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Living Radical Polymerization with Reversible Addition−Fragmentation Chain Transfer (RAFT Polymerization) Using Dithiocarbamates as Chain Transfer Agents

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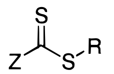
ABSTRACT: Living radical polymerization with reversible addition−fragmentation chain transfer (RAFT polymerization) can be achieved with the use of dithiocarbamate derivatives that have the nonbonded electron pair of the nitrogen included as part of an aromatic system. These compounds have been shown to be highly effective in RAFT polymerization of styrene and (meth)acrylate esters to produce polymers of predetermined molecular weight and narrow polydispersity (usually <1.2). By contrast, simple *N*,*N*-dialkyl dithiocarbamates (those compounds previously described as "photoiniferters") are ineffective as RAFT agents. The reasons for the different behavior are discussed.

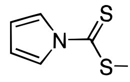
Radical polymerizations with living characteristics are of considerable interest since they offer numerous benefits over conventional free radical methods.[1−4] Several mechanisms to achieve this objective have been proposed.[3,5,6]

Recently, we described a mechanism for achieving living radical polymerization by a process of reversible addition−fragmentation chain transfer (the RAFT process, see Scheme 1).[7−10] The approach utilizes readily available thiocarbonylthio compounds as chain transfer agents (RAFT agents) to confer living character to the polymerization. The requirements for a thiocarbonylthio compound to be effective as a RAFT agent are (i) both rates of addition and fragmentation must be fast relative to the rate of propagation and (ii) the expelled radical ($R^\bullet$) must be capable of reinitiating polymerization (Scheme 1). The first requirement ensures the rapid consumption of the initial RAFT agent and fast equilibration of the dormant and active species while the second ensures the continuity of the chain process. In recent publications we have highlighted the effectiveness of dithioesters (**1**) as RAFT agents in radical polymerization. In this paper we report on the effectiveness and the benefits of appropriately substituted dithiocarbamates as RAFT agents.[11]



1

Z = Ph, CH_3
R = CH_2Ph, $C(CH_3)_2Ph$,
$C(CH_3)_2CN$



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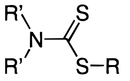
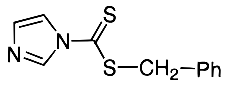
(a) R = CH_2Ph
(b) R = $C(CH_3)_2CN$



2 R = CH_2Ph; R' = C_2H_5
3 R = $C(CH_3)_2CN$; R' = CH_3



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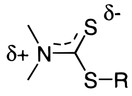

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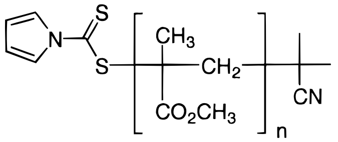

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S-Benzyl *N*,*N*-diethyldithiocarbamate (**2**)[6] has previously been reported as a "photoiniferter" in radical polymerization.[12] This and other similar dithiocarbamates such as *S*-(2-cyanoprop-2-yl) *N*,*N*-dimethyldithiocarbamate (**3**)[13] are not effective RAFT agents. For example, when styrene was heated at 100 °C in the presence of compound **2**, broadly dispersed polystyrene ($M_w/M_n = 1.86$) with $M_n = 317\,100$ was isolated after 6 h (Table 1). A similar lack of control was observed when methyl methacrylate (MMA) was polymerized in the presence of dithiocarbamate **3** (Table 1). These results show that propagating radicals under thermal conditions undergo neither reversible addition−fragmentation chain transfer with "iniferter" dithiocarbamates **2** and **3** nor the reversible termination that is observed under photochemical conditions.[12] The results also confirm that chain transfer to dithiocarbamates **2** and **3** is low,[14] despite having excellent homolytic leaving groups attached to the sulfur atom. We attribute the failure of **2** and **3** to undergo reversible addition−fragmentation to a less reactive double bond caused by the delocalization of the nonbonded electron pair on the nitrogen with the thiocarbonyl group[15] (as shown in **4**). This results in reduced double-bond character[16] in the thiocarbonyl bond, which lowers the rate of addition at sulfur and, consequently, the overall rate of chain transfer.

We have shown dithiocarbamate derivatives, which have the nonbonded electron pair on the nitrogen atom included as part of an aromatic system, to be effective RAFT agents. Examples of such dithiocarbamates are those derived from pyrrole (**5**)[13,17] and imidazole (**6**).[17]

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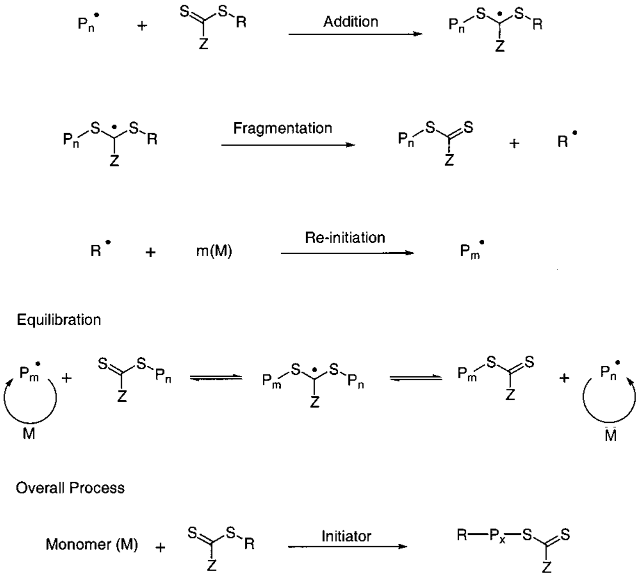
Table 1. Molecular Weight/Conversion Data for Polymers Formed by Polymerization of Various Monomers in the Presence of Dithio Compounds[a]

monomer[b] (concn in benzene, °C)	dithio compd (M × 10^2)	initiator[c] (M × 10^2)	time (h)	M_n[d]	M_n(calc)[e]	M_w/M_n	conv[f] (%)
styrene (bulk, 100)	**6** (2.93)	thermal[g]	16	8 700	9 500	1.14	30
styrene (bulk, 100)	none (control)	thermal[g]	3	319 600		1.62	15
styrene (bulk, 100)	**2** (2.97)	thermal[g]	6	317 100	4 700	1.86	15
styrene (bulk, 100)	**5a** (2.97)	thermal[g]	30	15 600	18 200	1.20	60
styrene (bulk, 60)	**7**[h] (1.03)	AIBN (0.18)	16	25 600	25 100	1.15	31
MMA (7.02 M, 60)	none (control)	AIBN (0.73)	2	274 900		1.67	23
MMA (7.02 M, 60)	**3** (1.12)	AIBN (0.73)	8	312 500	59 700	1.94	>95
MMA (7.02 M, 60)	**5b** (1.12)	AIBN (0.73)	16	51 500	59 700	1.19	>95
MA (2.22 M, 60)	**5a** (1.48)	AIBN (0.073)	16	8 800	9 800	1.17	74
MA (2.22 M, 60)	**6** (0.15)	AIBN (0.066)	4	82 600	84 100	1.14	66

[a] Reaction mixtures were prepared to give the concentrations shown, degassed through three freeze–thaw–evacuate cycles, sealed under vacuum, and heated in a constant-temperature bath for the stated time. [b] Abbreviations (monomers): MMA = methyl methacrylate, MA = methyl acrylate. [c] Abbreviations: AIBN = 2,2′-azobis(2-cyanopropane). [d] Molecular weight data were obtained by gel permeation chromatography (GPC) with 10^6, 10^5, 10^4, 10^3, 500, and 100 Å Waters Ultrastyragel columns connected in series. Tetrahydrofuran (1.0 mL/min) was used as eluent. Samples for GPC were prepared by evaporation of monomer and solvent (no fractionation or precipitation was performed). The system was calibrated with narrow polydispersity polystyrene standards and molecular weights are reported as polystyrene equivalents. [e] Theoretical molecular weights were calculated using the expression $M_n(\text{calc}) = ([\text{monomer}]/[\text{CTA}]) \times \text{conversion} \times \text{MWt of monomer}$. The above expression does not include the small number of chains formed from the initiator. It also assumes complete consumption of the chain transfer agent. [f] Conversions were determined gravimetrically following evaporation of monomer and solvent. Conversions were those obtained for the time indicated and are not a limiting conversion. [g] No added initiator. [h] Poly(methyl methacrylate) **7** (prepared by heating 7.02 M MMA, 11.2×10^{-2} M **5b**, and 0.73×10^{-2} M AIBN in benzene at 60 °C for 8 h) was used in this experiment.

Scheme 1. The RAFT Process[a]



[a] M is monomer; R is a radical that can initiate polymerization; P_n, P_m, and P_x are polymer chains.

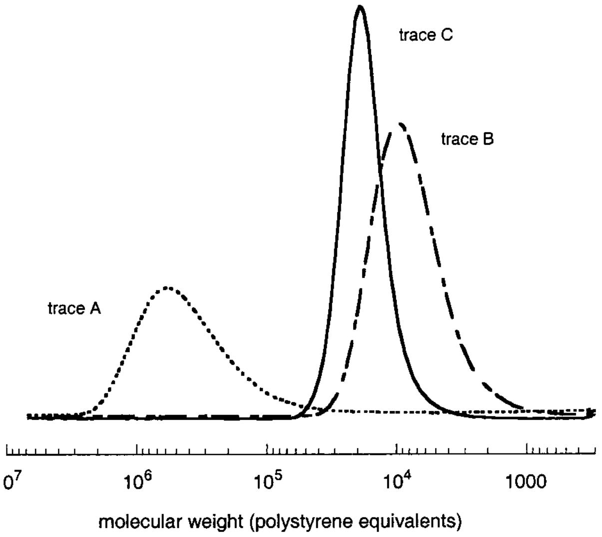


Figure 1. GPC traces for polystyrene prepared by heating bulk monomer at 100 °C in the presence of 2.97×10^{-2} M *S*-benzyl *N*,*N*-diethyldithiocarbamate (**2**) for 6 h (trace A: M_n = 317 100, M_w/M_n = 1.86) and 2.97×10^{-2} M *S*-benzyl *N*-pyrrolocarbodithioate (**5a**) for 6 h (trace B: M_n = 6480, M_w/M_n = 1.46), and 30 h (trace C: M_n = 15 600, M_w/M_n = 1.20).

Other dithiocarbamate derivatives that allow for such delocalization (e.g., derived from indoles) are expected to behave similarly. In these dithiocarbamates, the nonbonded electron pair on nitrogen is involved in the aromatic system and thus less available for conjugation with the thiocarbonyl group. As a result, reversible radical addition–fragmentation, similar to that observed with dithioesters, becomes more favorable. The GPC traces illustrated in Figure 1 show the difference between poly(styrene) prepared using the iniferter **2** and the RAFT agent **5a** under the same conditions.

A range of controlled molecular weight styrenic and acrylic polymers with narrow polydispersity (less than 1.2) has been synthesized using the dithiocarbamates **5** and **6**. The experimentally measured molecular weights (M_n), the calculated molecular weights [M_n(calc)], and the polydispersities of these polymers are listed in Table 1. The results of experiments in the absence of chain transfer agents are also tabulated for comparison. These

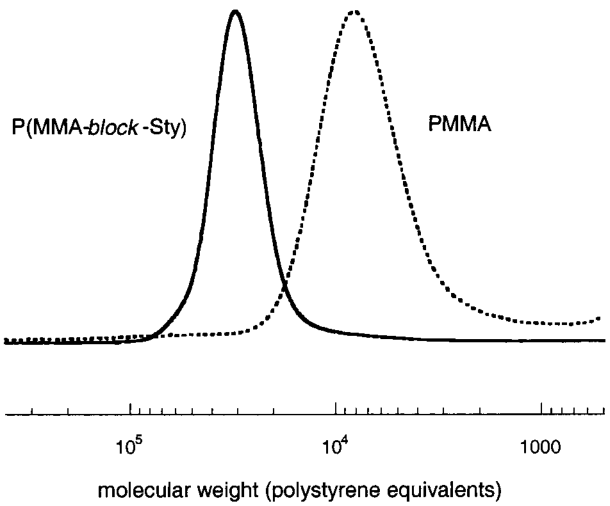


Figure 2. GPC traces for P(MMA-*block*-Sty) (M_n = 25 600, M_w/M_n = 1.15) prepared from PMMA **7** (M_n = 6700, M_w/M_n = 1.27). The PMMA was prepared as in footnote *h* of Table 1.

results demonstrate the excellent degree of control achievable with the RAFT process.

Dithiocarbamates **5** and **6** can also be used to prepare block copolymers. The ability to chain extend with different monomers demonstrates the living character of the polymerization and indicates that the product is predominantly composed of dithiocarbamate terminated polymer chains which can be reactivated when required. For example, poly(methyl methacrylate) (**7**) of M_n = 6700 and polydispersity 1.27 (prepared using **5b** as in footnote *h* of Table 1) when heated at 60 °C in the presence of styrene and AIBN afforded P(MMA-*block*-Sty) of M_n = 25 600 and polydispersity 1.15 (Figure 2).

Evidence for the presence of the dithiocarbamate group in PMMA (**7**) can be gathered from ^{1}H NMR data (Figure 3, spectrum A). The signals at δ 6.3 and 7.6 are characteristic of the pyrrolocarbodithioate moiety. (In compound **5b** these protons appear at δ 6.3 and 7.7.) The absence of signals in the region δ 4–6 in the ^{1}H NMR of **7** is consistent with the pyrrolocarbodithioate group being attached to the tertiary end of the polymer chain. Clearer evidence for the incorporation of the chain transfer agent fragments as end groups in the polymer chains is obtained from the ^{1}H NMR of poly(methyl acrylate) **8** prepared with **5a** (Figure 3, spectrum B). In this, the one proton multiplet at δ 4.8, in addition to the pyrrole signals at δ 6.3 and 7.6, demonstrates that the pyrrolocarbodithioate moiety is attached to the methine terminus of the polymer chains. The broad triplet at δ 2.5 and the aromatic proton signals at δ 6.9–7.4 are respectively assigned to the benzyl CH_2 and aromatic protons of the benzyl group. In addition, the multiplicity (triplet) of the signal at δ 2.5 is consistent with the presence of the benzyl moiety at the methylene terminus of the polymer chain. The sharp singlet at δ 3.8, labeled "a", is assigned to the three methyl ester protons of the monomer unit attached to sulfur. These observations are consistent with the RAFT mechanism proposed in Scheme 1.

In conclusion, simple dithiocarbamates (e.g., **2**) that have been used previously as photochemical iniferters do not undergo reversible addition–fragmentation chain transfer with propagating radicals under thermal conditions and are thus ineffective in controlling radical polymerization. However, dithiocarbamates in which the nitrogen lone pair forms part of an aromatic system (e.g., **5** and **6**) are very effective RAFT agents and provide polymers of controlled molecular weight and narrow polydispersity.

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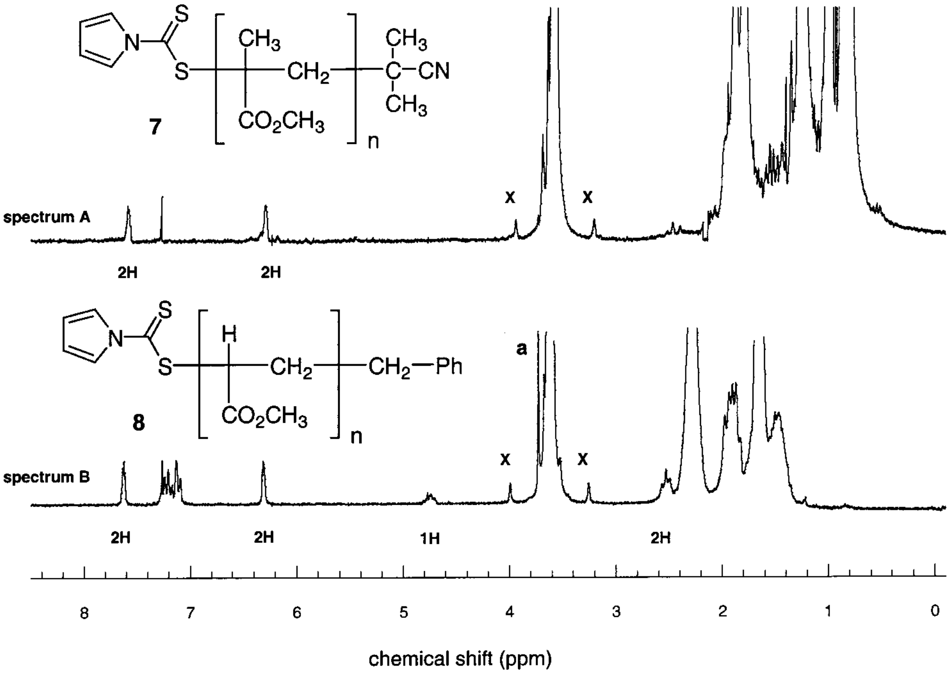

Figure 3. The 200 MHz ^{1}H NMR. Spectrum A: PMMA (**7**) prepared using **5b** as in footnote *h* of Table 1. Spectrum B: PMA **8** (M_n = 3400) prepared by heating 2.22 M MA, 1.5 × 10^{-2} M **5a**, and 0.06 × 10^{-2} M AIBN in benzene at 60 °C for 4 h. The signals labeled "X" are ^{13}C satellites.

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