Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Living Radical Polymerization in Homogeneous System by Using Iniferter: Design of Block Copolymers

T. Otsu[a]; A. Kuriyama[a]
[a] Department of. Applied Chemistry, Faculty of Engineering, Osaka City University, Osaka, Japan

To cite this Article Otsu, T. and Kuriyama, A.(1984) 'Living Radical Polymerization in Homogeneous System by Using Iniferter: Design of Block Copolymers', Journal of Macromolecular Science, Part A, 21: 8, 961 — 977
To link to this Article: DOI: 10.1080/00222338408056585
URL: http://dx.doi.org/10.1080/00222338408056585

J. MACROMOL. SCI.—CHEM., A21(8&9), pp. 961-977 (1984)

Living Radical Polymerization in Homogeneous System by Using Iniferter: Design of Block Copolymers

T. Otsu and A. Kuriyama

Department of Applied Chemistry,
Faculty of Engineering, Osaka City University
Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

ABSTRACT

Benzyl N-ethyldithiocarbamate(BEDC) and xylylene bis(N-ethyldithiocarbamate)(XEDC) were prepared, and used as mono- and bifunctional photoiniferters, respectively, of the polymerization of styrene and methyl methacrylate. These photopolymerizations were performed via a living radical polymerization mechanism in homogeneous system. The polymers obtained by BEDC and XEDC still contained one and two reactive N-ethyldithiocarbamate end groups, respectively, bonded at their chain ends. When these polymers were reacted with nucleophiles and copper(II) ion, the chain extension reactions were observed to occur depending on their functionality. By using the polymers obtained by BEDC and XEDC as mono- and bifunctional polymeric photoiniferters, the AB and ABA block copolymers were also obtained, respectively. Similar results were obtained by using benzyl N,N-diethyldithiocarbamate(BDC) and xylylene bis(N,N-diethyldithiocarbamate)(XEDC) as mono- and bifunctional photoiniferters, respectively. These results were also compared and discussed.

INTRODUCTION

Since the termination in bulk polymerization of styrene(St) with azobisisobutyronitrile at temperatures below 80°C [1] occurs by recombination, the polymer obtained has two initiator fragments

0022-233X/84/2108-0961$3.50/0

bonded at its chain ends. However, in radical polymerization of many monomers, the termination by disproportionation and the chain transfer reactions to the compounds existed in the system occur importantly, and hence the number of the initiator fragment per one polymer molecule is always less than 2.

If the initiator (R-R') used has high chain transfer to the initiator and/or primary radical termination reactivities, the polymer with two initiator fragments can be obtained [eq.(1)].

$$\mathrm{R{-}R' + n\,M \longrightarrow R\!\left(M\right)_{n}R'} \tag{1}$$

In such cases, the polymer formation is defined as insertion reaction of the monomer molecules (M) into the R-R' bond of the initiator. In a previous paper[2],we proposed to call such initiators initiator-transfer agent-terminator(iniferter). The concept of initiator-transfer agent(inifer) in cationic polymerization has already been proposed by Kennedy[3].

From the above definition, the iniferters can be classified into various types, such as monofunctional iniferter, bifunctional iniferter; thermal iniferter, photoiniferter; monomeric iniferter and polymeric iniferter, etc.

Many initiators which have been used seem to be able to serve as iniferters, if monomers and polymerization conditions are selected. Some examples which may give mono- and bifunctional oligomers or polymers are shown as follows:

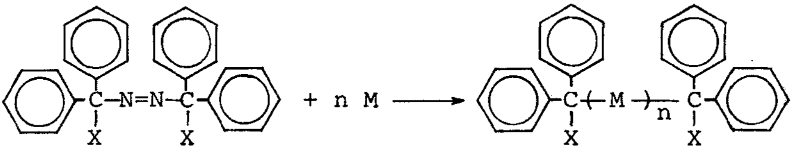
a) Peroxides — These compounds show relatively high chain transfer reactivities[1].

$$\mathrm{RO{-}OR + n\,M \longrightarrow RO\!\left(M\right)_{n}OR} \tag{2}$$

$$\mathrm{RO{-}OR' + n\,M \longrightarrow RO\!\left(M\right)_{n}OR'} \tag{3}$$

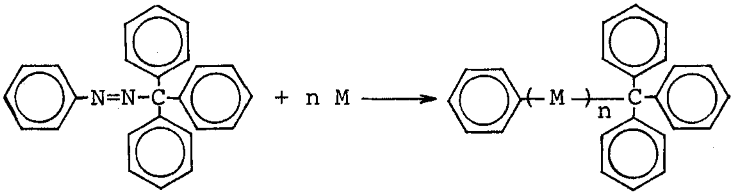
Where R and R' are hydrogen, alkyl and acyl groups.

b) Azo compounds — Aliphatic azo compounds show no chain transfer reactivity (1), but in some tetraphenyl and unsymmetric azo compounds, primary radical termination has been known to occur importantly[4,5].

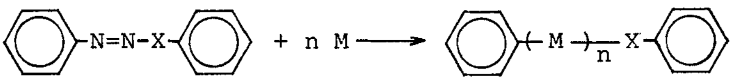


(4)

Where X is alkyl and other groups.



(5)



(6)

Where X is S and NH groups.

c) Organic sulfur compounds — These compounds show high chain transfer reactivity[6-12] and a part of thiyl radicals produced may undergo primary radical termination[9], because they are not so reactive for initiation.

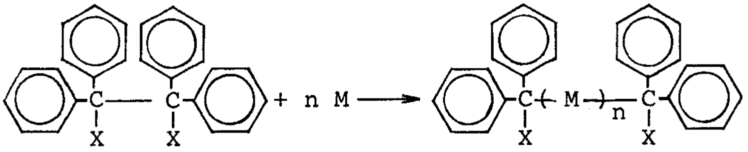
$$RS{-}R' + n\,M \xrightarrow{h\nu} RS\left(M\right)_n R' \qquad (7)$$

$$RS{-}SR + n\,M \xrightarrow[\text{or } \Delta]{h\nu} RS\left(M\right)_n SR \qquad (8)$$

$$RS{-}SR' + n\,M \xrightarrow[\text{or } \Delta]{h\nu} RS\left(M\right)_n SR' \qquad (9)$$

Where R and R' are hydrogen, alkyl, acyl and thiocarbonyl groups.

d) Tetraphenylethane derivatives — Hexaphenylethanes easily dissociate into triphenylmethyl radicals which are so stable and they can not enter into initiation[13]. However, some diphenylmethyl radicals can participate into both initiation and termination.

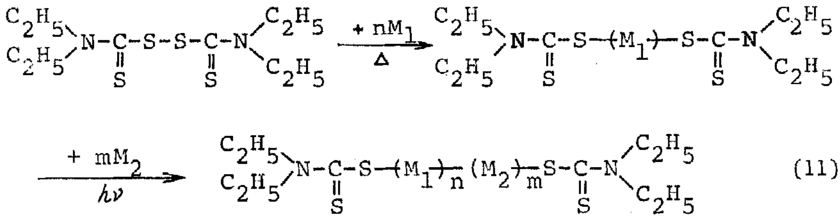


(10)

Wher X is CN[14], C_2H_5[15], OC_6H_5 groups[16].

Thus, when such iniferters were used for radical polymerization of vinyl monomers, various mono- and bifunctional oligomers or polymers might be obtained, and used for synthesizing of the other functional and block polymers.

In 1957, we reported that the polymers obtained by tetraethylthiuram disulfide could induce radical polymerization of second monomers leading to block copolymers[17,18], as follows.

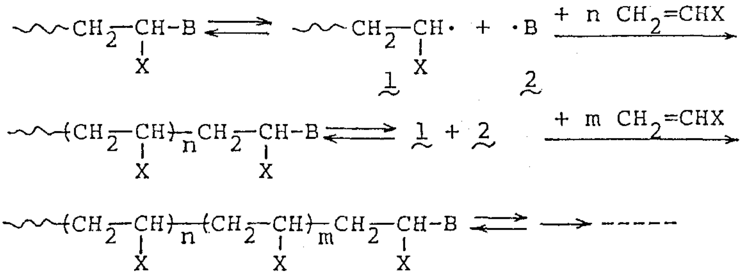


$$(C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-N(C_2H_5)_2 \xrightarrow[\Delta]{+\,nM_1} (C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-S-(M_1)-S-\underset{\underset{S}{\|}}{C}-N(C_2H_5)_2$$

$$\xrightarrow[h\nu]{+\,mM_2} (C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-S-(M_1)_n(M_2)_m-S-\underset{\underset{S}{\|}}{C}-N(C_2H_5)_2 \qquad (11)$$

Although this reaction scheme was not ascertained, some block copolymers as polystyrene-b-polymethyl methacrylate[17], polystyrene-b-polyvinyl acetate[18] and polystyrene-b-polyvinyl alcohol[18] were prepared by this technique. Recently, the end group in this polymer was confirmed to be diethyldithiocarbamate sensitive for photodissociation, and the number of this end group per one polymer molecule was found to be kept constant as nearly 2 during the polymerization[19]. If these were true, the photopolymerization of vinyl monomers with tetraethylthiuram disulfide is expected to proceed via a living radical mechanism[20] even in homogeneous system which is similar to living ionic polymerization which was discovered in 1956 by Szwarc[21,22].

From such results and consideration, we recently proposed a model for living radical polymerization in homogeneous system by using phenylazotriphenylmethane and tetraethylthiuram disulfide as thermal and photoiniferters, respectively[20]. This idea is attributed to that a short-lived unstable radical including propagating radical is only existed as its dimer consisting of covalent bond, and if this bond can dissociate, the unstable radical may be supplied into the system. Therefore, this model can be expressed as follows:



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

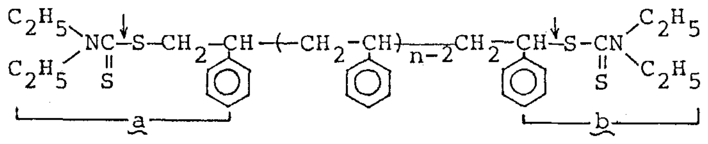
$$\sim\!\sim(CH_2-\underset{X}{CH})_n CH_2-\underset{X}{CH}-B \rightleftarrows 1 + 2 \xrightarrow{+\ m\ CH_2=CHX}$$

$$\sim\!\sim(CH_2-\underset{X}{CH})_n(CH_2-\underset{X}{CH})_m CH_2-\underset{X}{CH}-B \rightleftarrows \longrightarrow ----- \qquad (12)$$

Namely, the propagating chain ends which can dissociate thermally or photochemically into a propagating radical(1) and a small radical(2) which must be stable enough not to initiate new polymer chain, and recombine easily with propagating radical. If these dissociation, monomer addition and recombination cycles are repeated, such a radical polymerization proceeds apparently via a living radical mechanism. The polymerizations by phenylazotriphenylmethane and tetraethylthiuram disulfide as thermal and photo-iniferters are clear to be an example for such polymerization.

Therefore, in the polymerization of styrene and methyl methacrylate with these iniferters, the yield and average molecular weight of the polymers were found to increase as a function of the polymerization time[20]. The efficient formation of two or multi component block copolymers [23,24] might support that these polymerizations proceeded via living radical mechanism in homogeneous system, as shown in eq.(12).

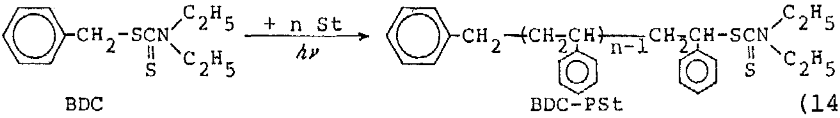
However, the structure of the polystyrene obtained by tetraethylthiuram disulfide, as an example, is expressed by eq.(13)[19].



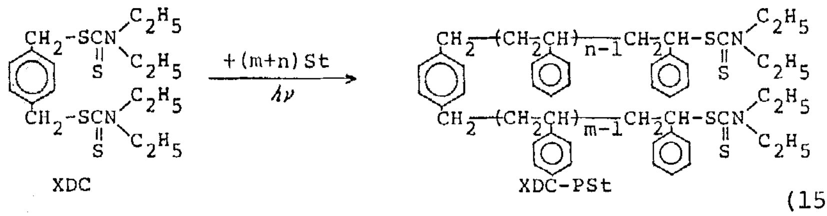
(13)

From this equation, the diethyldithiocarbamate groups are bonded to both polymer chain ends with a different linkage, a and b, which are expected to show different reactivities for photodissociation and initiation. In fact, phenylethyl diethyldithiocarbamate and benzyl diethyldithiocarbamate, model compounds for a and b end groups, respectively, were observed to show a different reactivity for initiation as the result of photodissociation at the different C-S bonds[25] which are shown by an arrow in eq.(13), i.e. the latter model compound was effective photoiniferter rather than the former[24].

To design the AB and ABA type structure of block copolymers by this technique, therefore, we must choose mono- and bifunctional polymeric photoiniferters, respectively, which consisted of identical bonds. For this purpose, benzyl N,N-diethyldithiocarbamate (BDC) and xylylene bis(N,N-diethyldithiocarbamate)(XDC) were synthesized, and used as mono- and bifunctional photoiniferters, respectively, in the polymerization of styrene and methyl methacrylate[26]. If these styrene polymerizations proceed according to a living radical mechanism [eq.(12)], the polymers with an identical chain end group seems to always be formed during the polymerization, as is shown in eqs.(14) and (15).



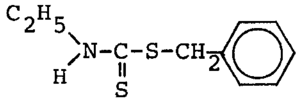
(14)



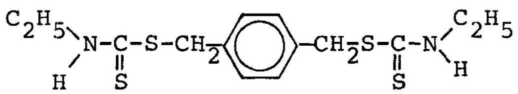
(15)

These possibilities were confirmed, and AB and ABA block copolymers were obtained by using polymers obtained by BDC and XDC(BDC-PSt and XDC-PSt), respectively[26]. The results will describe in this paper.

To clarify further these points, benzyl N-ethyldithiocarbamate (BEDC) and xylylene bis(N-ethyldithiocarbamate)(XEDC) were also prepa prepared, and used as photoiniferter of the polymerization of styrene (St) and methyl methacrylate(MMA).



BEDC



XEDC

Moreover, the polymers, (BEDC-PSt or BEDC-PMMA and XEDC-PSt or XEDC-PMMA), were used as telechelic(end-reactive) polymers for chain extension reaction, and as polymeric photoiniferters of the polymerization of second monomers in order to obtain AB and ABA block copolymers. The results will also shown in this paper.

EXPERIMENTAL

BDC and XDC were prepared according to the previous paper[26]. BEDC was prepared by the reaction of benzyl chloride with sodium N-ethyldithiocarbamate dihydrate in ethanol at room temperature. The crude BEDC was then purified by using column chromatography [column: silicagel(Wakogel C-200), solvent: benzene : n-hexane= 3 : 7]. The colorless viscous liquid thus obtained was confirmed by TLC, IR and NMR spectra(Fig. 1) to be pure. XEDC was prepared by the reaction of p-xylene dichloride with sodium N-diethyldithiocarbamate anhydrate in benzene/methanol (1 : 1) mixed solvent at 0°C, and recrystallized from chloroform/n-hexane mixture. XEDC thus obtained was also confirmed to be pure by TLC, IR, NMR(Fig. 1) and elementary analysis:

Obsd. C 48.50, H 5.94, N 8.06%; Calcd. C 48.79, H 5.86, H 8.13%

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

Polymerizations of St and MMA were carried out in a sealed glass tube at 30°C under irradiation of Toshiba SHL-100 UV lamp from a distance of 10cm. 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 whole polymers into two homopolymers, PSt and PMMA, and block copolymer was carried out by extracting them with cyclohexane/benzene (9 : 1- 7 : 3 vol%), acetonitrile and benzene, respectively. The fractions thus separated were checked by IR spectra.

The intrimsic viscosities, $[\eta]$, were determined viscometrically in benzene at 30°C, and the average-molecular weight($\overline{M}$) was calculated by the following equations:

$$\text{For PSt [27]: } [\eta] = 8.5 \cdot 10^{-5}\, \overline{M}^{0.75}$$
$$\text{For PMMA [28]: } [\eta] = 6.27 \cdot 10^{-5}\, \overline{M}^{0.76}$$

The number of the N,N-diethyldithiocarbamate group bonded at polystyrene end was determined by average-molecular weight and UV spectrum in comparison with that of BDC [λ_{max} 282 nm and ε=10500 in cyclohexane].

RESULTS AND DISCUSSION

Photopolymerizations with BEDC, BDC, XEDC and XDC

Figs. 1 and 2 show the time-conversion and time-$\overline{M}$ relations in the photopolymerizations of St and MMA, respectively, by BEDC, BDC, XEDC and XDC as photoiniferters.

From these figures, the yield and $\overline{M}$ of the polymers formed are observed to increase as a function of reaction time, indicating that the polymerizations proceed via a living radical mechanism in homogeneous system[20]. Similar results were reported already for the photopolymerizations of St and MMA with tetraethylthiuram disulfide[19,20], and for the polymerization of MMA with phenylazotriphenylmethane[20], in which the time-$\overline{M}$ relations were observed to increase from an original point with the time.

The time-$\overline{M}$ relation observed for the St polymerization with BDC is similar to the above cases reported, but that found for the other photoiniferters does not cross the original point, i.e. the extent of increasing in $\overline{M}$s against the time decreases. This reason seems to come from that a part of the polymer chain ends effective to a living radical propagation is destroyed.

As is shown in Figs.1 and 2, when the concentration of the $(C_2H_5)_2NCSS$- end group in BDC and XDC used was selected to be iden-

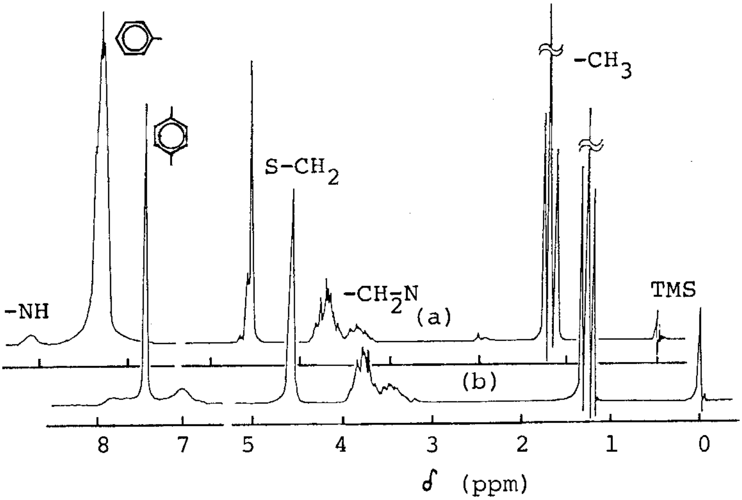


Fig. 1 H-NMR spectra of BEDC(a) and XEDC(b)

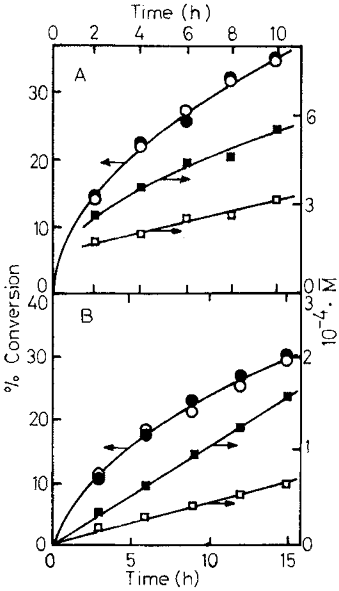


Fig. 2 Time-conversion and time-$\bar{M}$ relations in photopolymerization of St with BEDC, XEDC, BDC and XDC as photoiniferters;

A: [BEDC]=$2.0\cdot10^{-2}$mol/l (○,□)

[XEDC]=$1.0\cdot10^{-2}$mol/l (●,■)

B: [BDC]= $7.8\cdot10^{-3}$mol/l (○,□)

[XDC]= $3.8\cdot10^{-3}$mol/l (●,■)

[St]=6.9mol/l in benzene at 30°C.

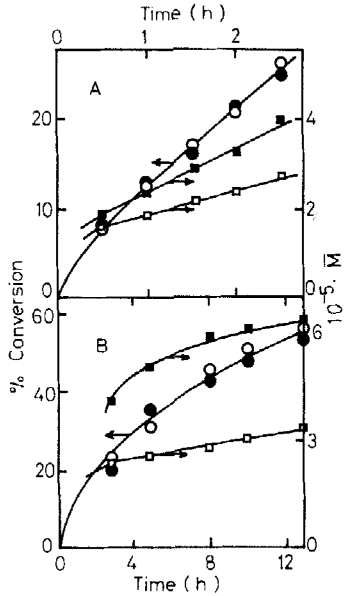


Fig 3 Time-conversion and time-$\bar{M}$ relations
in photopolymerization of MMA with BEDC, XEDC,
BDC and XDC as photoiniferters;
A: [BEDC] = 1.0 · 10^{-3}mol/l (○, □),
[XEDC] = 0.5 · 10^{-3}mol/l (●, ■),
B: [BDC] = 7.9 · 10^{-3}mol/l (○, □),
[XDC] = 3.9 · 10^{-3}mol/l (●, ■),
[MMA] = 2.8mol/l at 30°C in benzene.

tical, i.e. [BDC]=[XDC]/2, the observed time-conversion relations for both BDC and XDC are quite identical each other, indicating that all the $(C_2H_5)_2NCSS-C$ bonds in XDC and XDC-polymer may dissociate photochemically with a probability similar to those in BDC and BDC-polymer into radicals which have identical reactivities. Similar results were also obtained for photopolymerizations with BEDC and XEDC.

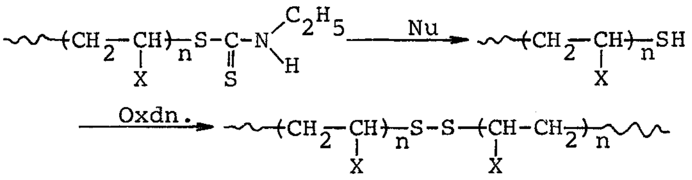
However, the $\bar{M}$s of the polymers obtained with XDC are always two times larger than those with BDC. In the case of XEDC, the increase in $\bar{M}$s is somewhat less than two times of the $\bar{M}$s obtained with BEDC. This may be due to that a part of the effective polymer chain end is deactivated.

To confirm whether these polymerizations proceed via a living radical mechanism, the number of the end groups of the polymers produced in photopolymerizations of St with BDC and XDC was determined. The results are shown in Tables 1 and 2.

From these tables, although the $\overline{M}$s of the polymers produced by BDC and XDC increase with the time, the number of the $(C_2H_5)_2NCSS$- end groups per one polymer molecule are found to be almost constant (1.0 for BDC and 2.0 for XDC) independent of the reaction time. These results strongly suggest that the polymerizations with BDC and XDC proceed via a living mono- and biradical polymerization mechanisms, respectively [see eq.(12)].

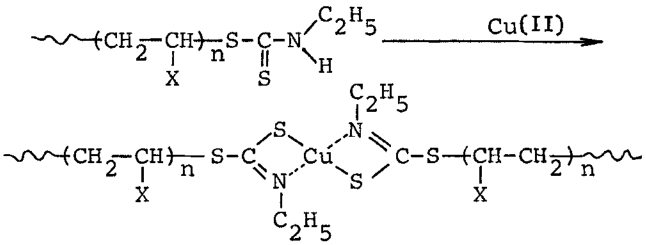
Chain Extension Reactions of the Poly(St)s Obtained by BEDC and XEDC

Okawara and coworkes[29] have reported that the N-ethyldithiocarbamate ester group in the polymer of St is easily hydrolyzed with some nucleophiles as sodium hydroxide and dimethylamine to the thiol group which is then oxidized, and it also forms a chelate bond with divalent metal ions such as Cu(II) ion. If these reactions are applied to mono- and bifunctional polymers obtained by BEDC and XEDC, respectively, the following chain extension reactions seem to occur.



$$\sim\!\!\sim(CH_2-\underset{X}{CH})_n-S-\underset{S}{\overset{\|}{C}}-N\begin{smallmatrix}C_2H_5\\H\end{smallmatrix} \xrightarrow{Nu} \sim\!\!\sim(CH_2-\underset{X}{CH})_n-SH \xrightarrow{Oxdn.} \sim\!\!\sim(CH_2-\underset{X}{CH})_n-S-S-(\underset{X}{CH}-CH_2)_n\sim\!\!\sim$$

(16)



(17)

Table 1 Number of $(C_2H_5)_2NCSS$- End Groups of the Polymers Produced in Photopolymerization of St with BDC and XDC[a)]

Iniferter	Time (h)	$\overline{M}$ $\times 10^{-4}$	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]=6.9mol/l in benzene at 30°C.

b) The numbers of the $(C_2H_5)_2NCSS$- end group per polymer molecule was determined from data of UV and $\overline{M}$.

Table 2 $\overline{Mn}$, $\overline{Mw}$, $\overline{Mw}/\overline{Mn}$ and Number of $(C_2H_5)_2NCSS$- End Groups of the Polymers Produced in Photopolymerization of St with BDC at 30°C[a)]

Time (h)	$\overline{Mn}$[b)] $\times 10^{-4}$	$\overline{Mw}$[b)] $\times 10^{-4}$	$\overline{Mw}/\overline{Mn}$	Number of end group[c)]
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 condition; [St]=7.2mol/l, [BEDC]=7.7 mol/l.

b) Determined by gel permeation chromatography.

c) The number of the $(C_2H_5)_2NCSS$- end group per one molecule was determined from both data of UV and $\overline{Mn}$.

The results of the reactions with nucleophiles are shown in Table 3. The polymers with one and two thiol groups bonded at the chain ends were not isolated, but the chain extension reaction of the polymers was observed to occur through a disulfide bond formation. When the monofunctional polymer obtained by BEDC was used, the $\overline{M}$ of the polymer obtained after reaction increases about two times as compared with that before reaction. However, in the cases of the bifunctional polymers obtained by XEDC, their $\overline{M}$s increase about 3-5 times rather than those before reaction.

Similar results were also obtained for chain extension reactions by a chelate bond formation as is shown in Table 4. If the polymers consist of mono- and bifunctional structure and the reactions occur completely, the $\overline{M}$ must increase to two times and infinite quantity, respectively. As is seen from Tables 1 and 2, the observed functionalities of the polymers are somewhat lower than those expected (1.0 and 2.0 for BEDC- and XEDC-polymers, respectively). Therefore, the observed results (Tables 3 and 4) seem to come from these reasons.

Block Copolymerizations — Synthesis of AB and ABA Block Copolymers

Table 5 shows the results of block copolymerizations of MMA with the polymers of St obtained by BDC and XDC (BDC-PSt and XDC-PSt) as mono- and bifunctional polymeric photoiniferters, respectively. From this table, when the $\overline{M}$s of BDC-PSt and XDC-PSt increased, i.e. the concentration of the end group decreased, the yields of MMA polymerized were observed to decrease. However, the yields of the block copolymers with XDC-PSt(~90%) were higher than those with BDC-PSt (~70%).

To synthesize AB and ABA block copolymers, the polymers obtained by BDC or BEDC and XDC or XEDC as photoiniferters were used as mono- and bifunctional polymeric photoiniferters, respectively of the polymerizations of second monomers. The results are shown in Table 6.

From comparison of the $\overline{M}$s of the block copolymers determined (see footnote of Table 6) with those calculated, AB and ABA block

Table 3 Chain Extention Reaction of BEDC- and XEDC-Polymers by Disulfide Bond Formation[a)]

Polymer	Before reaction $\bar{M}_o \cdot 10^{-4}$	After reaction $\bar{M} \cdot 10^{-4}$	$\bar{M} / \bar{M}_o$
BEDC-PSt	2.5	4.2	1.7
XEDC-PSt	2.6	6.3	2.4
XEDC-PSt	4.6	26.2	5.7
XEDC-PSt[b)]	4.6	16.2	3.5
XEDC-PSt[c)]	4.6	23.8	5.2

a) Reaction conditions: polymer 0.3g in dioxane(10ml) was reacted with 10% aq. NaOH(1ml) at 60°C for 8h, and then oxidized by air at room temp. for 1 day.

b) 50% aq. $(CH_3)_2NH$ was added as nucleophile instead of aq. NaOH.

c) SeO_2(20mg) was added as oxidation catalyst.

Table 4 Chain Extention Reaction of BEDC- and XEDC-Polymers by Chelate Formation[a)]

Polymer	Before reaction $\bar{M}_o \cdot 10^{-4}$	After reaction $\bar{M} \cdot 10^{-4}$	$\bar{M} / \bar{M}_o$
BEDC-PSt	2.1	3.6	1.7
BEDC-PSt	2.5	4.4	1.8
XEDC-PSt	2.6	12.7	4.9
XEDC-PSt[b)]	2.6	14.7	5.6
XEDC-PSt	4.6	18.9	4.1

a) Chelating reaction: polymer 0.2g, $Cu(CH_3COO)_2$ 0.2g, DMF 5ml, at room temp. for 2 days.

b) Chelating reaction was performed for 6 days.

Table 5 Block Copolymerization of MMA with BDC- and XDC-PSts[a)]

Polymeric photoini-ferter(M_1)	$\bar{M} \cdot 10^{-4}$	Total yield (g)	Fractions extracted (%)		
			Homo-poly(M_1)	Homo-poly(M_2)	Block copolymer
BDC-PSt	3.2	0.78	7	15	78
	4.3	0.64	8	16	76
	5.5	0.56	9	17	74
	6.3	0.50	13	16	71
	8.6	0.42	16	20	64
XDC-PSt	3.8	1.10	0	8	92
	6.3	0.99	2	9	89
	12.0	0.58	6	6	88
	15.0	0.49	0	8	92
	28.0	0.45	9	1	90

a) Polymerization at 30°C under irradiation of UV light from a distance of 10cm; polymeric photoiniferter 0.2g, [MMA]=4.7mol/l in benzene.

Table 6 Results of Block Copolymerizations[a)]

Polymeric photoini-ferter(M_1)	Functiona-lity	Second(M_2) monomer (mol/l)	Time (h)	Total yield (g)	Fractions extracted						Type of block copolymer[c)]
					HomoM$_1$ polymer		HomoM$_2$ polymer		Block copolym.		
					Wt(%)	$\bar{M}\cdot10^{-5}$	Wt(%)	$\bar{M}\cdot10^{-5}$	Wt(%)	$\bar{M}\cdot10^{-5}$[b)]	(calcd.$\bar{M}\cdot10^{-5}$)
BEDC-PSt	1	MMA(4.7)	3	0.59	17.8	0.24	29.1	3.7	53.1	4.0	AB (3.9)
BEDC-PMMA	1	St (6.5)	6	0.29	41.0	1.56	12.8	1.3	46.2	3.0	AB (2.9)
XEDC-PSt	2	MMA(4.7)	3	0.79	8.7	0.36	25.0	1.7	66.3	3.8	ABA (3.8)
XEDC-PMMA	2	St (6.5)	6	0.29	19.4	2.36	16.4	1.2	64.2	4.3	ABA (4.8)
BDC-PSt	1	MMA(4.7)	3	0.78	7.0	0.32	15.0	2.4	78.0	2.4	AB (2.7)
BDC-PMMA	1	St (6.5)	6	0.33	35.0	0.35	23.0	1.0	42.0	1.3	AB (1.4)
XDC-PSt	2	MMA(4.7)	3	0.99	2.0	0.63	9.0	2.5	89.0	4.9	ABA (5.6)
XDC-PMMA	2	St (6.5)	6	0.34	31.0	0.65	19.0	0.9	50.0	2.2	ABA (2.5)

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

b) Calculated by the following equation:

$$[\eta]^{2/3}_{block}=x(8.5\cdot10^{-5}\,\bar{M}^{0.75})^{2/3}+(1-x)(6.27\cdot10^{-5}\,\bar{M}^{0.76})^{2/3}$$

x: weight fraction of St unit.

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

copolymers were produced when the polymers obtained by BDC or BEDC and XDC or XEDC were used as mono- and bifunctional polymeric photo-iniferters, respectively.

By using this technique, we have recently synthesized the AB and ABA block copolymers consisting of random and alternating copolymer sequences, and the star-type block copolymers. These results will be described in a future publication.

REFERENCES

[1] J. C. Bevington, "Radical Polymerization", Academic Press Inc., New York 1961, p.136

[2] T. Otsu and M. Yoshida, Makromol. Chem., Rapid Commun., 3, 127 (1982)

[3] J. P. Kennedy, J. Macromol. Sci., Chem., 13, 695(1979)

[4] K. Ito, M. Omi and T. Ito, Polym. J., 14, 115(1982)

[5] D. H. Hey and G. S. Misra, J. Chem. Soc., 1949, 1807

[6] T. Otsu, J. Polym. Sic. 21, 559(1956)

[7] T. Otsu, K. Nayatani, I. Muto, M. Imai, Makromol. Chem., 27, 142 (1958)

[8] T. Otsu and K. Nayatani, Makromol. Chem., 27, 149(1958)

[9] T. Otsu, Mem. Fac. Eng., Osaka City Univ., 3, 205(1961); Chem. Abstr., 57, 12689f(1962)

[10] T. Otsu, Y. Kinoshita and M. Imoto, Makromol. Chem., 73, 225 (1964)

[11] K. Tsuda and T. Otsu, Bull. Chem. Soc. Jpn., 39, 2206(1966)

[12] K. Tsuda, S. Kobayashi and T. Otsu, Bull. Chem. Soc. Jpn., 38, 1517(1965)

[13] M. Gomberg, J. Am. Chem. Soc., 22, 757(1900)

[14] G. V. Schulz, Z. Electrochem., 47, 265(1941)

[15] E. Borsig, M. Lazar and M. Capla, Makromol. Chem., 105, 212 (1967)

[16] D. Braun and A. Bledzki, Makromol. Chem., 182, 1047(1981)

[17] T. Otsu, J. Polym. Sci. 26, 236(1957)

[18] M. Imoto, T. Otsu, J. Yonezawa, Makromol. Chem., 36, 93(1960)

[19] T. Otsu, M. Yoshida and A. Kuriyama, Polym. Bull., 7, 45(1982)

[20] T. Otsu, M. Yoshida and T. Tazaki, Makromol. Chem., Rapid Commun., 3, 133(1982)

[21] M. Szwarc, Nature(London), 198, 1168(1956)

[22] M. Szwarc, M. Levy and Milkovich, J. Am. Chem. Soc., 78, 2656 (1956)

[23] T. Otsu and M. Yoshida, Polym. Bull., 7, 197(1982)

[24] T. Otsu and A. Kuriyama, Kobunshi Ronbunshu, 40, 583(1983)

[25] M. Okawara, T. Nakai, K. Morishita and E. Imoto, Kogyo Kagaku Zasshi, 67, 2108(1964)

[26] T. Otsu and A. Kuriyama, Polym. Bull., in contribution
[27] T. Altares, D. P. Wyman and V. R. Allen, J. Polym. Sci., A2, 4533(1964)
[28] T. G. Fox, J. B. Kinsinger, H. F. Mason and E. M. Schnele, Polymer, 3, 71(1962)
[29] T. Nakagawa, Y. Taniguchi and M. Okawara, Kogyo Kagaku Zasshi, 70, 2382(1967)