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Living Radical Polymerizations in Homogeneous Solution by Using Organic Sulfides as Photoiniferters

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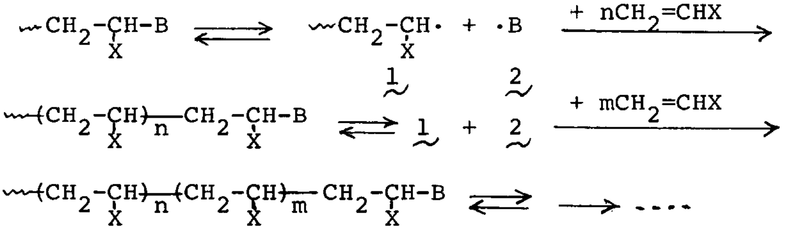
Summary

Some examples for living radical polymerization in homogeneous solution by four organic sulfides as photoiniferters have been proposed. In the photopolymerization of styrene(St) with diphenyl disulfide(DPD), tetraethyl thiuram disulfide(TD), benzyl diethyldithiocarbamate(BDC) and 2-phenylethyl diethyldithiocarbamate(PEDC), both the yields and the average-molecular weights of the polymers were found to increase as a function of the reaction time. The results obtained suggested that these polymerizations proceeded via a living radical mechanism. When these photoiniferters except DPD were used, the propagating polymer chain end was confirmed to be always the diethyldithiocarbamate[$(C_2H_5)_2NCSS$] group, which can further photodissociate into a reactive propagating radical and a less reactive small radical[$(C_2H_5)_2NCSS\cdot$] in order to result in successive insertion of monomer molecules into the dissociated bond.

Introduction

In a previous paper[OTSU et al., 1982a], the concept of initiator-transfer agent-terminator(iniferter) in radical polymerization to synthesize monofunctional and α,ω-bifunctional oligomers and polymers was proposed, and some organic disulfides such as TD and dibenzoyl disulfide were found to be excellent thermal or photoiniferters. This concept was extended to a new model for living radical polymerization in homogeneous solution by using iniferters[OTSU et al., 1982b]. Namely, if the propagating polymer chain ends which can dissociate into a reactive propagating radical(1) and a small radical(2), which is stable enough not to initiate a new polymer chain, such a radical polymerization would proceed via a living mechanism, according to eq.(1):



$$\sim CH_2-\underset{X}{CH}-B \rightleftarrows \underset{1}{\sim CH_2-\underset{X}{CH}\cdot} + \underset{2}{\cdot B} \xrightarrow{+\,nCH_2=CHX}$$
$$\sim\!(CH_2-\underset{X}{CH})_n\!-CH_2-\underset{X}{CH}-B \rightleftarrows 1 + 2 \xrightarrow{+\,mCH_2=CHX}$$
$$\sim\!(CH_2-\underset{X}{CH})_n\!(CH_2-\underset{X}{CH})_m\!-CH_2-\underset{X}{CH}-B \rightleftarrows \longrightarrow \cdots\cdot \quad (1)$$

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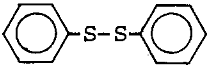
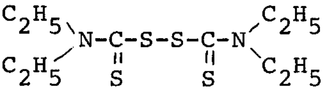
For these examples, the polymerizations of methyl methacrylate(MMA) by phenylazotriphenylmethane as a thermal iniferter and BDC as a photoiniferter were shown to proceed via a living radical mechanism[OTSU et al., 1982b]. More recently, a number of examples were observed in the cases which organic sulfur compounds were used as photoiniferters.

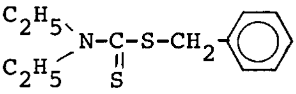
In this paper, the recent results of living radical polymerizations of St by DPD, TD, BDC and PEDC will be described. BDC and PEDC are used as model compounds for the poly(St) obtained by TD which is a polymeric photoiniferter.



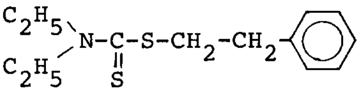
DPD



TD



BDC



PEDC

Experimental

The commercial TD and DPD were recrystallized from ethanol; mp 73-74°C and 61°C, respectively. BDC and PEDC were prepared and distilled in a reduced pressure; bp 154-155°C and 159-160°C, respectively. St, benzene and other reagents were used after ordinary purifications.

The bulk polymerizations of St were carried out in sealed tube under irradiation of Toshiba SHL-100 UV lamp from a distance of 10 cm. After polymerization for a given time, the contents of the tube were poured in a large amount of methanol to precipitate the polymer.

The yield of the polymers was determined from the weight of the resulting polymers dried. The intrinsic viscosities, $[\eta]$ were determined in benzene at 30°C, and the average-molecular weights($\bar{M}$) were then calculated from eq.(2)[ALTARES et al., 1964].

$$[\eta] = 8.5 \times 10^{-5}\ \bar{M}^{0.75} \qquad (2)$$

The diethyldithiocarbamate group in the polymer chain ends was determined by UV spectra in comparison with those of the model compound, methyl N,N-diethyldithiocarbamate[λ_{max} (>N-C=S) 278 nm, ε = 13,500 l/mol·cm in cyclohexane].

Results and Discussion

The results of photopolymerizations of St by DPD, TD, BDC and PEDC at 30°C are shown in Figs. 1 - 4, respectively. From Figs. 1 - 3, the yields and the $\bar{M}$ values of the polymers are observed to increase from an original point as a function of the reaction time. These results strongly suggest that these polymerizations proceed via a living radical mechanism according to eq.(1), in where **2** is a radical[$(C_2H_5)_2NCSS\cdot$]. However, the result by PEDC(Fig. 4) is somewhat different from the above systems, i.e. the values of $\bar{M}$ increase in little extent

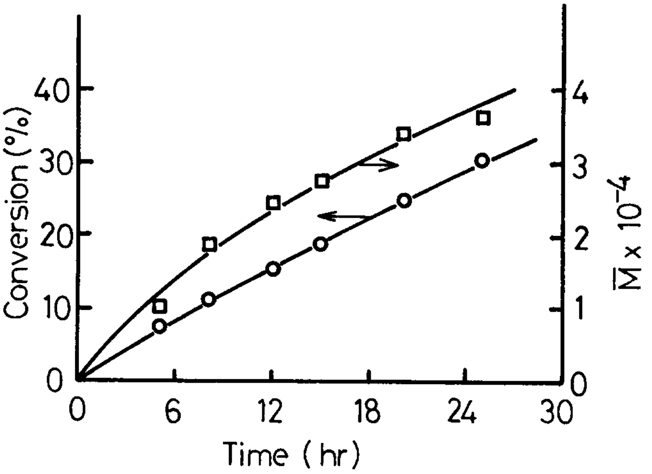


Fig. 1.Photopolymerization of St by DPD at 30°C: [St]= 6.5 mol /l, [DPD]= 33 mmol/l

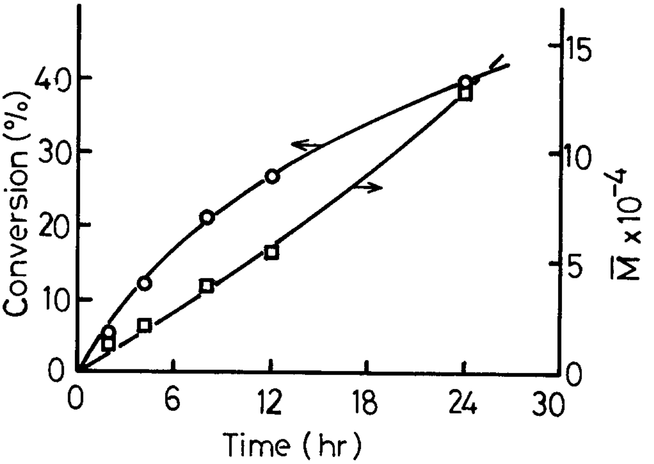


Fig. 2.Photopolymerization of St by TD at 30°C: [St]= 7.2 mol/l, [TD]= 7.7 mmol/l

with the time but the observed time-$\bar{M}$ relation does not cross an original point. This reason will be discussed later.

Table 1 shows the results of number- and weight-average molecular weights($\bar{M}_n$ and $\bar{M}_w$, respectively) of the polymers obtained by TD and BDC as a function of the polymerization time. From this table, the values of $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ are also observed to increase with reaction time. Contrary to living anionic polymerizations which give polymers with a narrow molecular weight distribution like $\bar{M}_w/\bar{M}_n \leq 1.1$-$1.2$[SZWARC, 1956; SZWARC et al., 1956], radical polymerizations have been known to proceed by a slow radical dissociation(initiation) of the initiator. Moreover, the living radical polymerizations in emulsion system are successful if the initiation rate is controlled as become slower [BIANCHI et al., 1957; Mikulášvá et al., 1974a and 1974b; INOUE et al., 1977]. However, since this living radical polymerization in homogeneous solution is performed by a successive insertion of monomer molecules into the dissociated bond, the molecular weight distribution of the polymers seems to become broader with the polymerization time(i.e. conversion).

As can be also seen from Table 1, the numbers of diethyldithiocarbamate end groups per one polymer chain are almost constant(nearly 2.0 for TD and 1.0 for BDC), independent of polymerization time. This result strongly suggests that the polymerization is performed by a living radical mechanism, i.e. a successive dissociation, monomer addition and recombination, as is shown in eq.(3).

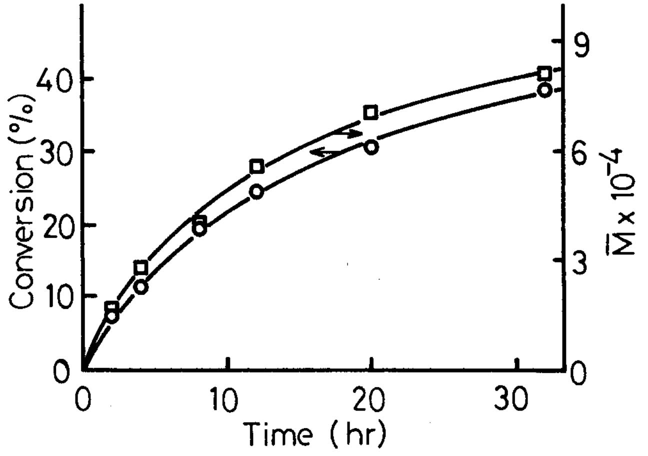


Fig. 3. Photopolymerization of St by BDC at 30°C: [St]= 7.2 mol/l, [BDC]= 7.7 mmol/l

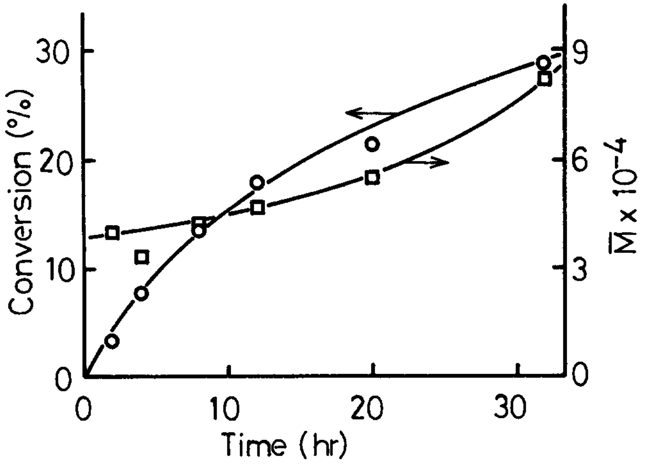


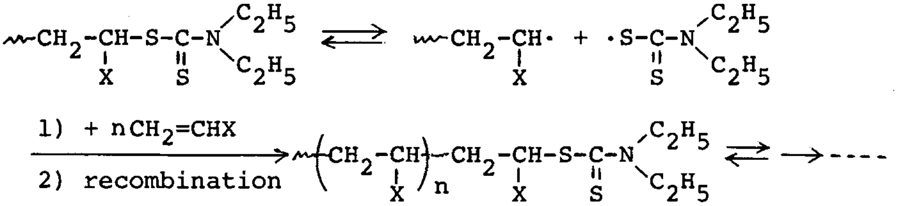
Fig. 4. Photopolymerization of St by PEDC at 30°C: [St]= 7.2 mol/l, [PEDC]= 7.2 mmol/l

Table 1. Photopolymerization of St by TD and BDC at 30°C[a)]

Iniferter	Time (hr)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	Number of end group[b)]
TD	8	2.1	5.3	2.5	1.7
	12	3.1	9.8	3.2	1.9
	24	5.7	30.4	5.4	2.0
BDC	2	0.7	1.2	1.7	0.9
	4	1.1	2.3	2.2	0.8
	8	1.7	4.5	2.7	1.0
	12	2.0	6.8	3.4	1.1

a) Polymerization conditions are identical to Figs. 2 and 3. $\bar{M}_n$ and $\bar{M}_w$ were determined by gel permeation chromatography.

b) The numbers of the $(C_2H_5)_2NCSS$- end group per one polymer molecule were determined from both data of UV and $\bar{M}_n$.

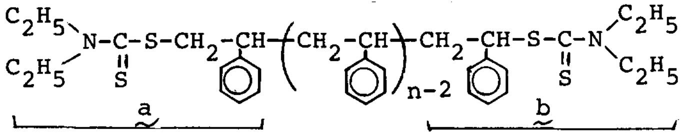


$$\sim CH_2-\underset{X}{CH}-S-\underset{\underset{S}{\|}}{C}-N\begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix} \rightleftarrows \sim CH_2-\underset{X}{CH}\cdot + \cdot S-\underset{\underset{S}{\|}}{C}-N\begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix}$$

$$\xrightarrow[\text{2) recombination}]{\text{1) + n}CH_2=CHX} \sim\left(CH_2-\underset{X}{CH}\right)_n-CH_2-\underset{X}{CH}-S-\underset{\underset{S}{\|}}{C}-N\begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix} \rightleftarrows \longrightarrow ---- \qquad (3)$$

This mechanism was also supported from the fact that the polymers obtained by TD can further photochemically dissociate into radicals[see eq.(3)] to give a chain-extended high molecular weight polymer or a block copolymer[OTSU, 1957, 1959; OTSU et al., 1960, 1982a, 1982b].

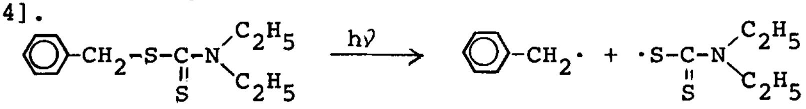
As described in the previous paper[OTSU et al., 1982a], the polymerization of St by TD gives polymer consisting of two diethyldithiocarbamate groups bonded with a different manner to polymer chain end, as is shown by the structure 3:



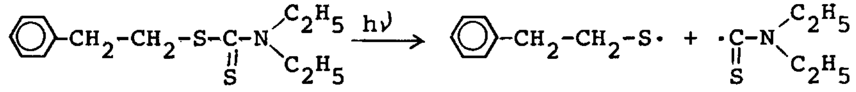
3

in which the end group attached to a styryl unit, a and b consist of similar structure to PEDC and BDC, respectively. Therefore, both the groups seem to dissociate into radicals which react with monomers, according to different mechanism and reactivity.

The photolysis of PEDC and BDC has been shown to proceed by the following bond scission[eqs.(4) and (5)][OKAWARA et al., 1964].

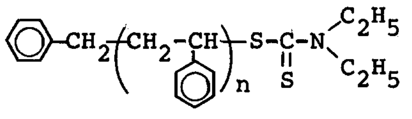


(4)



(5)

Although both BDC and PEDC show identical UV spectra, the polymer yields observed in the photopolymerization of St by PEDC are somewhat lower than those by BDC, as shown in Figs. 3 and 4. However, if the carbon-centered radicals can participate into initiation, the structure of the polymers obtained by both iniferters may be different as 4 and 5.



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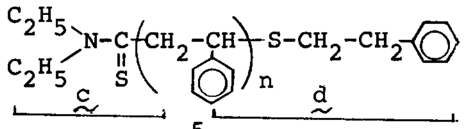

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The structure of the end group in 4 is always similar to that in BDC during polymerization. However, the photolysis of 5 seems to be different. When N,N-diethylthioacetamide and dibenzyl sulfide as model compounds for the end groups, c and d, respectively, were used as photoiniferter, the polymerizations of St were found to be hardly induced under the present conditions[OTSU, 1956; OTSU et al., 1958]. Therefore, the increase in $\bar{M}$ during polymerization by PEDC seems to be lower than that by BDC, similarly to the polymer yields.

Although in the photopolymerization of St by TD, the yields and $\bar{M}$ of the polymers obtained were observed to increase more than those by BDC or PEDC alone, it seems to proceed with a combined effect of both photoiniferters, i.e. this polymerization seems to be performed through a combined living mono- and biradical propagations.

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