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Poly(styrene disulfide) and poly(styrene tetrasulfide) as chain transfer agents in the radical polymerization of styrene

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This is a first report on the chain transfer behaviour of polysulfide polymers, namely poly(styrene disulfide) (PSD) and poly(styrene tetrasulfide) (PST), in the radical polymerization of styrene. It was observed that while PSD acts as a conventional chain transfer agent, PST acts as a retardant. Comparison of the chain transfer constants of PSD and PST with that of the corresponding simple sulfides indicates that polysulfide polymers are better chain transfer agents. Copyright © 1996 Elsevier Science Ltd.

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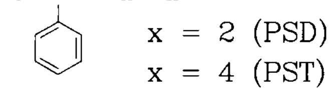
Introduction

Organic sulfur compounds are industrially important materials as vulcanizing agents for rubbers. In addition, they are commonly used as chain transfer agents (CTA) in vinyl polymerization, especially thiols and disulfides[1–4]. The role of sulfide compounds as CTA has been quite intriguing. While disulfides act as conventional CTA, tetrasulfides act as retardants of radical polymerization[5,6]. Notwithstanding earlier attempts to elucidate the role of disulfides as CTA, similar studies on tetrasulfides are limited.

In order to further broaden our understanding of sulfide compounds as CTA, we have chosen in the present study to examine the role of polymeric disulfides and tetrasulfides as CTA and compare their efficiency with low molecular weight counterparts. Hitherto no studies were available on the chain transfer behaviour of polysulfide polymers except some reports on disulfide polymers for synthesizing block copolymers[7,8]. The most fascinating feature of these polymeric sulfides is the influence of long chains on the reactivity of sulfide linkages and the formation of sulfide blocks, as a result of chain transfer reactions, which could be used to our advantage in making block copolymers.

We examine the role of poly(styrene disulfide) (PSD) and poly(styrene tetrasulfide) (PST) as CTA for the free radical polymerization of styrene and compare their efficiency with the corresponding simple sulfides. We believe these studies may provide further input on the degradative behaviour of weak-link polymers of group VIA elements.


$-(-CH_2-CH(C_6H_5)-S_x-)_n-$

x = 2 (PSD)
x = 4 (PST)

Experimental

Materials. The synthesis and characterization of PSD and PST are reported elsewhere[9]. The $\bar{M}_n$ of PSD and PST, as obtained from g.p.c., were 950 and 1950, respectively. Styrene was freed of inhibitor by washing with 5% NaOH and distilled under vacuum. The initiator 2,2′-azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol.

Low conversion styrene polymerization. Bulk polymerization of styrene initiated by AIBN in the presence of varying amounts of PSD or PST was carried out in evacuated sealed ampoules. Polystyrene was precipitated in excess methanol and further purified by repeated precipitation from the chloroform solution. Conversions were kept below 20%. The average degree of polymerization ($\overline{DP}_n$) was obtained using an Ubblehode viscometer using the following empirical equation (in benzene at 30°C)[10].

$$[\eta] = 4.61 \times 10^{-3}\overline{DP}_n^{0.73} \tag{1}$$

Results and discussion

Chain transfer behaviour of PSD. The results of the bulk polymerization of styrene using AIBN initiator in the presence of PSD are given in *Table 1*. The polymerization was carried out at 50, 60, and 80°C with varying amounts of PSD in order to calculate the chain transfer constants (C_{tr}). The rate of polymerization (R_p) of styrene does not vary much with different amounts of PSD (*Figure 1*). The C_{tr} values (*Table 1*) were calculated using the Mayo equation[11]:

$$\frac{1}{\overline{DP}_n} = \frac{1}{\overline{DP}_0} + C_{tr}\frac{[\mathrm{PSD}]}{[\mathrm{M}]} \tag{2}$$

where $\overline{DP}_n$ and $\overline{DP}_0$ represent the degree of polymerization in the presence and absence of the chain transfer agent, respectively. The C_{tr} values, obtained from the

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Table 1 Bulk polymerization of styrene initiated by AIBN in the presence of PSD as the chain transfer

Temp (°C)	[PSD] (mol-equiv l^{-1})	[PSD]/[M] × 10^3	$R_p \times 10^5$ (mol l^{-1} s^{-1})	$\overline{DP}_n$	$1/\overline{DP}_n \times 10^3$	$c_{tr} \times 10^2$
50^a	0.0238	2.82	4.95	735	1.36	8.9
	0.0476	5.64	4.25	642	1.56	
	0.1190	14.10	3.61	416	2.40	
	0.0000	0.00	5.56	866	1.16	
60^b	0.0476	5.69	7.56	563	1.78	8.1
	0.0714	8.54	7.16	501	2.00	
	0.1190	14.23	7.67	398	2.51	
	0.0000	0.00	8.68	738	1.36	
80^a	0.0238	2.90	55.57	303	3.30	6.6
	0.0476	5.80	56.59	293	3.41	
	0.0714	8.70	53.52	281	3.56	
	0.1190	14.51	56.13	241	4.15	
	0.0000	0.00	59.48	314	3.18	

[a] AIBN = 0.03 mol l^{-1}
[b] AIBN = 0.02 mol l^{-1}

plot of $1/\overline{DP}_n$ against [PSD]/[M], were found to decrease with rising temperature.

The quantity $(E_p - E_{tr})$, where E_p and E_{tr} are the activation energies for the propagation and chain transfer reactions, respectively, was obtained from the Arrhenius plot of ln C_{tr} vs $1/T$ according to equation (3),

$$C_{tr} = k_{tr}/k_p = A_{tr}/A_p \exp((E_p - E_{tr})/RT) \qquad (3)$$

The $(E_p - E_{tr})$ value was found to be 2.28 kcal mol^{-1}. By substituting the value of E_p reported in the literature for styrene polymerization (7.8 kcal mol^{-1})[12], E_{tr} was found to be 5.5 kcal mol^{-1}. The Arrhenius equation for the chain transfer process then can be written as

$$k_{tr}(\text{PSD}) = 5.55 \times 10^4 \exp(-5480/RT) \qquad (4)$$

Chain transfer behaviour of PST. The results of the bulk polymerization of styrene using AIBN initiator in the presence of PST are given in *Table 2*. Unlike PSD, the rate of polymerization was found to decrease with the increase in the concentration of PST (*Figure 1*) and hence equation (2) was modified (see equation (5)) for calculating C_{tr},

$$\left(\frac{1}{\overline{DP}_n} - \frac{2k_t R_p}{k_p^2 [\text{M}]^2}\right) = C_M + C_{tr}\frac{[\text{PST}]}{[\text{M}]} \qquad (5)$$

where k_p, k_t and C_M are the rate constants for propagation and termination, and chain transfer to monomer, respectively. The k_t/k_p^2 values were taken from ref. 13. Similar to PSD, we also find a decrease of C_{tr} in PST with rising temperature, the Arrhenius equation for the chain transfer is

$$k_{tr}(\text{PST}) = 7.27 \times 10^5 \exp(-4915/RT) \qquad (6)$$

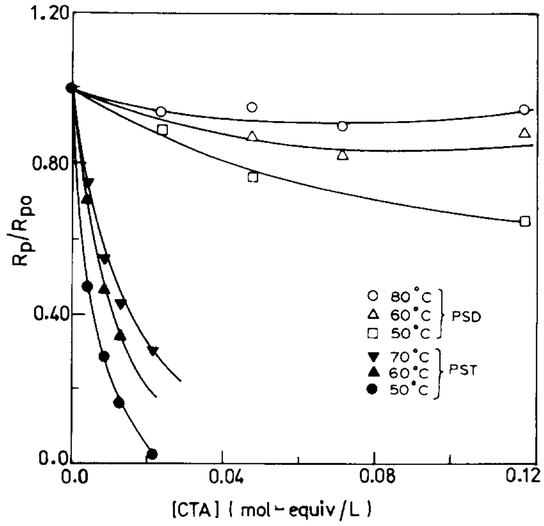
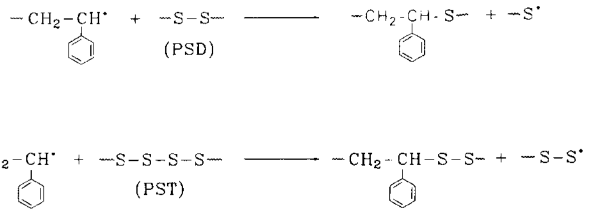


Figure 1 The effect of PSD and PST on the bulk polymerization of styrene; R_p and R_{p0} are the rate of polymerization in the presence and absence of CTA, respectively

Comparison between CTA behaviour of PSD and PST. The R_p values in the presence of PSD do not vary much with increasing [PSD], but decrease significantly with increasing [PST], this behaviour is explained in *Scheme 1*. It is known that the simple $-RS^{\cdot}$ radical is more reactive than $-RSS^{\cdot}$ radical as the latter radical is stabilized by resonance[5,6], and that is why we observe a difference between PSD and PST. A similar trend is observed for the MMA polymerization initiated by AIBN in the presence of dibenzyl sulfides ($C_6H_5CH_2 - S_n - CH_2C_6H_5$), where the compounds with sulfur rank (n) more than two were found to act as retarders[6].

Comparison of the C_{tr} values of PSD and PST (see *Tables 1* and *2*) indicate that the latter has a higher value



Scheme 1

Table 2 Bulk polymerization of styrene initiated by AIBN in the presemnce of PST as the chain transfer agent[a]

Temp (°C)	[PST] × 10^2 (mol-equiv l^{-1})	[PST]/[M] × 10^4	$R_p \times 10^5$ (mol l^{-1} s^{-1})	$\overline{DP}_n$	$1/\overline{DP}_n \times 10^3$	C_{tr}
50	0.431	5.11	2.20	469	2.13	
	0.862	10.21	1.31	328	3.05	
	1.290	15.28	0.74	223	4.48	2.76
	2.155	25.53	0.10	–	–	
	0.000	0.00	4.64	1085	0.92	
60	0.431	5.15	7.17	412	2.43	
	0.862	10.31	4.73	272	3.68	2.63
	1.290	15.43	3.48	218	4.59	
	0.000	0.00	10.24	672	1.49	
70	0.431	5.21	18.56	339	2.95	
	0.862	10.42	13.72	266	3.76	
	1.290	15.60	10.75	209	4.79	2.12
	2.155	26.06	7.50	160	6.25	
	0.000	0.00	25.02	452	2.21	

[a] AIBN = 0.02 mol l^{-1}

Table 3 The chain transfer constants and the rate constants for the reaction of polystyryl radicals with disulfides and tetrasulfides, at 60°C[4,14]

Compound	$C_{tr} \times 10^4$	$k_{tr}(C_{tr} \times k_p)^a$ (l mol^{-1} s^{-1})
CH_3SSCH_3	94	1.62
PrSSPr	23	0.39
BuSSBu	24	0.41
$C_{12}H_{25}SSC_{12}H_{25}$	2	0.04
$C_6H_5SSC_6H_5$	103	1.77
$C_6H_5CH_2SSCH_2C_6H_5$	100	1.72
$C_6H_5CH_2SSSSCH_2C_6H_5$[b]	840	14.45
PSD[c]	810	13.86
PST[c]	27460	472.30
Sulfur[d]	206900	3000.00

[a] k_p at 60°C = 172 mol^{-1} s^{-1} [12]
[b] For MMA polymerization at 60°C[6]
[c] This work
[d] At 81°C

compared to the former and is attributed the lability of the central S—S bond in PST[6]. The E_{tr} values were found to be 5.5 and 4.9 kcal mol^{-1} for PSD and PST, respectively. Although E_{tr} in the case of PST is lower than that of PSD the difference is only marginal. However, the frequency factor in PST was found to be more than an order of magnitude greater than PSD and that is why the chain transfer to PST is more facile.

Finally, the C_{tr} and k_{tr} values (at 60°C) of PSD and PST are compared with that of the simple di- and tetrasulfides (*Table 3*). Simple alkyl disulfides have very low chain transfer constants ($2–100 \times 10^{-4}$), but the C_{tr} of PSD is relatively much higher (0.0810). Similarly, the C_{tr} (2.746) of PST was also found to be much higher than the corresponding simple tetrasulfide, for example benzyltetrasulfide has a C_{tr} of 0.084, for MMA polymerization[6] at 60°C. Hence it is clear from *Table 3* that both PSD and PST are better chain transfer agents than their corresponding low molecular weight analogues.

Conclusions

For the first time the chain transfer characteristics of polysulfide polymers namely PSD and PST have been studied for styrene polymerization, and it has been found that PST has a higher C_{tr} value than PSD. While PSD behaves like a normal chain transfer agent, PST on the other hand acts as a retardant. Both PSD and PST are found to be good chain transfer agents compared to the conventional low molecular weight sulfides and this unfolds new avenues for exploring the utility of polymeric sulfides as efficient chain transfer agents. It is hoped that block copolymers of the vinyl monomer and the sulfide polymer, resulting from the chain transfer reactions, could be used as potential vulcanizing agents.

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