (counter ion not shown).

Experimental Part

Solvents were of AR grade and were distilled before use. Azobisisobutyronitrile (AIBN, Vazo-64) and azobis(cyclohexanenitrile) (ACHN, Vazo-88) were obtained from DuPont and purified by crystallization from chloroform/methanol, 2,2′-azobis[2-(2-imidazolin-2-yl)propane] (Wako VA-044) was used as received. Monomers were purified by filtration through neutral alumina (70–230 mesh) to remove inhibitors and flash distilled immediately prior to use. The syntheses of RAFT agents **5**,[10]**16**[31] and **13**[16] are decribed elsewhere. RAFT agent **19** was synthesized by a procedure analogous to that used for synthesis of **5**.[10] Gel permeation chromatography (GPC) was performed on a Waters Associates liquid chromatograph equipped with differential refractometer and 3 × Mixed C and 1 mixed E PLgel column (each 7.5 mm × 30 mm) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 22 ± 2 °C and the columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories). Nuclear magnetic resonance spectra (NMR) were obtained with a Bruker AC200 or AC400 spectrometer. Chemical shifts are reported in ppm from external tetramethylsilane.

2-(Dodecylthiocarbonothioylthio)-2-phenylacetic Acid (11)

2-Bromo-2-phenylacetic acid (Aldrich, 98%) (2.17 g, 0.01 mol) was added to a stirred suspension of sodium dodecyl trithiocarbonate[10] (3.06 g, 0.01 mol) in diethyl ether (100 mL). The reaction mixture was then stirred at room temperature for 1 h. Water was added and the organic layer separated, extracted twice with water, dried over anhydrous magnesium sulfate and evaporated to leave a residue which was chromatographed on silica gel eluting with 3:7 ethyl acetate:*n*-hexane. The yield of yellow solid (**11**) was 2.9 g (70%) m.p. 60.5–61.5 °C. ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H, CH_3); 1.3 (br s, 18H); 1.7 (m, 2H, CH_2); 3.35 (t, 3H, CH_2); 5.9 (s, 1H, CH), 7.3–7.5 (m, 5H, ArH).

2-(Dodecylthiocarbonothioylthio)-2-phenylacetonitrile (*14*)

2-Bromo-2-phenylacetonitrile was prepared by bromination reaction of phenylacetonitrile with *N*-bromosuccinimide in carbon tetrachloride in the presence of AIBN. Thus, *N*-bromosuccinimide (5.3 g, 0.03 mol) and AIBN (100 mg) was added to a stirred solution of phenylacetonitrile (2.9 g, 0.025 mol) in carbon tetrachloride (50 mL) and the resultant solution heated to reflux. After 24 hours, the solution was cooled, filtered to remove the precipitated succinimide and the filtrate concentrated on a rotary evaporator. The residue was purified by silica gel column chromatography with 3:97 ethyl acetate:*n*-hexane as eluent to afford the 2-bromo-2-phenylacetonitrile as a colourless oil (3.1 g, 64%). ^{1}H-NMR ($CDCl_3$) δ 5.5 (s, 1H, CH); 7.3–7.6 (m, 5H, ArH).

2-Bromo-2-phenylacetonitrile (1 g, 0.0051 mol) was added to a stirred suspension of sodium dodecyl trithiocarbonate[10] (1.54 g, 0.0051 mol) in acetonitrile (10 mL). The reaction mixture was then stirred at room temperature for 1 h. Water (20 mL) was then added, the mixture extracted with ethyl acetate and the organic layer separated, dried over anhydrous magnesium sulfate and evaporated to leave a residue which was chromatographed on silica gel eluting with 4:96 ethyl acetate:*n*-hexane to provide **14** as a yellow oil that solidified during storage at −15 °C (1.65 g, 82%) ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H, CH_3); 1.3 (br s, 18H); 1.7 (m, 2H, $C\mathbf{H}_2CH_2S$); 3.4 (t, 3H, CH_2S); 6.2 (s, 1H, CH), 7.3-7.6 (m, 5H, ArH).

RAFT Polymerization of MMA

Procedures for RAFT polymerization have been described previously.[10,32] Conditions used are provided in the footnote to Table 1.

Radical-Induced Reduction with (17)

A mixture of PMMA ($\overline{M}_n$ 3400, $\overline{M}_w/\overline{M}_n$ 1.18, prepared with RAFT agent **5**, 170 mg), *N*-ethylpiperidine hypophosphite (45 mg) and ACHN (4 mg) in toluene (1 mL) was degassed and heated at 100 °C for 2 hrs. The solution was extracted with water and the toluene removed to give a colorless polymer $\overline{M}_n$ 3380, $\overline{M}_w/\overline{M}_n$ 1.16. The ^{1}H NMR spectrum of the product showed that the signals attributable to the dodecyl trithiocarbonate end group were no longer present. A similar procedure was used for other reductions. Details are provided in the legend to Figure 3.

RAFT Polymerization of MMA in the Presence of Scandium Triflate

The following procedure is typical. Aliquots (0.5 mL) of stock solution comprising MMA (7.5 mL), AIBN (11 mg), *S*-methyl-*S*-cyanoisopropyl trithiocarbonate (0.023 g) and benzene (2.5 mL) from the control experiment were transferred to ampoules containing scandium triflate (0.05g), degassed with three freeze-evacuate-thaw cycles and sealed. The ampoules were heated at 60 ± 1 °C in a thermostatted oil bath for the appropriate time. Conversions were determined by ascertaining the residual MMA in the reaction mixture by ^{1}H NMR. The excess monomer and solvent removed by evaporation at ambient temperature under vacuum and the residues were analyzed directly by GPC. Samples were then further purified by precipitation into methanol before NMR analysis. Triad distributions from ^{1}H NMR analysis are provided in Table 2.

RAFT Polymerization of Tetramethylammonium Methacrylate

Tetramethylammonium methacrylate is readily prepared by neutralisation of methacrylic acid with tetramethylammonium hydroxide. It is critical not to use an excess of base in this process because of the hydrolytic sensitivity of the RAFT agent. The purity of the tetramethylammonium hydroxide is also important. Polymerizations of other methacrylate salts (Na, K, Cs) were carried out using procedure (b).

(a) Polymerization of Tetramethylammonium Methacrylate

A stock solution comprising tetramethylammonium methacrylate (5g, 0.0314 mol), 2,2′-azobis(*N,N*′dimethyleneisobutyramidine) dihydrochloride (15mg, 4.64×10^{-5} mol) was prepared and made up to 20 mL with water. A reaction vessel was charged with the above stock solution (13.8 mL; 0.0217 mol of tetramethylammonium methacrylate), 4-cyano-4-(thiobenzoyl)sulfanylpentanoic acid (**18**) (43.8 mg, 1.57×10^{-4} mol) and methanol (1 mL), degassed by three freeze-evacuate-thaw cycles, sealed and heated under vacuum at 45°C for 44 hours. The vessel was opened, the water and methanol evaporated under vacuum. The residue was dissolved in methanol (15 mL) and an excess of methyl iodide (5 mL) added and the mixture stirred overnight at ambient temperature (~22 °C). Water was then added, the mixture extracted with chloroform and the extract dried over sodium sulfate. Evaporation of the solvent gave PMMA (1.25 g, 58% conversion). $\overline{M}_n$ 8,200; $\overline{M}_w/\overline{M}_n$ 1.17. ^{1}H NMR analysis indicated a triad distribution of *mm:mr:rr* 2:21:77.

(b) Polymerization with in situ Neutralization of Methacrylic Acid

A mixture of methacrylic acid (1.0g, 0.012 mol), tetramethylammonium hydroxide (2.11g, 0.012 mol), 2,2′-azobis(N, N′dimethyleneisobutyramidine) dihydrochloride (1.9 mg, 5.9×10^{-6} mol) , RAFT agent **19** (16.9 mg, 5.8×10^{-5} mol) and deionised water (2.0 g) was degassed by three freeze-evacuate- thaw cycles, sealed and heated under vacuum at 45 °C for 16 hours. The vessel was opened and the conversion of the monomer was 97% as determined by ^{1}H-NMR. The solution was then acidified by addition of excess aqueous HCl and dried under vacuum. The residue was dis–solved in methanol (15 mL) and an excess of diazomethane in diethyl ether added and the mixture stirred overnight at ambient temperature. Water was then added, the mixture extracted with chloroform and the extract dried over sodium sulphate. Evaporation of the solvent gave PMMA $\overline{M}_n$ 20,000; $\overline{M}_w/\overline{M}_n$ 1.11. ^{1}H NMR analysis indicated a triad distribution of *mm:mr:rr* 1:25:74.

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