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KINETICS OF THE PHOTOPOLYMERIZATION OF VINYL MONOMERS BY BIS(ISOPROPYLXANTHOGEN) DISULFIDE. DESIGN OF BLOCK COPOLYMERS

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ABSTRACT

Bis(isopropylxanthogen) disulfide (BX) has been used as a photoinitiator with various vinyl monomers at 30°C. The kinetics of polymerization of styrene (St) and methyl methacrylate (MMA) at 30°C were studied for various concentrations of monomer and initiator. The observed deviations in polymerization rate from simple kinetic theory could be explained in terms of primary radical termination. The fraction of primary radical terminating chains was obtained as a function of various concentrations. The ratio of the rate constants for chain initiation and chain termination by a primary radical was determined to be 3.34×10^7 for St and 2.60×10^7 for MMA. The number-average degree of polymerization ($\overline{DP}_n$) of polymers obtained by photopolymerization with BX was found to increase linearly with conversion. However, the $\overline{DP}_n$ extrapolated to zero conversion was in good agreement with that calculated on the basis of the kinetic scheme. It was found that BX had interesting properties for the design of block copolymers, i.e., BX acts as a terminator and a chain transfer agent as well as an initiator in these polymerizations. The polymers obtained with BX contained two reactive isopropyl xanthate groups bonded at their chain ends, which could also act as macrophotoinitiators.

INTRODUCTION

Bis(isopropylxanthogen) disulfide (BX) is widely used in the rubber industry as a vulcanization accelerator. In an earlier paper [1] we showed that BX acts as a chain transfer agent in the polymerization of styrene (St) initiated by AIBN in the dark.

Further, some observations of such polymers obtained by the polymerization of St and methyl methacrylate (MMA) [2] reveal the presence of terminal groups consisting of BX fragments.

Recently, the terminal functional group in these polymers was confirmed to be isopropylxanthate, which was itself sensitive as a photoinitiator. The functional polymers could induce polymerization of second vinyl monomers leading to block copolymers [2, 5], as in Scheme 1.

These investigations suggest that BX generates active free radicals on irradiation that can initiate polymerization of vinyl monomers at low temperature. If the initiator used has a high reactivity for chain transfer to the initiator, a polymer incorporating initiator fragments can be obtained. Therefore, the photopolymerization by BX opens the possibility of designing a polymer structure by radical polymerization. The concept of "inifer" in cationic polymerization and of "iniferter" in radical polymerization has already been proposed by Kennedy [3] and Otsu [4], respectively.

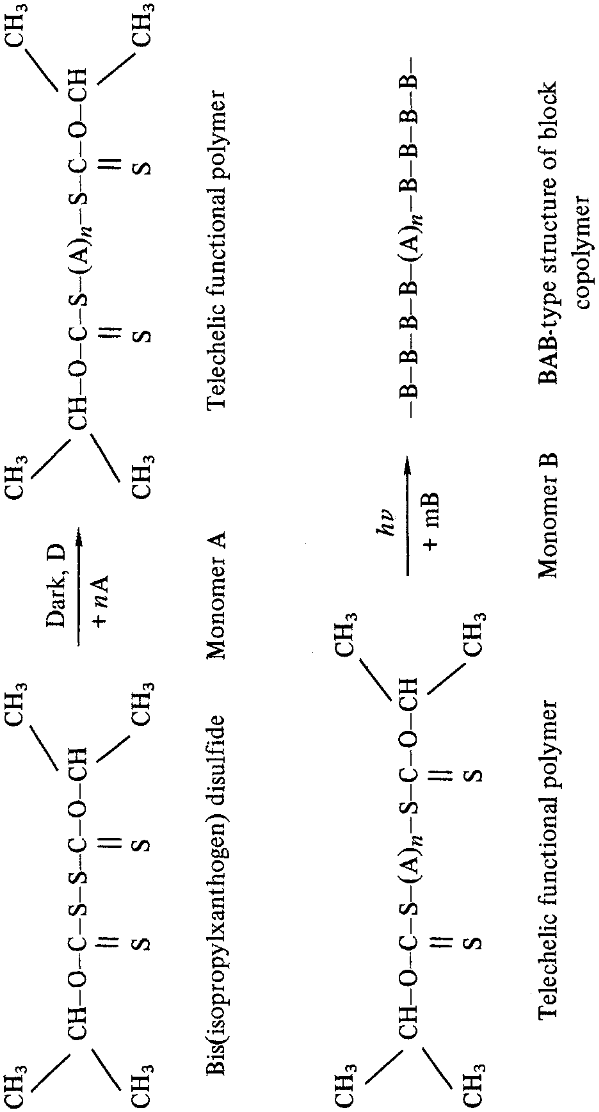
To obtain further information about design of block copolymers, we have studied in detail the photopolymerization of vinyl monomers initiated by BX. The present paper describes some results about the kinetics of the polymerization of MMA and St at 30°C. Examples of application of the resulting functional polymers are also described. Our conclusions are similar to those obtained recently for the photopolymerization of vinyl monomers with thiuram disulfides by Otsu [4].

EXPERIMENTAL

BX was obtained from K & K Laboratories, Inc. BX was recrystallized twice from acetone, mp 58.5°C.

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

Polymerizations were carried out in bulk and in benzene. To the monomer was added a given amount of BX in a hard-glass tube. The tube was degassed under vacuum by the usual freezing and thawing technique and then


Bis(isopropylxanthogen) disulfide
Dark, D
+ nA
Monomer A
Telechelic functional polymer
hν
+ mB
Monomer B
BAB-type structure of block copolymer
Telechelic functional polymer
—B—B—B—B—(A)n—B—B—B—B—

SCHEME 1.

sealed. The tubes were irradiated by a Rikosha low-pressure mercury lamp at a constant distance of 50 mm. The reaction temperature was maintained at 30°C during irradiation.

After polymerization for a given time, the content of the tube was poured into a large excess of a nonsolvent, such as petroleum ether or methanol. The precipitated polymer was reprecipitated several times from acetone solution into nonsolvent to remove unreacted monomer and BX. The polymer was dried in a vacuum oven at 60°C to constant weight.

The terminal functional group of the polymer was determined by the method described previously [2]. The UV spectrum was recorded with a Shimadzu UV-120 spectrophotometer using chloroform.

The number-average molecular weight of the polymer was measured with either a Knauer vapor-pressure osmometer (for samples with $\overline{M}_n < 20\ 000$) or a Knauer membrane osmometer.

Gel-permeation chromatograms were obtained with a Shimadzu LC-3A high-performance liquid chromatograph equipped with three polystyrene gel columns and dual UV and RI detectors. The number-average and weight-average molecular weights were obtained from GPC results by the usual procedures using the calibration curves.

RESULTS AND DISCUSSION

Photopolymerization of Vinyl Monomers Initiated by Bis(Isopropylxanthogen) Disulfide

Photopolymerization of five different vinyl monomers in the presence of BX was carried out in bulk at 30°C for 3 h. The results obtained are shown in Table 1. All monomers used in this experiment (St, MMA, acrylonitrile (AN), methyl acrylate (MA), and vinyl acetate (VAc)) were polymerized, and the conversion increased in the following order: MA > MMA >> AN = VAc > St. The polymerization of St, MMA, MA, and VAc proceeded homogeneously. However, as the polymerization of AN proceeded, the system became heterogeneous with the precipitation of poly(AN).

It is obvious that BX has the ability to initiate the photopolymerization of vinyl monomers.

Effect of BX Concentrations on the Rate of Polymerization

Figure 1 illustrates some examples of time-conversion curves for the bulk polymerization of MMA in the presence of BX at various concentrations. The

TABLE 1. Photopolymerization of Various Vinyl Monomers in the Presence of Bis(Isopropylxanthogen) Disulfide[a]

Vinyl monomer	Polymerization time, h	Polymer yield, %	$\overline{M}_n \times 10^{-3}$
Styrene	3.0	13.9	8.72
Methyl methacrylate	3.0	90.8	51.5
	0.25	10.5	25.2
Acrylonitrile	3.0	36.4	–
Methyl acrylate	3.0	96.3	71.5
	0.10	26.6	11.9
Vinyl acetate	3.0	34.6	20.5

[a] Polymerization in bulk at 30°C; BX concentration, 10.0 mmol/l.

rate of polymerization, which is very low in the absence of BX as shown by Line A in Fig. 1, rises markedly with BX concentration. BX is an excellent photoinitiator for the polymerization of MMA and St. Since the time-conversion plots were straight lines, the rate of polymerization, R_p, was determined from the slope of these lines. When the ln R_p values were plotted against logarithms of the BX concentrations, linear relationships were not obtained for both MMA and St, as seen from Fig. 2. The observed values of R_p at high [BX] fall below the values expected on the basis of the relationship

$$R_p = k[\mathrm{I}]^{1/2}[\mathrm{M}].$$

It is of interest that the rate equation does not agree with that of general catalyzed vinyl polymerization.

To confirm this point, R_p values were also plotted against the square root of the concentrations of BX, as shown in Fig. 3. The plot is strongly curved. The rate of polymerization rises rapidly with [BX] until a concentration of approximately 4 mmol/L is reached; further increases in the concentration have little effect on the rate. In both cases the relation has the familiar form. Accordingly, for BX initiation the dependence of initiator concentration on the rate of polymerization markedly deviated from the square-root rule.

Similar behavior has been observed with tetraalkylthiuram disulfide and

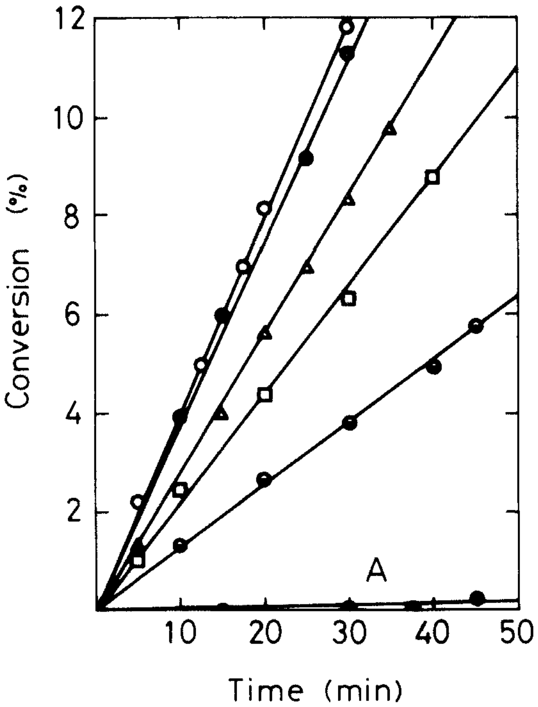


FIG. 1. Relationship between polymerization time and conversion for methyl methacrylate polymerization initiated by bis(isopropylxanthogen) disulfide (BX) at 30°C in bulk. [BX] in mmol/L: (A) 0; (○) 0.10; (□) 0.30; (△) 1.00; (●) 10.0; (○) 100; [M] = 9.28 mol/L.

phenylazotriphenylmethane. Tobolsky [6] indicated that the rate of polymerization is not proportional to the square root of the concentration of tetrathiuram disulfide. Otsu [7] indicated that the termination occurs due to reaction between the growing polymer radical and tetraalkylthiuram disulfide under thermal conditions. Misra et al. [8] dealt with the primary radical termination for the polymerization of St initiated by phenylazotriphenylmethane.

The possibility of such terminations was confirmed in this polymerization. For BX, the kinetic scheme is represented as follows:

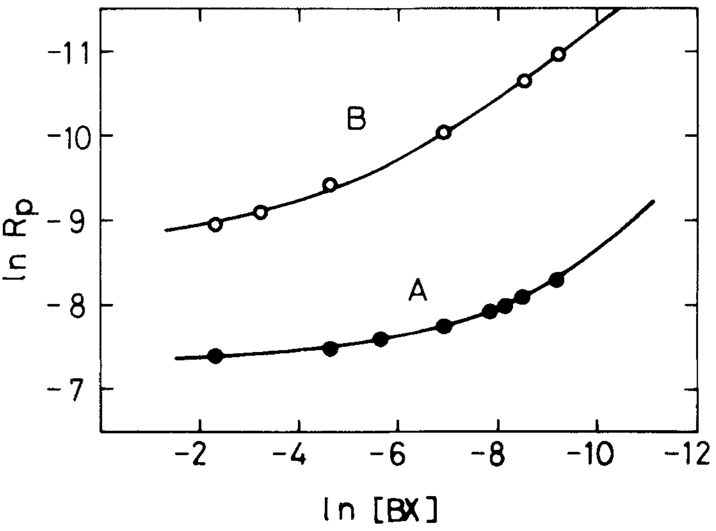


FIG. 2. Effect of concentrations of bis(isopropylxanthogen) disulfide (BX) on the rate of polymerization (R_p) of methyl methacrylate (A) and styrene (B) initiated by BX in bulk at 30°C.

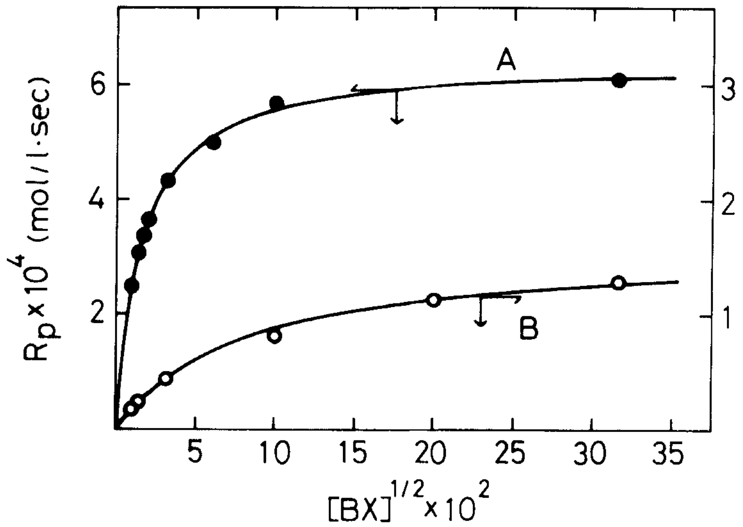


FIG. 3. Rate of polymerization as a function of bis(isopropylxanthogen) disulfide (BX) concentration. 30°C. A, [MMA] = 9.28 mol/L; B, [St] = 8.64 mol/L. Curves calculated from Eq. (3).

$$\mathrm{BX} \xrightarrow{k_d} m\mathrm{R}^*,$$

$$\mathrm{R}^* + \mathrm{M} \xrightarrow{k_i} \mathrm{P}_1{}^*,$$

$$\mathrm{P}_n{}^* + \mathrm{M} \xrightarrow{k_p} \mathrm{P}^*_{n+1},$$

$$\mathrm{P}_n{}^* + \mathrm{M} \xrightarrow{k_{fm}} \mathrm{P} + \mathrm{P}_1{}^*,$$

$$\mathrm{P}_n{}^* + \mathrm{BX} \xrightarrow{k_{fx}} \mathrm{PX} + \mathrm{X}^*,$$

$$\mathrm{P}_n{}^* + \mathrm{P}_m{}^* \xrightarrow{k_t} \mathrm{P},$$

$$\mathrm{P}_n{}^* + \mathrm{R}^* \xrightarrow{\sigma k_t} \mathrm{P},$$

$$\mathrm{R}^* + \mathrm{R}^* \xrightarrow{\sigma^2 k_t} \mathrm{Z},$$

where R* and $\mathrm{P}_n{}^*$ are the primary radical and the growing polymer radicals containing n monomer units, respectively. Here σ is a constant. The rate of polymerization R_p and the initiator efficiency Φ can be obtained for the expanded kinetic scheme involving primary radical termination reaction, as shown by Misra et al. [8] :

$$R_p = \frac{\Phi^{1/2}}{\lambda}\,[\mathrm{BX}]^{1/2}[\mathrm{M}], \tag{1}$$

$$\Phi^{1/2} = \frac{1}{1 + (\lambda[\mathrm{BX}]^{1/2}/\mu[\mathrm{M}])}, \tag{2}$$

where $\mu = (\sigma k_t/k_i k_p)$ and $\lambda = (k_t/mk_d)^{1/2}/k_p$.

From Eqs. (1) and (2), and the relationship between R_p and [M], [BX] is given by

$$\frac{[\mathrm{M}]}{R_p} = \lambda\,\frac{1}{[\mathrm{BX}]^{1/2}} + \mu\,\frac{1}{[\mathrm{M}]}. \tag{3}$$

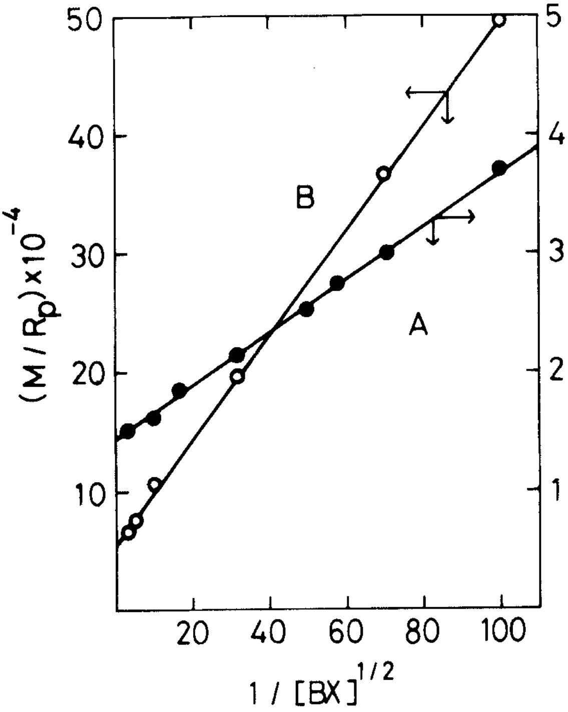


FIG. 4. Plots of Eq. (3) for the dependence of rate of polymerization on BX concentration. Polymerization of MMA (A) and St (B).

Equation (3) predicts a linear relationship between $[M]/R_p$ and the reciprocal of the square root of the BX concentration at constant monomer concentration [M]. The corresponding plot of the experimental results for the polymerization of St and MMA is shown in Fig. 4. In both cases these plots give good straight lines, and the relationship with Eq. (3) holds satisfactorily in these polymerizations. Accordingly, it is considered that BX also acts as terminator in the photopolymerization of vinyl monomers.

From the intercept and slope we calculate the values of kinetic parameters for the polymerization of St and MMA. The resulting values are shown in Table 2.

TABLE 2. Kinetic Parameters for the Polymerization of Styrene and Methyl Methacrylate Initiated by Bis(Isopropylxanthogen) Disulfide at 30°C

	St		MMA	
Concentration, mol/L	μ $\times 10^{-5}$	λ $\times 10^{-2}$	μ $\times 10^{-5}$	λ $\times 10^{-2}$
[M], bulk[a]	4.68	44.2	1.36	2.23
$[BX] = 1.0 \times 10^{-2}$	4.67	44.2	1.35	2.20
$[BX] = 1.0 \times 10^{-4}$	–	–	1.29	2.22
Mean	4.68	44.2	1.33	2.22

[a] [M] = 8.64 mol/L for St or [M] = 9.28 mol/L for MMA.

Effect of Monomer Concentrations on the Rate of Polymerization

The polymerization of St and MMA in the presence of a constant concentration of BX was carried out at 30°C in benzene with concentrations of monomer from 2.5 to 7.0 mol/L. Plotting $\ln R_p$ against $\ln$ [M], linear relationships were obtained as seen in Fig. 5. The rate of polymerization R_p can be written as

$$R_p = k'[\mathrm{M}]^y$$

where the reaction order of monomer is $y = 1.94$ for MMA and $y = 1.68$ for St at a constant BX concentration of 10.0 mmol/L. Keeping the concentration of BX constant at 0.100 mmol/L and varying the concentration of MMA, the polymerizations were carried out, and the results represented by the solid circles of Fig. 5 were obtained. In this case the value of y was 1.52. Therefore, the reaction order of the monomer seems to be affected by the concentration of BX.

Figure 6 shows plots of $[\mathrm{M}]/R_p$ against the reciprocal of monomer concentration according to Eq. (3). Although the plots show little scatter, there is an overall proportionality between $[\mathrm{M}]/R_p$ and $1/[\mathrm{M}]$. It can, therefore, be considered that the kinetic scheme as envisaged in Eq. (3) holds.

Kinetic Parameters and the Fraction of Termination by Primary Radicals

Kinetic parameters determined for the polymerization of St and MMA initiated by BX are summarized in Table 2. The agreement here is within experi-

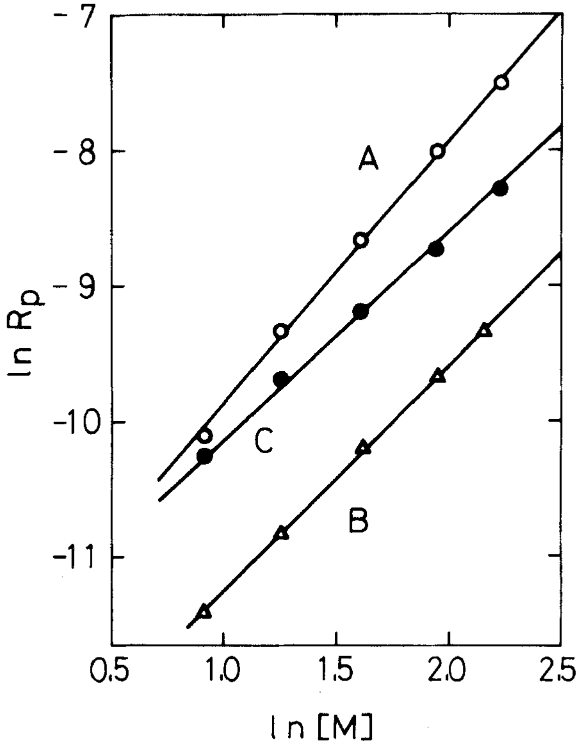


FIG. 5. Polymerization of MMA (A and C), and St (B) in benzene initiated by BX at 30°C. Values of [BX] in mmol/L: A and B, 10.0; C, 0.100. Curves calculated from Eq. (3).

mental error. The mean values obtained from the results in Table 2 were $\mu = 4.68 \times 10^5$ mol•s/L and $\lambda = 4\,420\ (\text{mol/L})^{1/2}\cdot$s for St, and $\mu = 1.33 \times 10^5$ mol•s/L and $\lambda = 2\,220\ (\text{mol/L})^{1/2}\cdot$s for MMA.

In order to indicate the extent to which Eq. (3) is consistent with the experimental observations, we have calculated the dependence of R_p on [BX] at constant [M] and the dependence of R_p on [M] at constant [BX] by using the mean values of the kinetic parameters. The relation calculated from Eq. (3), shown in Figs. 3 and 5, is in satisfactory agreement with the experimental points in each case. It is, therefore, clear that BX acts as terminator as well as initiator in the photopolymerization of vinyl monomers.

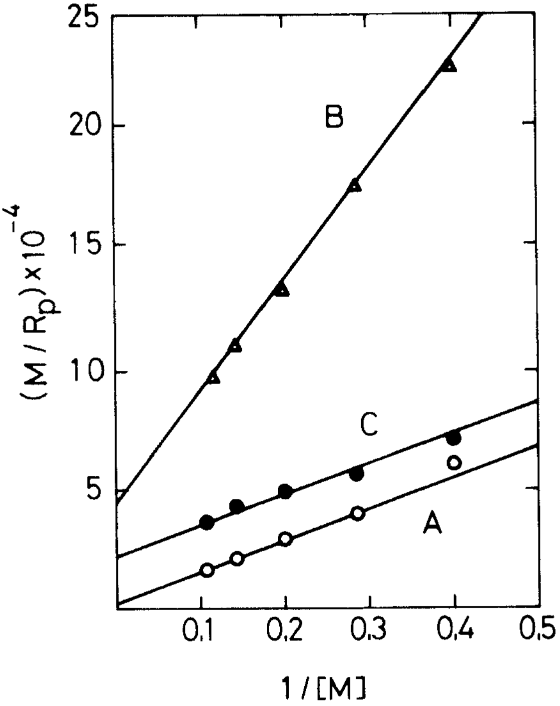


FIG. 6. Plots of Eq. (3) for dependence of rate of polymerization on [M]. Polymerization of MMA: A, [BX] = 10.0 mmol/L; C, [BX] = 0.100 mmol/L. Polymerization of St: B, [BX] = 10.0 mmol/L.

To evaluate degrees of the primary radical termination in these polymerizations, we have calculated the initiator efficiency Φ and the fraction β of primary radicals entering into termination; β is given by

$$\beta = \frac{\sigma R_t}{R_d} = \frac{\Phi^{1/2}}{1 + (\lambda[M]/\mu[I]^{1/2})}, \tag{4}$$

where σR_t and R_d are the rate of termination by primary radicals and the rate of initiator decomposition, respectively, while Φ is given in Eq. (2).

The values of Φ and β were calculated from Eqs. (2) and (4) and the kinetic parameters given above. The results are tabulated in Tables 3 and 4 for the polymerization of St and MMA.

TABLE 3. Initiator Efficiency (Φ) and Fraction of Primary Radical Terminating Chains (β) for the Polymerization of Styrene

Monomer concentration constant at [M] = 8.64 mol/L			BX concentration constant at [BX] = 10.0 mmol/L		
[BX], mmol/L	$\Phi^{1/2}$	β	[M], mol/L	$\Phi^{1/2}$	β
100	0.205	0.163	2.5	0.191	0.155
10	0.449	0.247	3.5	0.248	0.187
1.0	0.721	0.201	5.0	0.321	0.218
0.1	0.891	0.097	7.0	0.398	0.240

TABLE 4. Initiator Efficiency (Φ) and Fraction of the Primary Radical Terminating Chains (β) for the Polymerization of Methyl Methacrylate

Monomer concentration constant at [M] = 9.28 mol/L			BX concentration constant at [BX] = 10.0 mmol/L		
[BX], mmol/L	$\Phi^{1/2}$	β	[M], mol/L	$\Phi^{1/2}$	β
100	0.047	0.045	2.5	0.040	0.038
10	0.134	0.116	3.5	0.055	0.052
1.0	0.328	0.220	5.0	0.077	0.071
0.1	0.607	0.239	7.0	0.104	0.094

In both polymerizations the behavior observed is similar in that the initiator efficiency decreases markedly with BX concentration and increases with monomer concentration. However, the values of Φ in Table 3 for St were considerably higher than values for MMA (Table 4). For example, the value of $\Phi^{1/2}$ for St obtained at constant [BX] = 100.0 mmol/L is 0.205 compared to 0.047 for MMA obtained for the same condition.

On the other hand, the fraction of primary radical terminating the chain β increased with increasing the values of Φ in all cases except at very low [BX] (1.00 and 0.100 mmol/L) for the polymerization of St. In other words, β increases with BX concentration.

From the definition of the kinetic parameter μ and k_p for St and MMA at

30°C, the ratio ($\sigma k_t/k_i$) of the rate constants of termination and initiation by primary radicals can be obtained. Using the mean values at 30°C in Ref. 9, k_p(St) = 71.35 L/(mol·s) and k_p(MMA) = 195.8 L/(mol·s), we obtained ($\sigma k_t/k_i$) for St = 3.34 × 10^7 and for MMA = 2.60 × 10^7. The value for St can be seen to be somewhat larger than that for the polymerization of MMA.

The Number-Average Degrees of Polymerization

The number-average molecular weight $\overline{M}_n$ of the polymers prepared in the polymerization with BX is shown in Table 1, which shows that when the MMA or MA was polymerized to high conversion, the polymer obtained had markedly higher molecular weight. Then, the molecular weight of St and MMA poly-

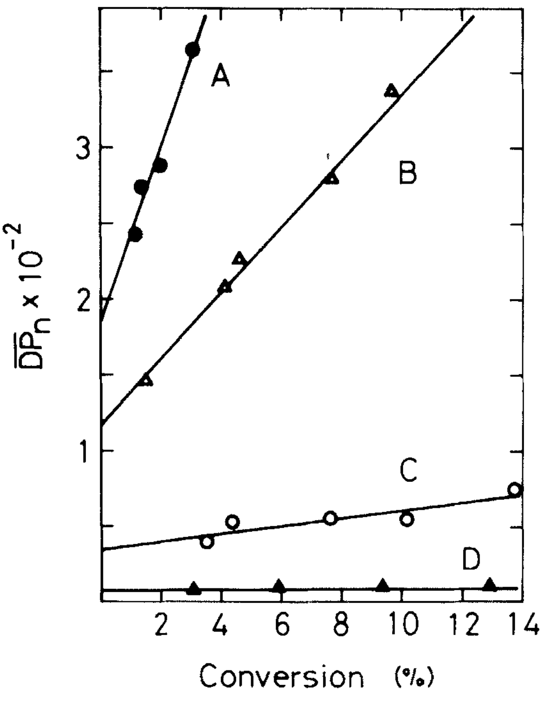


FIG. 7. Number-average degrees of polymerization ($\overline{DP}_n$) of the polymers obtained in the polymerization of St initiated by bis(isopropylxanthogen) disulfide (BX) as a function of conversion. [BX] in mmol/L: A, 0.10; B, 1.00; C, 10.0; D, 100; [M] = 8.64 mol/L.

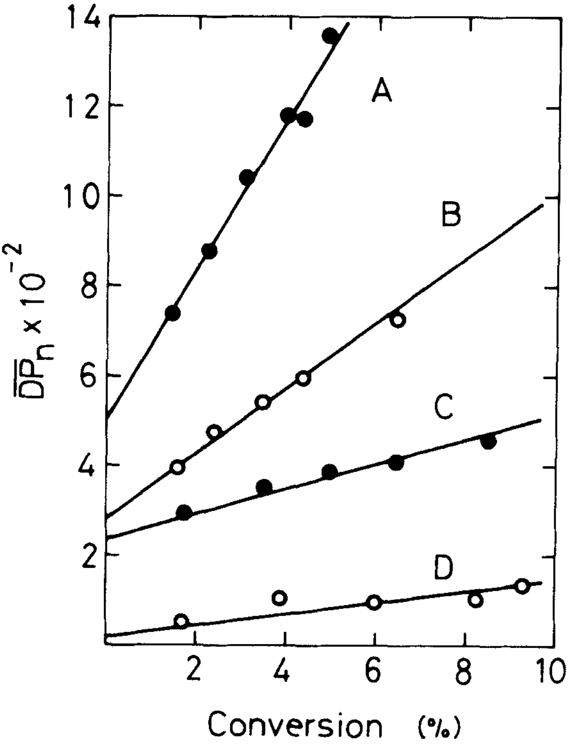


FIG. 8. $\overline{DP}_n$ of polymers obtained in the polymerization of MMA with BX as a function of conversion. [BX] in mmol/L: A, 0.10; B, 0.30; C, 0.40; D, 100; [M] = 9.28 mol/L.

mers were measured as a function of the conversion, with the results shown in Figs. 7 and 8. The number-average degrees of polymerization $\overline{DP}_n$ are found to increase almost linearly with the conversion. This is unusual in radical polymerization since the $\overline{DP}_n$ values of polymers obtained in typical radical polymerizations are known to remain constant, independent of the conversion. However, the $\overline{DP}_n$-conversion dependence for the lower BX concentration is remarkably steep; that at the higher concentration is less so, as shown in both figures. It is considered that the difference between this polymerization and the usual polymerizations is mainly due to the difference of the polymerization mechanism. It is also seen from Figs. 7 and 8 that $\overline{DP}_n$ of the polymers obtained at constant conversion falls as [BX] increases. The primary radical termination and chain transfer reactions are mainly responsible for the low $\overline{\mathrm{DP}}_n$ because BX has a high chain-transfer constant in the polymerization of St and MMA under thermal conditions, as we reported previously [1, 2].

The number-average degree of polymerization $\overline{\mathrm{DP}}_n$ of polymers produced instantaneously in the polymerizations is

$$\frac{1}{\overline{\mathrm{DP}}_n} = \frac{\chi \delta R_i^{1/2}}{[\mathrm{M}]} + C_{fm} + C_{fx} \frac{[\mathrm{BX}]}{[\mathrm{M}]} \tag{5}$$

and

$$\chi = \frac{\alpha - 1}{2} + \frac{1}{\Phi^{1/2}}, \tag{6}$$

where $\delta = k_t^{1/2}/k_p$ and the rate of initiation is $R_i^{1/2} = (\delta/\lambda)^2 \Phi [\mathrm{BX}]$; C_{fm} and C_{fx} are the chain-transfer constants for monomer and BX, respectively; and α is the fraction of bimolecular termination of growing polymer radicals that occurs by disproportionation. At 30°C, δ and α have the values 105.3 $(\mathrm{mol{\cdot}s/L})^{1/2}$ and 0 for St and 21.5 $(\mathrm{mol{\cdot}s/L})^{1/2}$ and 0.62 for MMA [9].

From Eqs. (5) and (6) and the values of the kinetic parameters (μ and λ), the degree of polymerization ($\overline{\mathrm{DP}}_n$) was calculated. The values of C_{fm} and C_{fx} used were 0 and 4.44 [1] for St and 0 and 0.286 [2] for MMA. As shown in Table 5, the experimental value of $\overline{\mathrm{DP}}_n$ obtained for an intercept of zero on the conversion axis in the plot of $\overline{\mathrm{DP}}_n$ against conversion is in good agreement with the calculated value of $\overline{\mathrm{DP}}_n$, except at very low BX concentration in the polymerization of St.

The number of the end groups of the polymers produced in the polymerization of St or MMA with BX was determined spectrophotometrically (see Table 6). Although the $\overline{M}_n$ increases with decreasing BX concentration, the number of xanthate end groups (N_x) per polymer molecule is found to be almost constant at 2.0, independent of the BX concentration. From this table it is obvious that there are two initiator fragments per polymer molecule.

These results, the agreement between experimental and calculated values of $\overline{\mathrm{DP}}_n$, and the formation of the above telechelic polymers again strongly support the idea that polymer formation follows the mechanism given above.

Photolysis of Telechelic Functional Polymers Obtained in the Presence of Vinyl Monomers

Photolysis was carried out in a sealed tube under irradiation with the same UV lamp. The results are shown in Table 7.

TABLE 5. Comparison of the Calculated[a] and Experimentally Observed[b] Number-Average Degree of Polymerization

	$\overline{DP}_n$ of poly(St)			$\overline{DP}_n$ of poly(MMA)	
[BX], mmol/L	Obs	Calc	[BX], mmol/L	Obs	Calc
100.0	6.8	7.48	100.0	18.8	13.61
40.0	14.0	14.3	0.40	240	242.0
10.0	34.6	36.2	0.30	285	281.7
1.00	118	156.5	0.20	340	348.8
0.10	186	602.0	0.10	508	502.6

[a] Calculated from Eq. (5).

[b] Obtained from the intercept at conversion = 0 of a plot of $\overline{DP}_n$ against conversion.

TABLE 6. Number of Xanthate End Groups (N_x) of the Polymers Produced in the Photopolymerizations with BX

Monomer	[BX], mol/L	Conversion, %	$\overline{M}_n \times 10^{-3}$	Xanthate,[a] mmol/g	N_x[b]
St	0.100	12.9	1.12	1.832	2.1
	0.200	43.5	2.36	0.832	2.0
	0.100	29.6	5.64	0.355	2.0
	0.001	4.22	19.86	0.098	2.0
MMA	0.100	12.2	10.38	0.194	2.0
	0.200	62.8	13.30	0.142	1.9
	0.150	87.1	21.48	0.084	1.8
	0.004	8.38	45.81	0.044	2.0

[a] Determined by UV analysis using λ_{max} = 288 nm.

[b] Number of the $(CH_3)_2CHOC(S)S-$ end groups per polymer molecule.

TABLE 7. Photopolymerization of Vinyl Monomers Initiated by the Functional Polymers[a]

	Functional polymer used			Monomer			Polymer obtained	
Run	Type	$\overline{M}_n \times 10^{-3}$	g	Type	g	Conversion of monomer, %	$\overline{M}_n' \times 10^{-3}$	$\overline{M}_n'/\overline{M}_n$
102	St	1.60	0.1	St	5.0	17.9	12.0	7.50
103	St	1.60	2.0	MMA	2.0	72.2	2.37	1.48[b]
112	St	1.60	0.1	MMA	5.0	35.5	21.2	13.3
113	St	1.60	0.1	MA	5.0	79.8	63.4	39.6
303	MA	4.65	2.0	St	3.0	81.2	6.35	1.37
305	MA	4.65	0.2	St	2.0	45.7	19.7	4.24
214	MMA	5.12	0.1	MA	5.0	28.8	46.5	9.08
211	MMA	5.12	0.1	St	5.0	27.9	67.4	13.2
218	MMA	5.12	2.0	St	2.0	56.7	6.19	1.21
219	Run 218		0.2	MMA	2.0	24.0	17.6	2.84

[a] Polymerization in benzene at 30°C.

[b] Number-average molecular weight ($\overline{M}_{n,b}$) of block copolymer obtained, 44.5×10^3; $\overline{M}_{n,b}/\overline{M}_n$, 27.8.

When the telechelic poly(St) was photolyzed in the presence of St monomer (Run 102 of Table 7), polymerization was induced and the average molecular weight ($\overline{M}_n'$) of the resulting polymer increased markedly. Similarly, when the telechelic poly(MMA) or poly(MA) obtained was used, chain extension polymerization of the functional polymer was observed. Moreover, when MMA or MA was used as the second monomer, block polymerization with the same telechelic poly(St) as a macrophotoinitiator took place (Runs 103, 112, and 113 of Table 7). In this case, when the amount of the functional polymers increased, the $\overline{M}_n'$ of the resulting polymer was observed to decrease. Similar results were also found for the functional poly(MMA), poly(MA), and the resulting blocked polymer (Run 219).

From Table 7 it is evident that the telechelic functional polymers obtained by the above photopolymerizations with BX are useful as chain-extending backbone polymers, applied to photochemical design of block copolymers and chain-extended polymers. More detailed results for the block copolymerizations using these telechelic functional polymers as macroinitiators will be described in a future publication.

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