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Living Mono- and Biradical Polymerizations in Homogeneous System Synthesis of AB and ABA Type Block Copolymers

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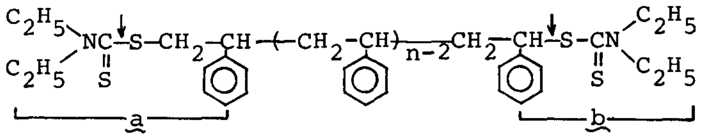
Summary

To design the structure of the block copolymers by radical polymerization, benzyl N,N-diethyldithiocarbamate(BDC) and p-xylylene N,N-diethyldithiocarbamate(XDC) were used as mono- and bifunctional photo-iniferters, respectively, for the polymerizations of styrene(St) and methyl methacrylate(MMA). These polymerizations proceeded via a living radical mechanism. When the ratio of the concentration of the diethyldithiocarbamate group to that of a photo-iniferter molecule was kept constant, the yields of the polymers obtained by both BDC and XDC were identical, and their molecular weights($\bar{M}$) by XDC were two times as high as those by BDC. This observation strongly suggested that the polymerizations by BDC and XDC were performed by living mono- and biradical mechanisms, respectively. By using the polymers obtained by BDC and XDC as polymeric photo-iniferters of the polymerization of second monomers, the AB and ABA type block copolymers were obtained, respectively.

Introduction

In previous papers[OTSU et al., 1982a,1982b,1982c], when some organic sulfur compounds such as tetraethylthiurum disulfide(TD) were used as a photo-iniferter, the polymerizations of vinyl monomers such as St and MMA were found to proceed via a living radical mechanism in homogeneous system. Moreover, the polymers thus obtained were observed to serve as a polymeric photo-iniferter in order to give efficiently block copolymers [OTSU et al., 1957,1960,1982d,1983].

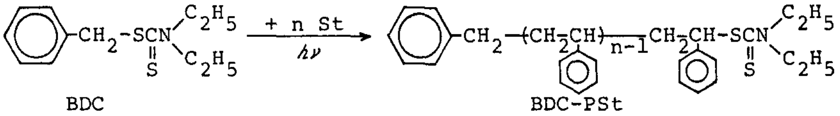
However, this technique was not so effective to control the AB and ABA type structures of the resulting block copolymers. For this reason, it was suggested in a previous paper[OTSU et al., 1982c] that the presence of two diethyldithiocarbamate groups linked by a different bonding to both poly(St) chain ends, a and b, in eq.(1), was important. Namely, BDC which was used as a model compound of the bond b acts as an effective photo-



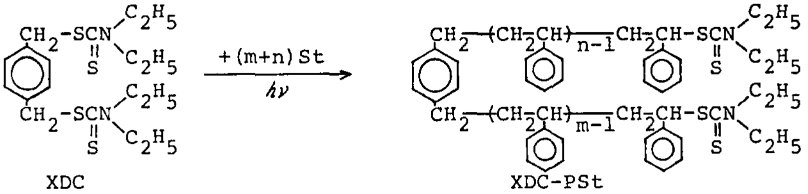
(1)

iniferter rather than phenylethyl N,N-diethyldithiocarbamate, a model compound of the bond **a**, because the photochemical dissociation of these compounds occurs at different C-S bonds [OKAWARA et al., 1964], and hence the radicals produced show different reactivities toward the monomer.

To design the AB and ABA type structures of block copolymers by this technique, therefore, we must choose mono- and bifunctional photo-iniferters, respectively, which consisted of identical bonds. In the present paper, BDC and XDC were synthesized and used for the polymerization of St and MMA. According to the living radical mechanism reported in previous papers[OTSU et al., 1982b,1983c][see eq.(8)], the polymerization of St, for an example, seems to be expressed by the following equations[eqs.(2) and (3)].

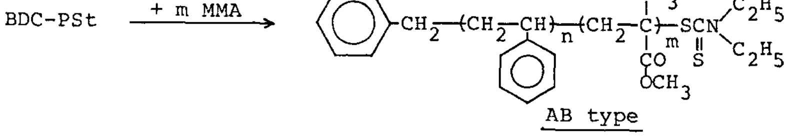


BDC BDC-PSt (2)



XDC XDC-PSt (3)

Both monomeric photo-iniferters(BDC and XDC) and polymeric photo-iniferters(BDC-PSt and XDC-PSt) consist of identical benzyl N,N-diethyldithiocarbamate structure. Therefore, if these BDC-PSt and XDC-PSt are used as polymeric mono- and bifunctional photo-iniferters, respectively, in the polymerization of second monomers, AB and ABA type block copolymers, respectively, seem to be produced[eqs.(4) and (5)]. The results are described in this paper.



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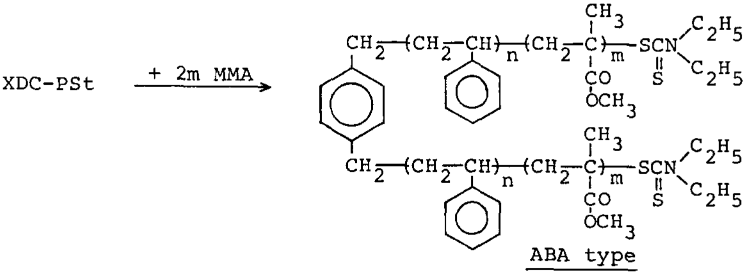

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Experimental

BDC was prepared by the reaction of benzyl chloride with sodium N,N-diethyldithiocarbamate in ethanol at room temperature, and distilled in a reduced pressure; bp 154-155°C/1 mmHg. XDC was prepared similarly from p-xylylene dichloride, and recrystallized from methanol; mp 84-84.5°C. These compounds were identified by elementary analysis, and TLC to be pure.

Monomers, solvents and other reagents were used after ordinary purifications.

Polymerizations of St and MMA were carried out in a seald tube at 30°C under irradiation of Toshiba SHL-100 UV lamp from a distance of 10 cm. After polymerization for a given time, the content of the tube was poured into a large amount of methanol to isolate the polymer. The yield of the polymers was determined from the weight of the dried polymers obtained.

Similar procedure was used for block copolymerizations. The separation of the resulting whole polymers into two homopolymers, PSt, PMMA, and block copolymer was carried out by extracting them with cyclohexane-benzene (9:1-7:3 vol%), acetonitrile and benzene, respectively. The polymer fractions thus extracted were examined by IR spectra.

The intrinsic viscosities, $[\eta]$, were determined viscometrically in benzene at 30°C, and the average-molecular weights ($\bar{M}$) were calculated by the following equations[eqs. (6) and (7)].

For PSt [ALTARES et al., 1964]: $$[\eta]= 8.5\cdot 10^{-5}\ \bar{M}^{0.75} \qquad (6)$$

For PMMA [FOX et al., 1962] : $$[\eta]= 6.27\cdot 10^{-5}\ \bar{M}^{0.76} \qquad (7)$$

The number of the N,N-diethyldithiocarbamate[$(C_2H_5)_2NCSS$-] group bonded at PSt chain ends was determined by UV spectrum in comparison with that of BDC[λ_{max}=282nm, ε=10500 in cyclohexane].

Results and Discussion

Figs. 1 and 2 show the time-conversion and time-$\bar{M}$ relations in the photo-polymerization of St and MMA, respectively, by BDC and XDC as photo-iniferters. From Fig.1, the polymer yield and $\bar{M}$ of the resulting PSt are observed to increase from an original point as a function of the reaction time. Similar results were also shown in the previous papers[OTSU et al., 1982b,1983c].

Although the yield and $\bar{M}$ of the PMMA also increase with the time, a remarkable increase of $\bar{M}$ is observed in the early stage of polymerization. This result seems to come from the difference in C-S bond structures between BDC or XDC and BDC-PMMA or XDC-PMMA[see eqs.(4) and (5)], contrary to the case of the St polymerization[see eqs.(2) and (3)], i.e. the C-S bond in BDC or XDC seems to dissociate photochemically more easily than that in BDC- or XDC-PMMA end. Moreover, the increas of $\bar{M}$ against the time observed in the later stage of polymerization is not so large, as compared with that of St polymerization. This point will be described later. In any event, it is evident that these polymerizations proceed via a living radical mechanism in homogeneous system as well as that reported by TD as photo-iniferter[OTSU et al., 1982b,1982c].

In Figs. 1 and 2, since the same concentration of the $(C_2H_5)_2NCSS$- group in BDC and XDC was used, i.e. [BDC]=[XDC]/2, the observed time-conversion relations by both BDC and XDC are

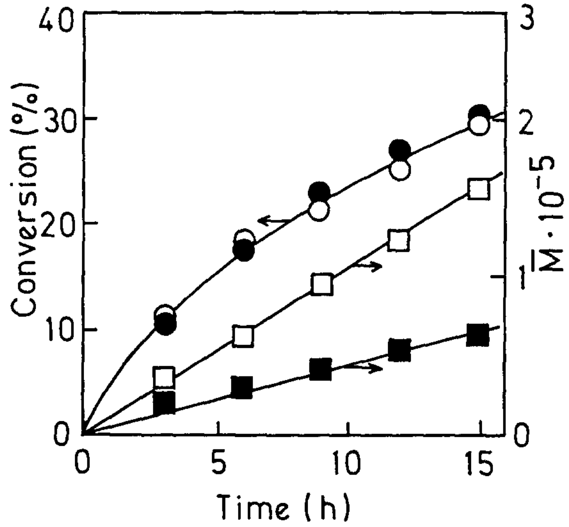


Fig. 1 Time-conversion and time-$\bar{M}$ relations in photo-polymerization of St with BDC and XDC as photo-iniferters at 30°C; [BDC]=$7.8\cdot10^{-3}$mol/l (●,■), [XDC]=$3.8\cdot10^{-3}$mol/l(○,□), [St]=6.9 mol/l in benzene.

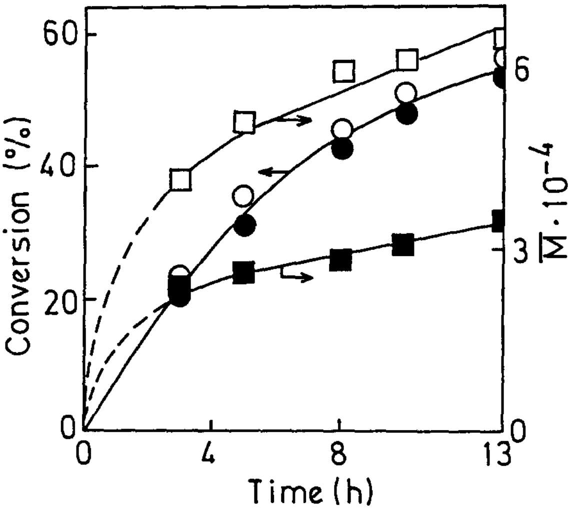


Fig. 2 Time-conversion and time-$\bar{M}$ relations in photo-polymerization of MMA with BDC and XDC as photo-iniferters; [BDC]=$7.9\cdot10^{-3}$mol/l(●,■), [XDC]=$3.9\cdot10^{-3}$mol/l(○,□), [MMA]=2.8mol/l at 30°C in benzene.

quite identical, indicating that two C-SCSN$(C_2H_5)_2$ bonds in XDC and XDC-Polymers may dissociate photochemically with a probability similar to those in BDC and BDC-Polymers into radicals which have identical reactivities.

However, the $\overline{M}$ of the polymers obtained by XDC are always two times as high as those by BDC. This result seems to also suggest that the polymerizations by BDC and XDC proceed via living mono- and biradical mechanisms, respectively, to give the BDC- and XDC-Polymers [see eqs.(2) and (3)].

To confirm further these points, the numbers of the $(C_2H_5)_2$-NCSS- group bonded at polymer chain ends were determined. The results obtained are shown in Table 1.

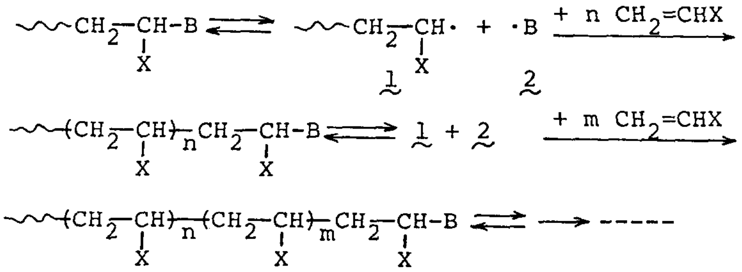
Table 1 Photo-polymerization of St by BDC and XDC[a)]

Iniferter	Time (h)	$\overline{M}$ x 10^{-4}	Number of end group[b)]
BDC	3	2.1	0.9
	6	3.2	0.9
	9	4.3	1.0
	12	5.5	1.1
	15	6.3	1.0
XDC	3	3.8	1.8
	6	6.3	1.7
	9	9.5	1.9
	12	12.2	2.0
	15	15.4	2.0

a) Polymerization conditions: [BDC]=$7.8\cdot10^{-3}$mol/l, [XDC]=$3.8\cdot10^{-3}$mol/l, [St]=6.9 mol/l in benzene at 30°C.(see Fig.1)

b) The numbers of the $(C_2H_5)_2$NCSS- end group per polymer molecule were determined from data of both UV and $\overline{M}$.

From this table, the numbers of the $(C_2H_5)_2$NCSS- end groups per one PSt chain are found to be almost constant (1.0 for BDC and 2.0 for XDC) independent of the polymerization time. These results also support the living mono- and biradical polymerization mechanisms according to eq.(8)[OTSU et al., 1982b, 1982c].



$$\sim\!\sim CH_2-\underset{X}{CH}-B \rightleftharpoons \underset{\mathbf{1}}{\sim\!\sim CH_2-\underset{X}{CH}\cdot} + \underset{\mathbf{2}}{\cdot B} \xrightarrow{+\ n\ CH_2=CHX}$$

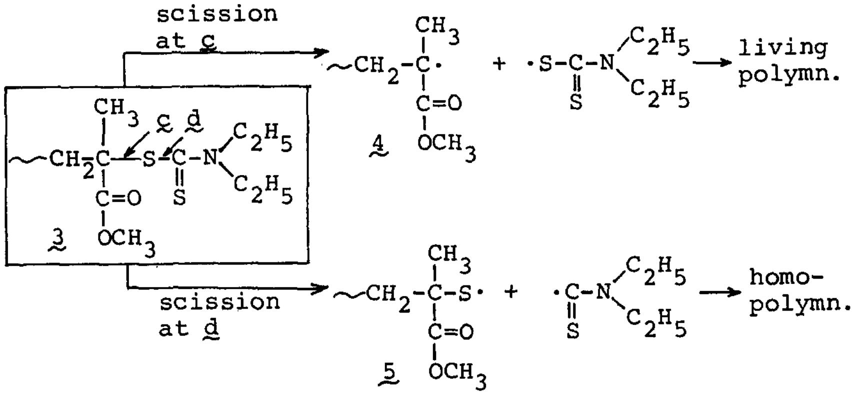
$$\sim\!\sim(CH_2-\underset{X}{CH})_n CH_2-\underset{X}{CH}-B \rightleftharpoons \mathbf{1} + \mathbf{2} \xrightarrow{+\ m\ CH_2=CHX}$$

$$\sim\!\sim(CH_2-\underset{X}{CH})_n(CH_2-\underset{X}{CH})_m CH_2-\underset{X}{CH}-B \rightleftharpoons \longrightarrow \text{-----} \qquad (8)$$

Where 1 and 2 are reactive propagating and unreactive N,N-diethyldithiocrabamate radicals, respectively.

Therefore, if the BDC-Polymers and XDC-Polymers were used as polymeric photo-iniferter of the polymerization of second monomers, the AB and ABA type block copolymers, respectively, seems to be produced. The results obtained are summarized in Table 2.

As is seen from this table, the block copolymers are produced in high yield of above 70% from block copolymerization of MMA by using BDC- and XDC-PSt. In the case of St by BDC- and XDC-PMMA, however, the yields of the block copolymers are lower about 20% than those of the above systems. These results seem to be originated from the photo-dissociation at different C-S bonds, c and d, in the PMMA end, 3, as is shown in eqs.(9) and (10).



(9)

(10)

Although living radical polymerization is performed by successive dissociation of the C-S bond, c, in 3[see eqs.(8) and (9)], a part of the PMMA end may be dissociated at the C-S bond, d, to give unreactive polymeric thiyl radical, 5, and reactive carbon radical, 4, which undergoes homopolymerization [eq.(10)]. Such photo-dissociation may be also related to somewhat low increasing tendency in the observed time-$\bar{M}$ relations in the polymerization of MMA by BDC and XDC(Fig.2).

From Table 2, however, it is evident that AB and ABA type block copolymers are produced when BDC- and XDC-Polymers were used as polymeric mono- and bifunctional photo-iniferters, respectively. Recently, we have prepared AB and ABA block copolymers consisting of random and alternating copolymer sequences by this technique, and the results will be reported in a future publication.

Table 2 Results of Block Copolymerization a)

Polymeric photo-ini-ferter(M_1)	Functi-onality	Time (h)	Second M_2 monomer (mol/l)		Fractions extracted						
					Homopoly(M_1)		Homopoly(M_2)		Block copolymer		
					Wt(%)	$\overline{M}$ 10^{-5}	Wt(%)	$\overline{M}$ 10^{-5}	Wt(%)	$\overline{M}$ 10^{-5} b)	Type c)
BDC-PSt	1	7	MMA	4.7	7	0.32	15	2.4	78	2.4	AB
BDC-PSt	1	7	MMA	4.7	13	0.63	16	3.8	71	4.0	AB
BDC-PMMA	1	10	St	6.5	31	0.26	28	0.8	41	1.0	AB
BDC-PMMA	1	10	St	6.5	35	0.35	23	1.0	42	1.3	AB
XDC-PSt	2	7	MMA	4.7	2	0.63	9	2.5	89	4.9	ABA
XDC-PSt	2	7	MMA	4.7	0	1.5	8	3.3	92	7.5	ABA
XDC-PMMA	2	10	St	6.5	14	0.51	23	0.8	62	1.9	ABA
XDC-PMMA	2	10	St	6.5	31	0.65	19	0.9	50	2.2	ABA

a) Polymerized at 30°C under irradiation of UV light from a distance of 10cm; polymeric photo-iniferter 0.2g, monomer 3ml, benzene 2ml.

b) Calculated by the following equation: $[\eta]^{2/3}_{block} = X\,(K\,\overline{M}^{\alpha})^{2/3}_{PM_1} + (1-X)(K\,\overline{M}^{\alpha})^{2/3}_{PM_2}$ [KOTAKA et al., 1975]
where X is weight fraction of M_1 unit, and K and α are reported values in molecular weight-viscosity relationships [eqs. (1) and (2)] for respective homopolymers.

c) Determined by comparing of molecular weight calculated from $[\eta]_{block}$ with that calculated for AB or ABA type block copolymer.

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