Functional Polymers from Novel Carboxyl-Terminated Trithiocarbonates as Highly Efficient RAFT Agents

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Introduction. Recent development of controlled radical polymerization leads to the synthesis of many well-defined architectures with predictable molecular weights. The most important methodologies reported include reversible addition−fragmentation transfer[1] (RAFT) polymerization, atom transfer radical polymerization[2] (ATRP), and nitroxide-mediated radical polymerization.[3] Among them, RAFT has arguably the most important commercial significance because it only involves organic substances and works very well with most acrylic derivatives, including acrylic acid.

RAFT, however, has some shortcomings of its own. To be effective, RAFT agents have to carry a good leaving group that is attached to the S atom(s).[4] These compounds are difficult to synthesize.[5,6] They would suffer from either low yields or the handling of dangerous chemicals such as Grignard reagents. The most promising products are usually liquids which are difficult to purify in order to remove the impurities associated with strong mercaptan odor. Another drawback is the difficulty to introduce functional groups on the RAFT agents without elaborate procedures.

Polymers bearing functional groups are highly sought after. In radical polymerizations the end functional groups are usually originated from initiators or transfer agents.[7] High functionalities are not easily achieved, especially when telechelic polymers are desired, as they are often at the mercy of how efficient the functionalized polymer chain radicals can recombine themselves. In reality, chain transfer to solvent molecules or monomers in addition to disproportionation will always occur. The chain lengths in those polymers are usually not very uniform, resulting in wide molecular weight distributions (high polydispersities).

In this paper we would like to report an easy synthesis of carboxyl-terminated trithiocarbonates. These trithiocarbonates have extremely high chain-transfer efficiency and control over the radical polymerization because the carbon attached to the labile sulfur atom is tertiary and bears a radical-stabilizing carboxyl group. Telechelic carboxyl-terminated polymers are easily obtained when dicarboxyl trithiocarbonate is employed. Bulk or solution polymerizations of alkyl acrylates, acrylic acid, and styrene are well-controlled. Some disproportionation at chain ends are observed with methyl methacrylate. Well-defined block copolymers can also be synthesized.

Results and Discussion. We found that when carbon disulfide is reacted with hydroxide ions, followed by alkylation with chloroform and acetone in a phase-transfer catalyzed (PTC) reaction, the *S,S*′-bis(α,α′-dimethylacetic acid) trithiocarbonate, **1**, is isolated in very good yield after acidification. With simple purification, the yellow crystalline solid carries a low or no mercaptan odor. Similarly, when 1 equiv each of alkyl mercaptan and carbon disulfide are reacted with hydroxide ions, followed by chloroform and acetone, and then acidification, the monocarboxyl-terminated trithiocarbonate derivative, **2**, is obtained in high yield. Since the dodecyl derivative of **2** (R = $C_{12}H_{25}$) is crystalline and easily purified, it is used entirely in this study. These reactions are an extension of our ketoform reaction methodology to synthesize hindered molecules.[8] Their scope and mechanism will be discussed elsewhere.

Both **1** and **2** are very efficient chain-transfer RAFT agents, due to the carboxyl-stabilized tertiary carbon radical produced when the carbon−sulfur single bond is broken during polymerizations. None of the polymers synthesized from **1** or **2** have any mercaptan odor. The polymerization can be initiated thermally or more practically at much lower temperatures with a small amount of a known initiator such as AIBN, usually in the amount of less than 3 mol % equivalent of **1** or **2**. Carboxyl-terminated azo-initiator ACVA (4,4′-azobis(4-cyanovaleric acid)) can be used to add to the end-functionality. The end-functionalities are very high as evidenced by MALDI and H NMR spectra. In the latter, the hydrogen atom on the carbon right next to the sulfur has a chemical shift at around 4.6 ppm downfield from TMS.[1] The ratio of the peak integration of that proton to that of the carboxylic acid proton at the polymer end is always found to be equal or very close (within 4%) to one. When percent conversion and M_n are plotted against each other, the result is always close to a straight line. The polydispersity is usually close to 1.1, when the monomers are alkyl acrylates, acrylic acid, and styrene. Block copolymers are easily made by polymerizing the first monomer, removing residual monomers if less than 95% converted, followed by chain extension with the second monomer. Their structures are confirmed by the progress of the GPC curves and MALDI spectra.

We have found that most common solvents would work with the controlled polymerization. *tert*-Butyl alcohol, acetone, methyl ethyl ketone, toluene, xylene, water (for acrylic acid), and DMF are all suitable solvents. Bulk polymerizations are also successful. Methyl methacrylate gives polymers with higher polydispersities due to some disproportionation at the polymer chain ends, as indicated by MALDI spectra. Lower temperatures seem to help control that polymerization better. Table 1 and Table 2 demonstrate some of the polymers and block copolymers prepared with radical polymerizations as mediated by RAFT agents **1** or **2**.

Experimental Section. All monomers are purchased from Aldrich Chemicals. All other chemicals are purchased from Aldrich or Acros. NMR spectra are recorded on a Bruker WH-200 spectrometer. Infrared spectra are plotted on a Nicolet MX-1 FT spectrometer. Mass spectra were obtained from a Finnigan MAT spectrometer. MALDI spectra were acquired from University of Akron on a Bruker Reflex III MALDI−TOF mass spectrometer. Gel permeation chromatography (GPC) was carried out using a Waters model 510 pump and a model 410 refractive index detector. The columns are a PLgel guard 5 m 50 × 7.5 mm, followed by two Plgel mixed-C 10 m 300 × 7.5 mm columns at 50 °C. Tetrahydrofuran is used as eluent, and calibration is

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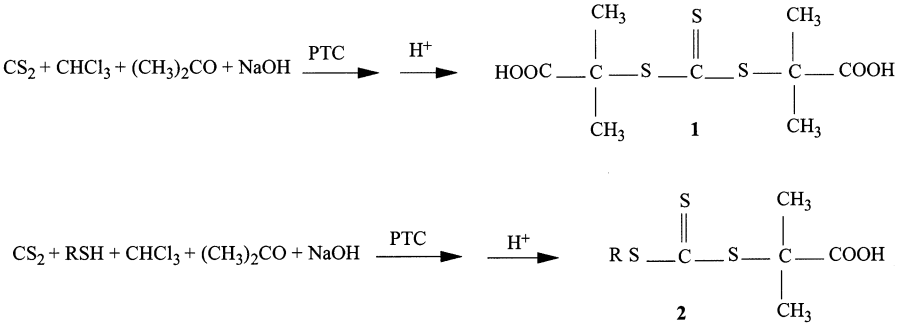
Scheme 1. Synthesis of Carboxyl-Terminated Trithiocarbonates



Scheme 2. Polymerization with Carboxyl-Terminated Trithiocarbonates

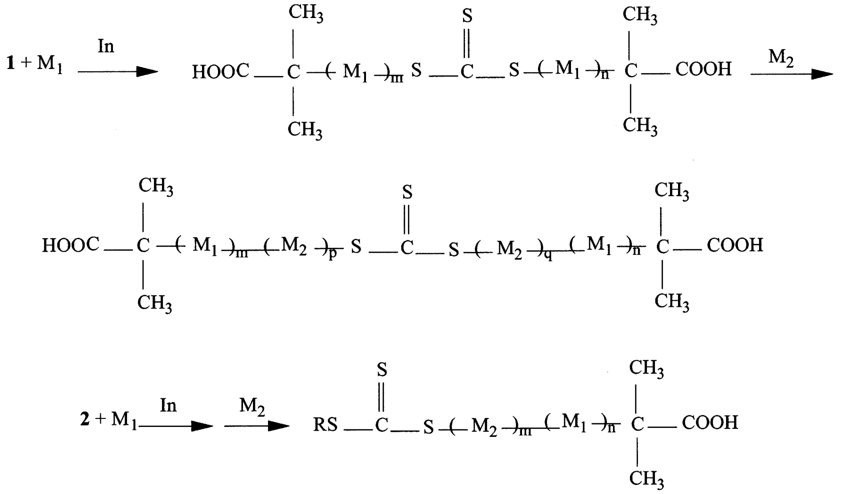


Table 1. Polymerizations with 1 or 2

monomer[a] (g)	solvent[b] (mL)	**1** or **2** (g)	initiator[c] (g)	temp (°C)	time (h)	M_n [e]	M_w/M_n	conv[d] (%)
EA(10.5)	bulk	**2** (3.69)	AIBN(0.02)	80	4.5	1169	1.07	100
EA(20.0)	bulk	**1** (5.00)	ACVA(0.12)	60	6	1132	1.06	99
AA(8.5)	DMF(20)	**2** (3.69)	AIBN(0.02)	80	7.5	1375	1.08	96
AA(20)	H_2O(100)	**1** (0.60)	ACVA(0.02)	70	6	9480	1.15	97
HEA(10.0)	*t*BOH(10)	**1** (1.13)	AIBN(0.02)	80	2.5	2560	1.12	99
BA(25.0)	bulk	**1** (1.13)	AIBN(0.07)	80	2	6755	1.10	99
EA(100)	bulk	**1** (0.14)	AIBN(0.02)	80	2.5	58175	1.43	93
*t*BAm(10)	*t*BOH(20)	**2** (0.91)	AIBN(0.02)	80	2	3805	1.15	95
Sty (50)	bulk	**1** (1.45)		140	5	6709	1.16	75
MMA(20)	xyln(23)	**1** (1.20)	BPO(0.52)	75	5	5732	1.72	65

[a] EA = ethyl acrylate; AA = acrylic acid; BA = butyl acrylate; HEA = 2-hydroxylethyl acrylate; tBAm = *tert*-butyl acrylamide; Sty = styrene; MMA = methyl methacrylate. [b] *t*BOH = *tert*-butyl alcohol. [c] AIBN = 2,2′-azobis(isobutyronitrile); ACVA = 4,4′-azobis(4-cyanovaleric acid), 75% in water, BPO = benzoyl peroxide. [d] Measured by GC with undecane as internal standard. [e] Measured by GPC, molecular weight in g/mol; theoretical M_n = [(weight of monomer/mol of **1** or **2**) + molecular weight of **1** or **2**] × conversion.

Table 2. Block Copolymers from 1 or 2[a]

M_1[b] (g)	solvent[c] (mL)	**1** or **2** (g)	time (h)	conv (%)	M_n	M_w/M_n	M_2 (g)	time (h)	M_n	M_w/M_n	conv (%)
AA(7.3)	MEK(20)	**1** (2.8)	4.5	98	1068	1.10	EA (10.2)	3	1804	1.10	71
AA(7.3)	*t*BOH (20)	**2** (3.6)	4.5	97	1433	1.10	EA (10.2)	3	2442	1.12	96
Sty(10)	*t*BOH (10)	**1** (2.8)	4.0	75	818	1.05	AA (7.2)	6	1313	1.10	85
AA(20)	*t*BOH (30)	**2** (9.5)	5	98	1048	1.09	Sty (7.5)	5	1441	1.08	55
EHA(12)	Epon (45 g)	**1** (3.6)	3.5	99	1195	1.08	EA (48)	5	5118	1.08	93

[a] All reactions were at 80 °C with 0.01−0.07g of AIBN in the specified solvents, except when M_1 was styrene, where the polymerization was bulk at 140 °C without initiator. [b] EHA = 2-ethylhexyl acrylate. [c] MEK = methyl ethyl ketone; Epon = Epon 828, from Resolution Performance Products, which is mostly diglycidyl ether of bisphenol A.

done with polystyrene standards. Data acquisition is performed with Waters Millennium 32 software. Gas chromatography (GC) was performed on a Hewlett-Packard 6890 machine.

Synthesis of S,S′-Bis(α,α′-dimethyl-α″-acetic acid)-trithiocarbonate, ***1***. Carbon disulfide (27.4 g, 0.36 mol), chloroform (107.5 g, 0.9 mol), acetone (52.3 g, 0.9 mole), and tetrabutylammonium hydrogen sulfate (2.41 g, 7.1 mmol) were mixed with 120 mL of mineral spirits in a 1 L jacketed reactor cooled with tap water under nitrogen. Sodium hydroxide (50%) (201.6 g, 2.52 mol) was added dropwise over 90 min in order to keep the temperature below 25 °C. The reaction was stirred overnight. 900 mL of water was then added to dissolve the solid, followed by 120 mL of concentrated HCl (*caution! gas, mercaptan odor*) to acidify the aqueous layer. Stir for 30 min with nitrogen purge. Filter and rinse the solid thoroughly with water. Dry to constant weight to collect 41.3 g of earth-colored product. It can be further purified by stirring in toluene/acetone (4/1) or by recrystallizations from 60% 2-propanol or acetone to afford a yellow crystalline solid; mp 173−8 °C (dec). IR (KBr, cm^{-1}): 1710, 1060. H NMR (DMSO-d_6, ppm from TMS): 1.59 (s, 12H), 12.91 (s, 2H). C-13 NMR ($MeOD_4$): 25.76, 57.25, 176.26, 220.50. MS (chemical ionization): calcd for $C_9H_{13}O_3S_3$ ($M^+ - OH$): 265.0027. Found: 265.0015.

Synthesis of S-1-Dodecyl-S′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate, ***2***. 1-Dodecanethiol (80.76 g, 0.40 mol), acetone (192.4 g, 3.31 mol), and Aliquot 336 (tricaprylylmethylammonium chloride, 6.49 g, 0.016 mol) were mixed in a jacketed reactor cooled to 10 °C under a nitrogen atmosphere. Sodium hydroxide solution (50%) (33.54 g, 0.42 mol) was added over 20 min. The reaction was stirred for an additional 15 min before carbon disulfide (30.42 g, 0.40 mol) in acetone (40.36 g, 0.69 mol) was added over 20 min, during which time the color turned red. Ten minutes later, chloroform (71.25 g, 0.60 mol) was added in one portion, followed by dropwise addition of 50% sodium hydroxide solution (160 g, 2 mol) over 30 min The reaction was stirred overnight. 600 mL of water was added, followed by 100 mL of concentrated HCl (*caution! gas, odor*) to acidify the aqueous solution. Nitrogen was purged through the reactor with vigrous stirring to help evaporate off acetone. The solid was collected with a Buchner funnel and then stirred in 1 L of 2-propanol. The undissolved solid was filtered off and was identified as *S*,*S′*-bis(1-dodecyl)trithiocarbonate. The 2-propanol solution was concentrated to dryness, and the resulting solid was recrystallized from hexanes to afford 92.5 g of yellow crystalline solid; mp 62−3 °C. IR (KBr): 1725, 1075. H NMR: 0.99 (t, 3H), 1.37−1.47 (m, 20H), 1.75 (s, 6H), 3.42 (t, 2H), 13.05 (s, 1H). MS (MH^+, chem. ion.): calcd for $C_{17}H_{33}O_2S_3$: 365.1642. Found: 365.1626.

Polymerization with ***1***. All monomers were stripped off the inhibitors by passing through a short column packed with the inhibitor removal from Aldrich. No further purification was performed. In the polymerizations, nitrogen was bubbled for 10−15 min in the mixture of monomers, **1** or **2**, initiator, and solvent in a reactor immersed in an oil bath. The reaction mixture was then allowed to warm under a nitrogen atmosphere to the desired temperature. In bulk polymerization caution is still needed toward the reaction exotherm, since the total heat of the reaction is essentially the same as random radical polymerization. The exotherm is much easier to control, nevertheless, due to the slower propagation. For RAFT polymerization with **1** or **2** which was initiated by an initiator, the temperature was first set at 65 °C where the exotherm showed. Dropping the oil bath or using a water bath was sometimes needed to cool the polymerization and control the temperature between 65 and 80 °C. When the exotherm subsided, the temperature was then maintained at 80 °C. Conversions were calculated from GC with undecane as the internal standard. Samples taken during the course of the reactions were drawn from a rubber septum inserted on one arm in the reactor.

Block Copolymers from ***1*** *or* ***2***. The first monomer was polymerized with **1** or **2** and a small amount of initiator in solution or bulk as described above. If the first monomer was not >95% converted, it was removed by a rotary evaporator. The second monomer was added with a small amount of initiator, and the polymerization was repeated.

Conclusion. Highly active RAFT agents **1** and **2** can be synthesized practically. Controlled radical polymerizations with **1** and **2** yield polymers with narrow molecular weight distributions and predictable molecular weights. Block copolymers including many amphiphilics are successfully made. These polymers can be telechelic dicarboxyl-terminated (from **1**) or monocarboxyl-terminated (from **2**). Applications with these functional polymers are being explored, as are the transformations of the carboxyls into other functionalities such as hydroxyls.

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References and Notes

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