Living Radical Polymerization of Styrene with Tetramethylene Disulfide

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Introduction. It has long been considered that the synthesis of polymers having a controlled structure by radical polymerization in homogeneous systems is almost impossible, because control of short-lived unstable radicals such as initiating and propagating radicals is quite difficult. For this problem, a significant breakthrough is the "iniferter" concept proposed by Otsu in 1982.[1] When an iniferter (I–I′) with a very high reactivity for chain transfer and/or primary radical termination is used, a polymer bearing iniferter fragments at both chain ends is obtained as shown in eq 1. If the end groups of the polymers

$$\text{I–I}' + n(\text{monomer}) \rightarrow \text{I–(monomer)}_n\text{–I}' \qquad (1)$$

obtained in this polymerization still have an iniferter function, the polymerization shows a feature of a living mechanism:[2,3] i.e., both polymer yields and molecular weights of the polymers increase with reaction time.

Polymerizations with this mechanism were reported in the polymerizations of styrene (St) and methyl methacrylate (MMA) with tetraalkylthiuram disulfide and dithiocarbamate as photoiniferters.[2,3] Such polymerizations were also reported in the polymerization of MMA with thermal iniferters such as highly substituted ethanes and (phenylazo)triphenylmethanes.[4,5] Despite these studies, one of the goals for complete living polymerization has not been reached: polymer with a narrow molecular weight distribution cannot be obtained.

Cyclic disulfides were reported to polymerize to give polymers containing a disulfide bond in the main chain[6–11] and to copolymerize with vinyl monomers.[12–16] Thus it is possible to introduce such bonds in a chain by polymerization. Since bond dissociation energies of carbon–sulfur and sulfur–sulfur bonds are generally lower than those of carbon–carbon bonds,[17,18] such groups may serve as thermal iniferters. Thus, living radical polymerization is expected to be induced.

Recently, we found that the polymerization of St in the presence of cyclic sulfide proceeds with a living radical mechanism. In this paper, we describe our preliminary results on the radical polymerization of St in the presence of a six-membered cyclic disulfide, tetramethylene disulfide (TMDS).

Results and Discussion. Polymerization of St in the presence of TMDS was carried out at 120 °C. The results are shown in Figure 1. Interestingly, the conversion and the number-average molecular weight ($\bar{M}_n$) of the polymers increased with reaction time. The enhancement of $\bar{M}_n$ of the polymers with reaction time is quite different from ordinary radical polymerization of St.

To further clarify this polymerization behavior, the $\bar{M}_n$ of the polymers was plotted as a function of conversion (Figure 2). The $\bar{M}_n$ of the polymers increased almost linearly with conversion. Moreover, as shown in Figure 3, the GPC elution curves of the polymers shifted to the higher molecular weight side with reaction time, and no significant change of the molecular weight distribution

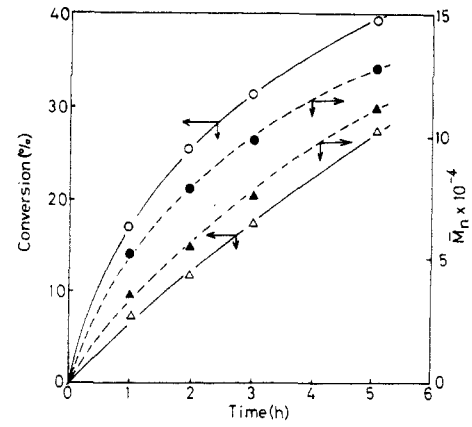

Figure 1. Polymerization of St in the presence of TMDS at 120 °C: St, 8.7 mol·dm^{-3}; TMDS, (▲,△) 0.5 mol·dm^{-3}, (●,○) 1.0 mol·dm^{-3}.

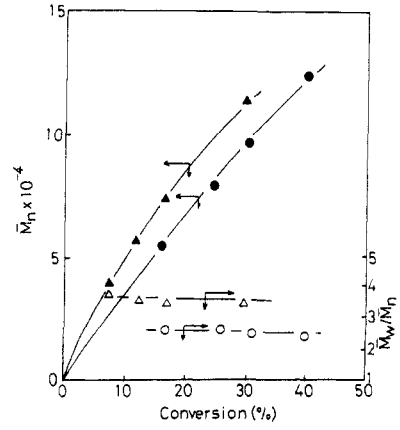

Figure 2. $\bar{M}_n$–conversion relations for the polymerization of St in the presence of TMDS: TMDS, (▲,△) 0.5 mol·dm^{-3}, (●,○) 1.0 mol·dm^{-3}; for other conditions, see legend to Figure 1.

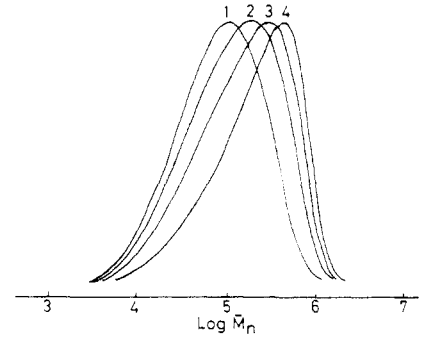

Figure 3. GPC elution curves for polymers obtained from the polymerization of St in the presence of TMDS for (1) 1, (2) 2, (3) 3, and (4) 5 h; TMDS, 0.5 mol·dm^{-3}; for other conditions, see legend to Figure 1.

($\bar{M}_w/\bar{M}_n$; $\bar{M}_w$ is the weight-average molecular weight) of the polymers determined by GPC measurement was observed (Figure 2).

The number of TMDS units per polymer chain did not change significantly as a function of reaction time as listed in Table I, suggesting that TMDS did not serve as a true comonomer, although some cyclic disulfides such as lipoamide were reported to copolymerize with St.[15,16]

On the basis of these results, we supposed that the polymerization of St in the presence of TMDS proceeds via a living radical mechanism.[2,3]

To elucidate the polymerization mechanism, the polymerization of St was examined under various conditions. Thermal polymerization of St was examined in the absence

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Table I
Bulk Polymerization of St in the Presence of TMDS[a]

		polymer		
time, h	conv, %	$10^{-3}\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	no. of TMDS units[c]
1.0	7.0	46.1	3.88	0.9
2.0	12.0	54.4	3.61	
3.0	30.5	92.0	3.48	1.1
5.0	39.2	128.1	3.40	1.3

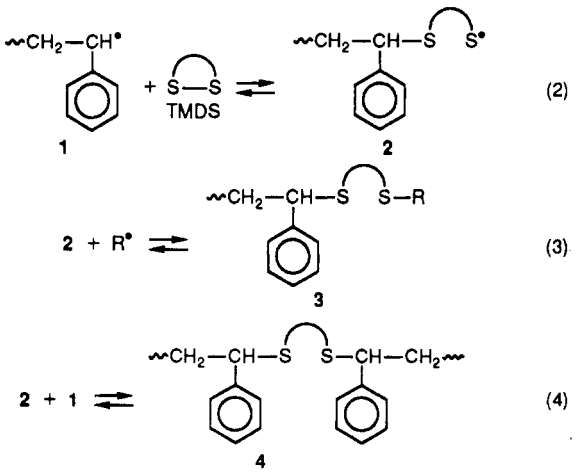
[a] St, 8.7 mol·dm^{-3}; TMDS, 0.5 mol·dm^{-3}; reaction temperature, 120 °C. [b] Determined by GPC. [c] Calculated from ^{1}H-NMR and $\bar{M}_n$ data of the polymer.

of TMDS at 120 °C, and the results are shown in Figure 4. Different from the polymerization of St in the presence of TMDS under similar conditions, the $\bar{M}_n$ of the polymers decreased with reaction time, suggesting that TMDS plays a role in the living radical polymerization.

The rate of polymerization of St in the presence of TMDS is not so different from that in the absence of TMDS (Figures 1 and 4). Moreover, thiyl radicals were reported to hardly initiate the polymerization of St.[19] Thus we supposed that the initiating radical (R•) is mainly produced by thermal reaction of St monomers.[20]

During the polymerization in the presence of TMDS, it is possible to produce dithiol compounds. Such compounds can cause an increase in the molecular weights of polymers by coupling chain-to-chain. To check this point, the polymerization of St was examined in the presence of 1,5-pentanedithiol. The results are shown in Figure 5. The $\bar{M}_n$ of the polymers increased with reaction time, but the $\bar{M}_w/\bar{M}_n$ became broad as a function of the time. Moreover, the plot of $\bar{M}_n$ against reaction time is not clearly linear. This suggests that the thiol compound is consumed rapidly due to a large chain transfer constant. Since these behaviors are different from the results of the polymerization in the presence of TMDS, a mechanism for coupling chain-to-chain by thiols may be excluded.

Thus we considered the following reactions to account for the living nature of the polymerization.



The styryl radical (1) attacks TMDS, giving the thiyl radical (2).[15,16] If such a radical couples with another radical to give 3 and 4 and the C–S bonds in 3 and 4 dissociate again into the styryl radical and the thiyl radical, the polymerization will show a living nature.

Since bond dissociation energies of the C–S bond in –CH(C_6H_5)–S– are lower than other related ones as listed in Table II,[17,18] a cleavage of the C–S bonds at relatively high temperature, e.g., 120 °C, may be possible. Thus the proposed mechanism of the polymerization of St in the presence of TMDS seems to be reasonable.

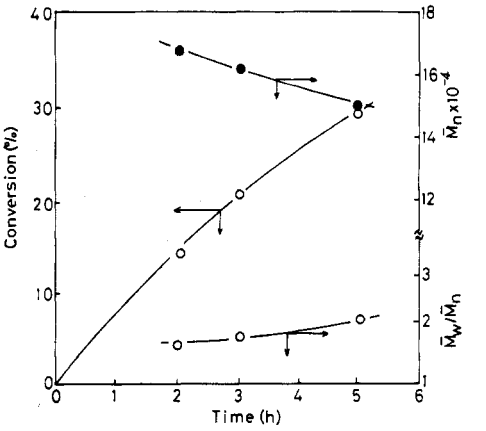


Figure 4. Thermal bulk polymerization of St in the absence of TMDS at 120 °C: (●) $\bar{M}_n$ of the polymer, (○) $\bar{M}_w/\bar{M}_n$ of the polymer.

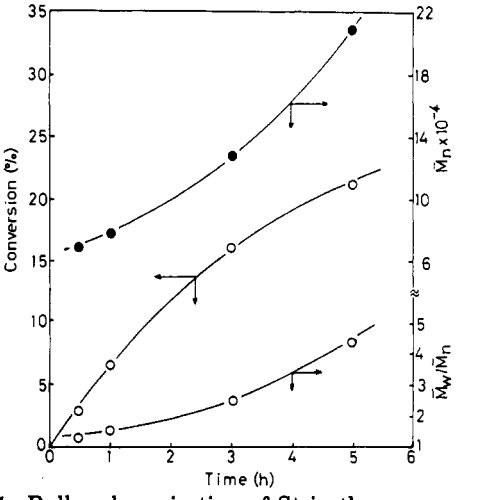


Figure 5. Bulk polymerization of St in the presence of 1,5-pentanedithiol at 120 °C: 1,5-pentanedithiol, 0.038 mol·dm^{-3}; (●) $\bar{M}_n$ of the polymer, (○) $\bar{M}_w/\bar{M}_n$ the polymer.

Table II
Bond Dissociation Energy (BDE) for Sulfur-Containing Compounds[a]

compound	BDE, kJ/mol
C–S Bond	
C_2H_5–SCH_3	301.2
CH_3–SC_6H_5	251.0
$C_6H_5CH_2$–SCH_3	217.6
S–S Bond	
C_2H_5S–SC_2H_5	292.9
$C_6H_5CH_2S$–$SCH_2C_6H_5$	259.4–284.5
$C_{18}H_{37}S$–$SC_{18}H_{37}$	251.0–276.1

[a] Data from refs 17 and 18.

However, some undesirable reactions for decreasing the living nature, e.g., an attack of the thiyl radical on the St monomer and bimolecular termination between styryl radical, cannot be excluded. This can be estimated from the divergence from linear for the relation of conversion against $\bar{M}_n$ of the polymers (Figure 2).

Experimental Section. Polymerizations were carried out in a sealed glass tube. After the required amounts of reagents were charged, the tube was degassed and then sealed under high vacuum. After the polymerization, the tube was opened, and the contents of the tube were poured into a large amount of methanol to precipitate the polymer formed. The number-average molecular weights ($\bar{M}_n$) and molecular weight distributions ($\bar{M}_w/\bar{M}_n$) of the polymers were determined by GPC (Tosoh CCPD RE-8000) in THF

at 38 °C. A standard poly(St) was used for calibration of the molecular weight of the polymers.

References and Notes

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Registry No. St, 100-42-5; TMDS, 505-20-4; PSt, 9003-53-6; 1,5-pentanedithiol, 928-98-3.