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Vinylogous Thionothio Compounds for RAFT Polymerization

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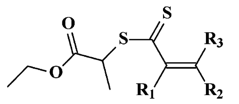
Introduction. In recent years, considerable attention has been paid to controlled/living radical polymerization.[1] Reversible addition−fragmentation chain transfer (RAFT) polymerization is a controlled radical polymerization method of choice for macromolecular engineering. It allows the synthesis of polymers with controlled architectures, predetermined molecular weights and narrow molecular weight distributions for a great number of monomers.[2,3] Its principle is based on the use of thiocarbonylthio reversible chain transfer agents RS(C═S)Z.[4] A high reactivity of the C═S bond and a weak R−S bond are necessary to promote an efficient RAFT polymerization. Our group contributed to understanding the relationship between the nature of the R and Z groups and the transfer ability of the RAFT agents.[5,6] According to the selection of the Z group, dithioester,[7] dithiocarbamate[5,7] RAFT agents, and xanthates—MADIX agents[6]—were synthesized and their performances evaluated in polymerization. The long list of commercially available alcohol and amino derivatives enabled the design of numerous xanthate and dithiocarbamate agents, respectively. In contrast, very few dithioesters with different Z groups were reported (mostly alkyl, phenyl, thiobenzyl,[7] and benzyl[8]).

The present work focuses on a novel range of dithioester RAFT agents **A** (Scheme 1) comprising one given (ethoxycarbonyl)ethyl leaving group and an unsaturated, potentially substituted Z group.

Also, preliminary results of polymerizations using the thioether−thione **B**[9] (Scheme 1) as a RAFT agent are presented. The peculiarities of this class of transfer agents are commented upon.

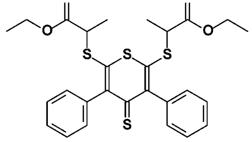
Results and Discussion. Dithioesters $\mathbf{A_{1-4}}$ were synthesized and evaluated in RAFT polymerization of ethyl acrylate (EA) and styrene (St). The polymerization of EA with $\mathbf{A_1}$ and $\mathbf{A_4}$ was strongly retarded in toluene at 80 °C. Under classical conditions for acrylate polymerizations, the conversions were less than 10% (entries 1 and 3 of Table 1), with formation of oligomers capped by the thiocarbonylthio group of **A**, as shown by the strong signal at $\lambda = 290$ nm given by the UV detection used for size exclusion chromatography (SEC). With $\mathbf{A_4}$, a much higher EA conversion (65%) was obtained at 130 °C after a 48 h reaction, using di-*tert*-butyl peroxide (DTBP) as an initiator (experiment 4, Table 1). A somewhat controlled molecular weight with a relatively narrow polydispersity index ($M_w/M_n = 1.38$) was obtained. A conversion equal to 44% was obtained after 24 h for polymerization of EA initiated with azobis(isobutyronitrile) (AIBN) at 60 °C using a low $\mathbf{A_3}$ initial concentration (experiment 2, Table 1). Under these conditions, M_n was controlled and the polydispersity index was low ($M_w/M_n = 1.35$). Bulk polymerization of styrene at 60 °C was initiated with AIBN using $\mathbf{A_1}$ as a RAFT agent (experiments 5−7, Table 1). Results reported in Table 1 and Figure 1 show that $\mathbf{A_1}$ is an efficient RAFT agent for styrene polymerization. M_n increases with monomer conversion with values approaching those predicted for a controlled RAFT polymerization. Polydispersities tend to decrease with time, and remain low throughout polymerization. The "living" character is shown in Figure 1, with the gradual shift toward the high molecular weight region of the polymer distribution over time. Like $\mathbf{A_1}$, $\mathbf{A_3}$ controls St polymerization (experiments 12−14, Table 1). $\mathbf{A_2}$ also induces a linear increase of M_n with conversion during St polymerization (experiments 8−11, Table 1), although M_n was always twice the theoretical value and polydispersity values were greater than for $\mathbf{A_1}$ and $\mathbf{A_3}$ ($1.41 < M_w/M_n < 1.49$). The latter result − combined with unusually low intensities in SEC/UV traces- was attributed to partial degradation of $\mathbf{A_2}$ before and during polymerization. Unlike the other RAFT agents of the series, the electrophilic and little hindered olefinic group of $\mathbf{A_2}$ is susceptible to cycloadditions and such derivatives undergo Diels−Alder reactions with themselves, leading to dimers where one thiocarbonyl group becomes a vinylic sulfide and is incorporated into a ring.[10] Thus, only "half" of the original thiocarbonyl groups remain available, and this explains the doubling of the M_n values. In addition, the conjugation between the olefin, thiocarbonyl and phenyl groups renders $\mathbf{A_2}$ sensitive to visible light and this could speed the cycloaddition process. Polymerization of St with $\mathbf{A_4}$ (experiments 15−17, Table 1) was much slower than for the other agents of the series. Although M_n increased gradually with conversion and low polydispersities were obtained ($1.25 < M_w/M_n < 1.41$), partial monomer conversion was obtained (30%). Also, M_n values were half of those predicted for an efficient RAFT process. With an increase of the reaction temperature up to 130 °C with the DTBP initiator, a high St conversion (92%) was reached (experiment 18, Table 1). But again, M_n was about half of that targeted, with a PDI equal to 1.39. All of the SEC traces of PSt-$\mathbf{A_4}$ exhibit a bimodal distribution (see Supporting Information).

Scheme 1. Vinylogous Dithioester A and Thioether−Thione B RAFT Agents



A

	R_1	R_2	R_3
$\mathbf{A_1}$	H	CH_3	CH_3
$\mathbf{A_2}$	H	Ph	H
$\mathbf{A_3}$	Ph	Ph	Ph
$\mathbf{A_4}$	H	$SCH(CH_3)(CO_2Et)$	$SCH(CH_3)(CO_2Et)$



B

Although some detailed experimental data is still missing, we believe that the strong retardation in rate observed with this

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Table 1. Reversible Addition−Fragmentation Chain Transfer Polymerization of Styrene (St) and Ethyl Acrylate (EA) with Vinylogous RAFT Agents A and B ($[St]_0 = 8.7$ M, $[EA]_0 = 4.6$ M, and Solvent = Toluene)

expt	monomer	RAFT Agent[a]	initiator	$[Ini]_0/[RAFT]_0$	T (°C)	t (h)	M_{nth} [b]	M_n [c]	M_w/M_n	convn (%)[d]
1	EA	**A_1**	AIBN[e]	0.03	80	20	750	775	1.39	6.3
2	EA	**A_3**	AIBN	0.2	60	24	79 000	73 800	1.35	44.3
3	EA	**A_4**	AIBN	0.06	80	10	790	<1000		4.3
4	EA	**A_4**	DTBP[f]	0.2	130	48	5400	3700	1.38	65.6
5	St	**A_1**	AIBN	0.2	60	24	18 700	17 200	1.29	22.7
6	St	**A_1**	AIBN	0.2	60	48	35 100	32 500	1.29	42.6
7	St	**A_1**	AIBN	0.2	60	120	58 000	50 000	1.24	70.7
8	St	**A_2**	AIBN	0.2	60	20	15 400	36 900	1.47	16.1
9	St	**A_2**	AIBN	0.2	60	25	19 600	44 000	1.49	20.6
10	St	**A_2**	AIBN	0.2	60	52	37 500	66 500	1.41	39.7
11	St	**A_2**	AIBN	0.2	60	69	41 600	89 900	1.42	44.1
12	St	**A_3**	AIBN	0.2	60	20	13 800	15 400	1.21	14.3
13	St	**A_3**	AIBN	0.2	60	52	26 400	27 500	1.24	27.6
14	St	**A_3**	AIBN	0.2	60	59	36 800	30 100	1.27	38.8
15	St	**A_4**	AIBN	0.2	60	23	5000	2100	1.43	4.8
16	St	**A_4**	AIBN	0.2	60	90	12 800	6500	1.26	13.1
17	St	**A_4**	AIBN	0.2	60	336	29 000	14 700	1.31	30.3
18	St	**A_4**	DTBP	0.2	130	48	8300	4500	1.38	92.9
19	EA	**B**	AIBN	0.2	80	24	1200	<1000		<5
20	EA	**B**	V-40[g]	0.2	80	144	1100	1000	1.16	7.4
21	EA	**B**	V-40	0.2	110	24	1850	1500	1.13	17
22	EA	**B**	V-40	0.4	110	65	3400	2700	1.59	35.3
23	St	**B**	thermal		110	65	9400	4500	1.37	69.7

[a] See Scheme 1 for definition. [b] $M_{nth} = ([M]_0/[RAFT]_0)(convn)M_w(M) + M_{W(RAFT)}$. [c] By size exclusion chromatography in tetrahydrofuran (based on polystyrene standards). [d] Conversion was determined gravimetrically. [e] Azobis(isobutyronitrile). [f] Di-*tert*-butyl peroxide. [g] 1,1′-Azobis(cyclohexane-1-carbonitrile).

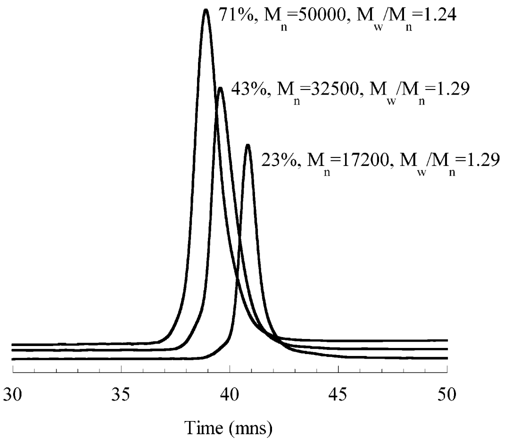
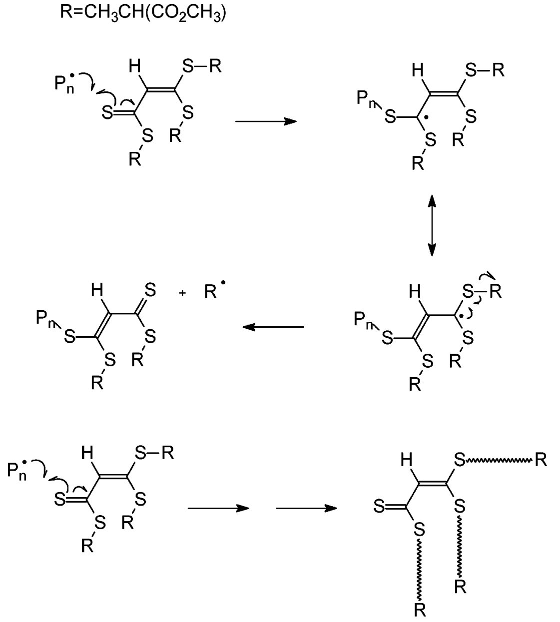


Figure 1. Size exclusion chromatography traces during bulk reversible addition−fragmentation chain transfer polymerization of styrene at 60 °C using **A_1** (structure shown in Scheme 1) as a transfer agent (experiments 5−7 of Table 1).

Scheme 2. Proposed Vinylogous Type Addition−Fragmentation Mechanism during A_4-Mediated Reversible Addition−Fragmentation Chain Transfer Polymerization with Potential Access to Three-Arm Star Polymers



series of RAFT agents is mainly due to slow fragmentation of the intermediate macro-RAFT radicals.[11] Recent ab initio quantum mechanical calculations from Coote's group[12] have shown that unsaturated π-accepting Z-substituents in RAFT agents greatly increase the stability of the macro-RAFT radical. In particular, the radical stabilization energies for the RAFT-adduct radicals were found to be significantly greater for Z = $(-CH{=}CH_2)$ than for Z = Ph.[12] The long lifetime of the macro-RAFT radical increases the probability that side reactions could occur like in the vinylogous type addition−fragmentation chain transfer mechanism proposed for RAFT agent **A_4** (Scheme 2), for which bimodal distributions were observed. This point is still being explored by our group.

The thioether−thione **B** was added to a bulk polymerization of EA initiated with AIBN at 80 °C. This led to the formation of low molecular weight polymers (<1000 g/mol) with very limited conversion after 24 h reaction (experiment 19, Table 1). The incorporation of the RAFT agent **B** into the oligomer chains was supported by the intense SEC response which was obtained with a UV detection at $\lambda = 290$ nm. The use of the V-40 azo initiator at 110 °C (experiments 21 and 22 of Table 1) led to an increased EA conversion (~35%) for prolonged reaction times. M_n was controlled, with a greater polydispersity index than for the other experiments of this series (M_w/M_n = 1.59). The observed dramatic retardation was further evidenced when the polymerization of EA was initiated at 130 °C with DTBP. After 67 h, oligomers (M_n = 840 g/mol) were formed with EA conversion close to 10%. Here again, SEC chromatograms revealed that **B** had reacted efficiently. Thermal bulk styrene polymerization was performed in the presence of thiother−thione **B** (last entry of Table 1). Long reaction times were necessary to reach a monomer conversion close to 70%.

M_n was about half of the theoretical value, and the polydispersity index remained low (M_w/M_n = 1.37). Although the RAFT mechanism involving thioether–thione **B** is still being investigated, we believe that the very strong retardation observed during polymerization is mainly due to the highly stabilized intermediate radical created by the addition of the oligomeric radicals to the C═S bond. This slows down the subsequent (vinylogous type) fragmentation step and therefore significantly decreases the overall rate of the polymerization.

Conclusion. RAFT polymerization of styrene and ethyl acrylate was efficiently conducted using novel vinylogous thionothio compounds. Controlled M_n with low M_w/M_n were obtained for most of the reported experiments. The vinylogous character of RAFT agents **A** and **B** caused a severe retardation during polymerization.

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Supporting Information Available: Text giving experimental details and schemes showing SEC traces during bulk RAFT polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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