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

Block Polymerizations of Vinyl Monomers Initiated by Telechelicisopropyl Xanthate-Terminated Polymers as Macrophotoinitiator. Design Of Block Copolymers. 2

Masazo Niwa[a]; Yasuhiro Sako[a]; Motoyuki Shimizu[a]
[a] Department of Applied Chemistry, Doshisha University Karasuma-Imadegawa, Kyoto, Japan

To cite this Article Niwa, Masazo , Sako, Yasuhiro and Shimizu, Motoyuki(1987) 'Block Polymerizations of Vinyl Monomers Initiated by Telechelicisopropyl Xanthate-Terminated Polymers as Macrophotoinitiator. Design Of Block Copolymers. 2', Journal of Macromolecular Science, Part A, 24: 11, 1315 — 1332

To link to this Article: DOI: 10.1080/00222338708076948

URL: http://dx.doi.org/10.1080/00222338708076948

J. MACROMOL. SCI.–CHEM., A24(11), pp. 1315-1332 (1987)

BLOCK POLYMERIZATIONS OF VINYL MONOMERS INITIATED BY TELECHELIC ISOPROPYL XANTHATE-TERMINATED POLYMERS AS MACROPHOTOINITIATOR. DESIGN OF BLOCK COPOLYMERS. 2

MASAZO NIWA, YASUHIRO SAKO, and MOTOYUKI SHIMIZU

Department of Applied Chemistry
Doshisha University
Karasuma-Imadegawa, Kamikyo-ku, Kyoto, 602 Japan

ABSTRACT

Both photopolymerization and thermal polymerization of a variety of vinyl monomers with bis(isopropylxanthogen) disulfide (BX) as initiator and as chain-transfer agent were carried out in benzene. The results of photopolymerizations to high conversion with BX support the polymerization mechanism given in a previous paper of this series. Telechelic isopropyl xanthate-terminated polymers (TXP) having a different backbone have been used as macroinitiator for the polymerization of vinyl monomers. The rate of polymerization of the functional polymers was found to be markedly dependent on the monomer species: block polymerization of methyl acrylate or methyl methacrylate proceeded rapidly compared to the chain-extension polymerization of styrene. However, in all cases the molecular weight of the polymers obtained was found to increase linearly with conversion, which is an interesting property for the design of block copolymers and which is similar in polymerization with BX. It is also found that the molecular weight of the block copolymers can be controlled by adjusting the concentration of the TXP macroinitiator.

INTRODUCTION

In previous papers [1-3] of this series, the polymerization of vinyl monomers in the presence of bis(isopropylxanthogen) disulfide (BX) was reported. Particularly, photopolymerization of styrene and methyl methacrylate with BX was studied kinetically, and it was found that BX is an effective initiator, chain-transfer agent, and primary radical terminator [3]. In these polymerizations the resulting polymers, which contain isopropyl xanthate end groups that can initiate the second monomer, were used to derive block copolymers. In the course of the investigations, we became interested in studying the molecular design of block copolymers through a photochemical reaction of the functional polymers. The photopolymerization of vinyl monomers using functional polymers has been examined at 30°C.

In this article we report on the preparation and characterization of telechelic isopropyl xanthate-terminated polymers of different molecular weights, and on the block polymerization of several vinyl monomers with the telechelic polymers as macrophotoinitiators.

EXPERIMENTAL

Materials

BX was obtained commercially and was recrystallized twice from acetone (mp, 58.5°C). Styrene (St), methyl acrylate (MA), ethyl acrylate (EA), and methyl methacrylate (MMA) were used after standard purification. AIBN, benzene, and polymer precipitants were purified in the usual ways.

Synthesis of Telechelic Isopropyl Xanthate-Terminated Polymers

Telechelic polystyrene, polymethyl methacrylate, polyethyl acrylate, and polymethyl acrylate (denoted here as TXS, TXM, TXE, and TXA, respectively), terminated with isopropyl xanthate ($(CH_3)_2-CH-O-C(=S)-S-$) groups, which were to be used as macrophotoinitiators and as backbone polymers, were synthesized by a procedure similar to that described in a previous paper [2]. Backbone polymer samples of different molecular weights were prepared by the method reported previously [4].

The required amounts of the monomer, BX, benzene, and AIBN (in the case of thermal polymerization) were placed into a glass tube which was then degassed by conventional freezing and thawing techniques, and sealed off under vacuum. After polymerization for a given time, the polymer was isolated by pouring the polymerization mixture into the precipitant. The polymers were purified by reprecipitating their benzene solutions in precipitants several times. The polymer was dried to constant weight in a vacuum oven at 60°C.

Block Polymerizations by Telechelic Functional Polymers

A similar procedure was applied to the block polymerization of vinyl monomers with the telechelic polymers as macroinitiators. Photopolymerizations in bulk and in benzene were carried out by irradiation with a Rikosha low-pressure mercury lamp from a constant distance of 50 mm. The polymerization temperature was maintained at 30°C during irradiation. The polymer obtained was purified by reprecipitation.

Characterization of the Polymers

The terminal isopropyl xanthate group of the telechelic polymer and the block copolymer was determined by its UV spectrum, using *O*-isopropyl-*S*-ethyl xanthate [$(CH_3)_2-CH-O-C(=S)-S-C_2H_5$] as the model compound ($\lambda_{max} = 282$ nm, due to the π-π^* transition of $-O-C(=S)-S-$), $\epsilon = 9620$ L/(mol·cm) in chloroform), as described previously. The UV spectrum was recorded with a Shimadzu spectrophotometer (Model UV-120-02).

Number-average molecular weights of the telechelic polymers and the block copolymers were determined by 37°C in benzene by osmometry. A Hitachi Perkin-Elmer vapor-pressure osmometer was used for samples with $\bar{M}_n$ up tp 20 000. The instrument was calibrated with benzil and polystyrene standard samples (from the Pressure Chemical Co.) by the procedures described previously [5]. Molecular weights higher than 20 000 were obtained with a Knauer membrane osmometer using regenerated cellulose membranes.

Molecular weight distributions of polymers were measured by using a Shimadzu LC-3A high-performance liquid chromatograph equipped with three polystyrene gel columns (HSG-15, HSG-30, and HSG-50), a UV absorbance detector, and a differential refractometer operated at 40°C. The flow of solvent (tetrahydrofuran) was maintained at 1 mL/min. A molecular weight calibration curve was obtained on the basis of the universal calibration with 12 standard polystyrene samples (from Pressure Chemical Co.). Number-average and weight-average molecular weights were obtained by the usual procedures with the aid of the calibration curve.

RESULTS AND DISCUSSION

High-Conversion Photopolymerization of Vinyl Monomers Initiated by Bis(isopropylxanthogen) Disulfide

We first examine the photopolymerizations initiated by BX at an advanced degree of conversion.

Time and conversion curves obtained from the photopolymerization of MA (concentration of monomer, [M], 3.50 mol/L) with different concentrations of BX at 30°C are shown in Fig. 1. The time-conversion relation in the polymerization of MA is almost independent of BX concentration, [BX], in the range investigated ([BX] = 35.0-140 mmol/L). An ultimate conversion of 100% was attained after 5.0 h polymerization time.

In MMA polymerization at a BX concentration higher than 35.0 mmol/L, results for the time-conversion relation were obtained similar to those for MA. The BX concentration exerts only a small effect on the time-conversion relations. These results support the polymerization mechanism we reported previously [3].

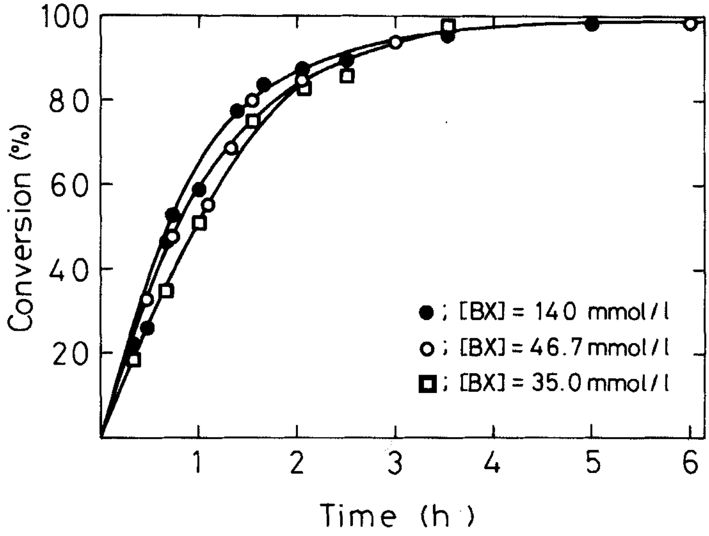

FIG. 1. Time and conversion curves for the polymerization of methyl acrylate ([MA] = 3.50 mol/L) with different concentrations of bis(isopropylxanthogen) disulfide (BX) as photoinitiator at 30°C.

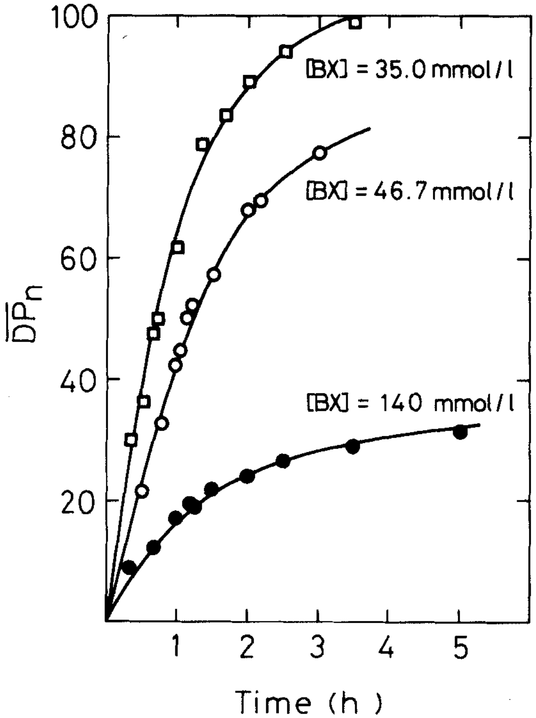

FIG. 2. Effect of BX concentrations on the relation of number-average degree of polymerization ($\overline{DP}_n$) and polymerization time for the polymerization of MA initiated by BX.

In the case of MA polymerization, $\overline{DP}_n$ is observed to increase with time, as shown in Fig. 2. The $\overline{DP}_n$-time relation depends markedly on the BX concentration: the rate of increase of $\overline{DP}_n$ is greater at lower BX concentration than at higher. However, the results for MMA at the same BX concentration (Fig. 3, Curves B and C) are markedly different from those for MA, i.e., $\overline{DP}_n$ decreases with time. However, at a much lower BX concentration in MMA polymerization, the $\overline{DP}_n$ increases with time as for MA polymerization (Fig. 3, Curve A).

Otsu and coworkers [6] reported that vinyl polymerization with some organic sulfides, such as tetraethylthiuram disulfide, as "photoiniferters" proceeded by a living-radical mechanism. The dependence of the molecular

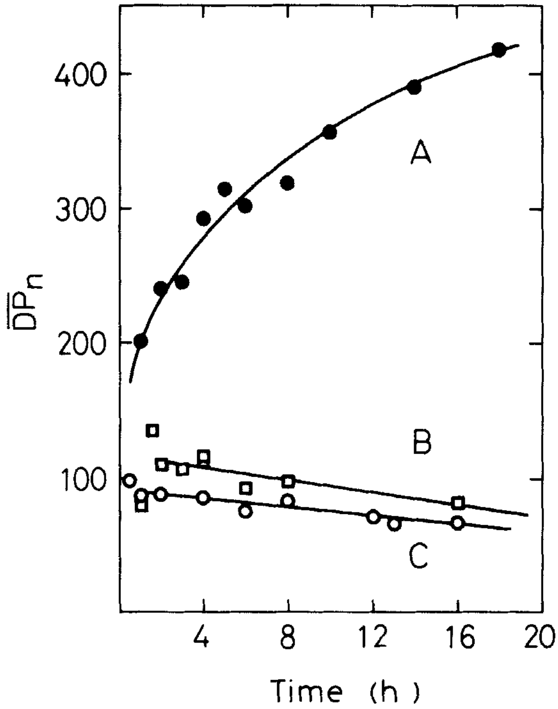

FIG. 3. Effect of BX concentrations on the relation of $\overline{DP}_n$ to polymerization time for the polymerization of methyl methacrylate (MMA) initiated by BX at 30°C. A: [MMA] = 5.0 mol/L, [BX] = 5.0 mmol/L. B: [MMA] = 3.5 mol/L, [BX] = 35.0 mmol/L. C: [MMA] = 3.5 mol/L, [BX] = 58.3 mmol/L.

weight on the polymerization time observed by us is roughly consistent with the results for the polymerization of MMA by tetraethylthiuram disulfide obtained by Otsu et al. [7], although it is uncertain whether the mechanism of the two polymerization systems is the same or not.

However, when our present results with BX are compared in detail with those reported by Otsu et al. for the photopolymerization of MMA, the former is shown to give a higher polymerization rate and about half the molecular weight increase with time, under similar conditions.

In all polymerizations with BX, $\overline{DP}_n$ was found to increase almost linearly

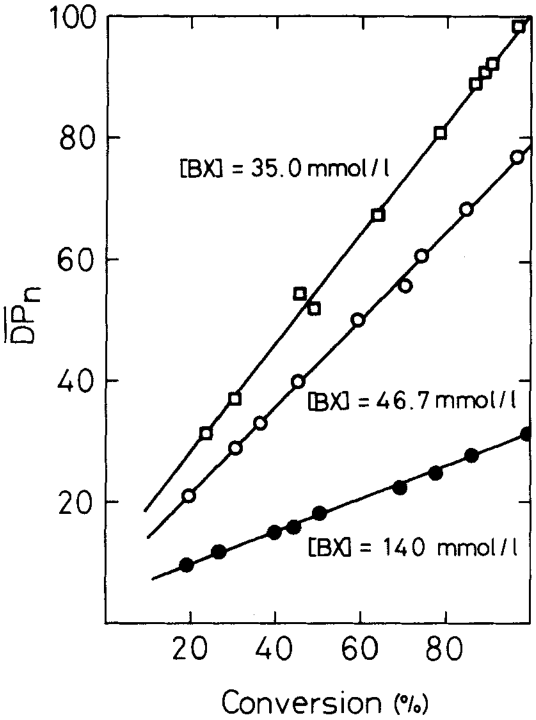

FIG. 4. Plots of number-average degree of polymerization as a function of conversion for the polymerization of MA initiated by BX.

with conversion (Fig 4), except for MMA at very high BX concentration range. The linear increase of $\overline{DP}_n$ with conversion is quite similar to what happens in polycondensation.

Isopropyl xanthate contents and $\overline{M}_n$ of some typical polymers are given in Table 1. The number of xanthate end groups per polymer molecule, N_x, is found to be almost constant to 2.0, independent of conversion, for both polymerizations. These results indicate that these polymerizations are an effective and useful synthetic method of telechelic polymers in which the molecular weight can be regulated by adjusting the conversion and the BX concentration.

TABLE 1. Results of Photopolymerizations of Methyl Acrylate and Methyl Methacrylate Initiated by Bis(isopropylxanthogen) disulfide (BX) at 30°C[a]

Methyl acrylate					Methyl methacrylate				
Run	Yield, %	$\bar{M}_n \times 10^{-3}$	X,[b] mmol/g	N_x,[c]	Run	Yield, %	$\bar{M}_n \times 10^{-3}$	X,[b] mmol/g	N_x,[c]
88	21.3	3.09	0.680	2.1	53	18.8	11.10	0.175	1.9
83	49.0	5.30	0.342	1.8	59	45.6	10.70	0.188	2.0
90	68.1	6.85	0.315	2.2	54	64.9	9.31	0.214	2.0
91	78.4	7.16	0.278	2.0	57	70.7	9.84	0.187	1.8
81	88.3	8.04	0.258	2.1	58	96.8	8.20	0.212	1.7

[a] [M] = 3.50 mol/L and [BX] = 35.0 mmol/L.

[b] Isopropyl xanthate content of the polymer, determined by UV analysis at 288 nm.

[c] Number of isopropyl xanthate terminal groups per polymer molecule, determined from X and $\bar{M}_n$.

TABLE 2. Synthesis and Characterization of Telechelic Isopropyl Xanthate-Terminated Polymers (TXP)

Functional polymer[a]	f_0[b]	Polymer[c] yield, %	$\bar{M}_n \times 10^{-3}$	End groups,[d] mmol/g	N_x[e]
TXS2	20.0	72.4	1.69	1.191	2.01
TXS1	90.0	35.8	5.08	0.379	1.92
TXS4	864	7.94	8.82	0.234	2.06
TXE1	66.0	30.8	3.18	0.614	1.95
TXA1	50.0	87.8	4.74	0.426	2.02
TXM4	30.0	28.5	5.12	0.364	1.86

[a] Telechelic isopropyl xanthate-terminated polymers: TXS, TXE, TXA, and TXM are polystyrene, poly(ethyl acrylate), poly(methyl acrylate), and poly(methyl methacrylate), respectively.

[b] f_0 = [monomer]/[BX] in feed.

[c] All polymerizations by AIBN were carried out in benzene at 70°C, except TXS4 prepared by photopolymerization with BX at 30°C.

[d] $(CH_3)_2CHOC(=S)S-$ end groups were determined by UV analysis at λ_{max} = 288 nm.

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

Synthesis and Characterization of Telechelic Isopropyl Xanthate-Terminated Polymers Used as Macrophotoinitiator

Preparation of the telechelic polymers containing two isopropyl xanthate groups by using BX as a chain transfer agent was described in the Experimental section. The telechelic functional polymers were prepared in good yield by thermal polymerizations initiated by AIBN. Like the above method of photopolymerization with BX, this method is a convenient route. Table 2 lists the characteristics of the resulting polymers. The products have molecular weights from1600 to 6000. The N_x value of these polymers, determined from the molecular weight and the isopropyl xanthate contents, indicates that the polymers have two xanthate groups per molecule.

TXE macroinitiator was a highly viscous liquid polymer, soluble in methanol.

We observed the UV spectrum of the TXS1 polymer in chloroform and the spectral changes during irradiation in a 10-mm quartz tube 50 mm from a low-

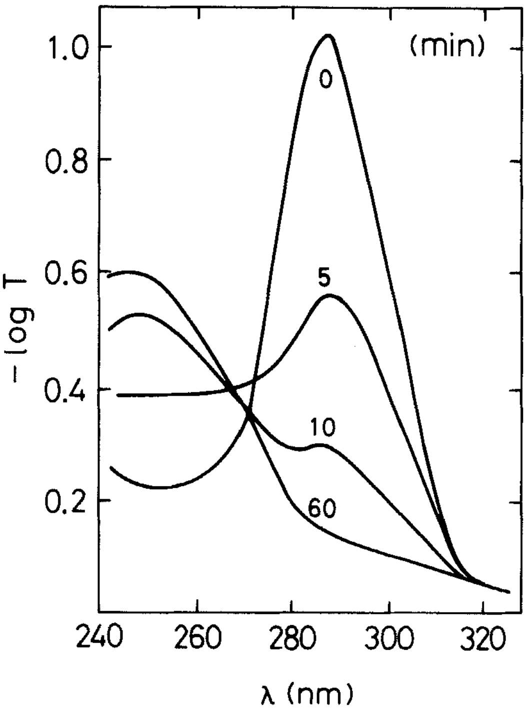

FIG. 5. Change of ultraviolet absorption spectra of telechelic isopropyl xanthate-terminated polystyrene (TXS1) by irradiation with a low-pressure mercury lamp of 0.10 mmol/L solution in chloroform. The numbers on the curves indicate the time of irradiation in minutes.

pressure mercury lamp. Figure 5 shows the UV spectra of irradiated and unirradiated TXS1. TXS1 shows the characteristic absorption maximum at 288 nm due to π-π^* transition of the –S–C(=S)–O– groups. The characteristic absorption λ_{max} varied markedly with irradiation time at the low isopropyl xanthate concentration. The rate of decomposition of the TXS1 polymer was determined quantitatively by the decrease in the absorption at λ_{max} for a given time. The result of a simple treatment of the rate of decomposition data from experiments conducted with the low concentration showed that the rate of decomposition obeyed the first-order kinetics up to 80% conversion.

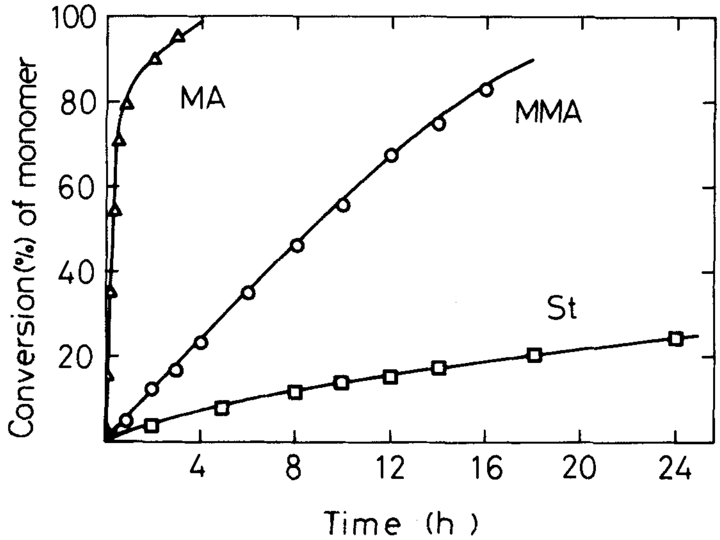

FIG. 6. Time and conversion curves for the polymerization of styrene (St), methyl methacrylate (MMA), and methyl acrylate (MA) by telechelic isopropyl xanthate-terminated polystyrene (TXS2) as a macrophotoinitiator at 30°C. [M] = 5.0 mol/L and [TXS2] = 5.0 mmol/L in benzene.

Polymerization of a Variety of Vinyl Monomers with Telechelic Isopropyl Xanthate-Terminated Polystyrene (TXS2) as a Macrophotoinitiator

Results for photopolymerization of St, MMA, and MA are shown in Fig. 6. All of polymerizations with TXS2 proceeded homogeneously, but the rates of polymerization are different from each monomer. As can be seen from Fig. 6, the block polymerization of MA onto TXS2 is very fast in the presence of 0.1 mol% TXS2. The rate of polymerization of MMA is higher than that of St. The photoinitiator behavior with TXS2 is almost the same as for polymerization initiated by BX, as reported previously [3]. The polymerization of MA and MMA reached higher conversions.

$\bar{M}_n$ increases with time in all cases from a point above the origin (Fig. 7), which represents the $\bar{M}_n$ of TXS2. This is similar to the polymerization by BX, except that there the curves start from the origin.

As shown in Fig. 8, $\bar{M}_n$ increases linearly with increasing conversion, which is a desirable characteristic for the polymerization and shows that chain-exten-

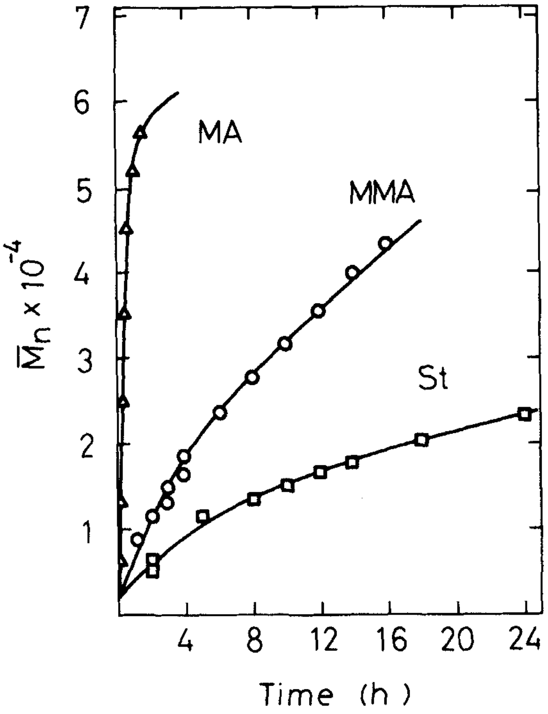

FIG. 7. Relationship between number-average molecular weight ($\bar{M}_n$) and polymerization time for polymerizations initiated by TXS2 macroinitiator.

sion polymerization and block polymerization occur. It can be seen by comparison of Figs. 7 and 8 that the relation of molecular weight to conversion depends only slightly on the type of monomer, though both of time-conversion and time-molecular weight relations vary markedly with it.

These results indicate that the polymer molecular weight, the block length, and the chemical composition of the block copolymer can be controlled by polymerization time and conversion at a constant concentration of macroinitiator.

As for chain-extension polymerization, the N_x values for the chain-extension and block polymerization appear to be almost constant to 2.0, independent of conversion (Table 3).

The chain-extended polystyrene has the same two xanthate terminal groups

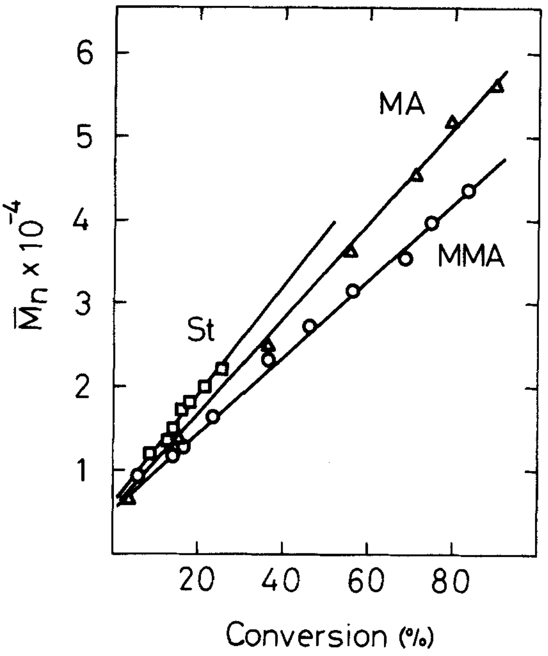

FIG. 8. Plots of $\bar{M}_n$ as a function of conversion for polymerizations with TXS2.

as the starting material TXS2 which is a telechelic functional polymer. It is interesting that chain-extended polystyrene can also be transformed into a block copolymer with a second or the third monomer by photoinitiation of isopropyl xanthate-terminal groups. However, the N_x value ranged from 1.4 to 1.5 for block polymerization of MA with TXS2, values far below what is usually found in polymerization of MA with BX, where N_x is commonly very close to 2.

Effect of Macroinitiator Concentration on the Molecular Weight of Polymer

To study the effect of initiator concentrations on the polymerization of MMA and St, the telechelic isopropyl xanthate-terminated polymethyl methacrylate macroinitiator, TXM4, was used. Figure 9 reports results obtained

TABLE 3. Results of Photopolymerizations of Styrene and Methyl Acrylate Initiated by TXS2[a]

Styrene				Methyl acrylate			
Run	Time, h	Yield,[b] %	N_x[c]	Run	Time, h	Yield,[b] %	N_x[c]
176	8	12.04	1.91	181	0.17	15.83	1.46
173	10	14.00	1.93	182	0.33	35.13	1.72
177	12	15.38	2.08	183	0.5	54.17	1.40
178	18	20.64	2.04	185	1.0	79.73	1.52
175	24	24.62	1.93	186	2.0	89.92	1.42

[a] Concentration of monomer, 5.0 mol/L, and concentration of TXS2, 5.0 mmol/L.

[b] Yield of monomer polymerized.

[c] Number of isopropyl xanthate terminal groups per polymer molecule.

at constant polymerization time. Polymerization without TXM4 gives only a small amount of polymer (up to 1.5%), but the addition of a small amount of macroinitiator induces efficient polymerization. These telechelic functional polymers indeed exhibited significant initiator activity, independent of the backbone polymer. Initially, the conversion rises steeply as the TXM4 concentration is increased, but at about 2.5-5.0 mmol/L the slope decreases for both St and MMA, as shown in Fig. 9. Similar behavior has been observed in the polymerization with BX, and it is therefore suggested that the telechelic isopropyl xanthate-terminated polymer plays roles not only as an initiator but also as a terminator and as a chain-transfer agent in the polymerization of vinyl monomers.

As can also be seen in Fig. 9, the molecular weight of polymer initially rose rapidly but then decreased with increasing TXM4 concentration. These results support the above conclusions.

Table 4 demonstrates the dependence of molecular weight of polymer on the TXS2 concentration for comparison with TXM4 which has a different molecular weight and backbone species. The rate of polymerization, reflected in the yield of polymer, increased with increasing TXS2 concentration. A similar relationship holds for the polymerization with TXM4. On the other

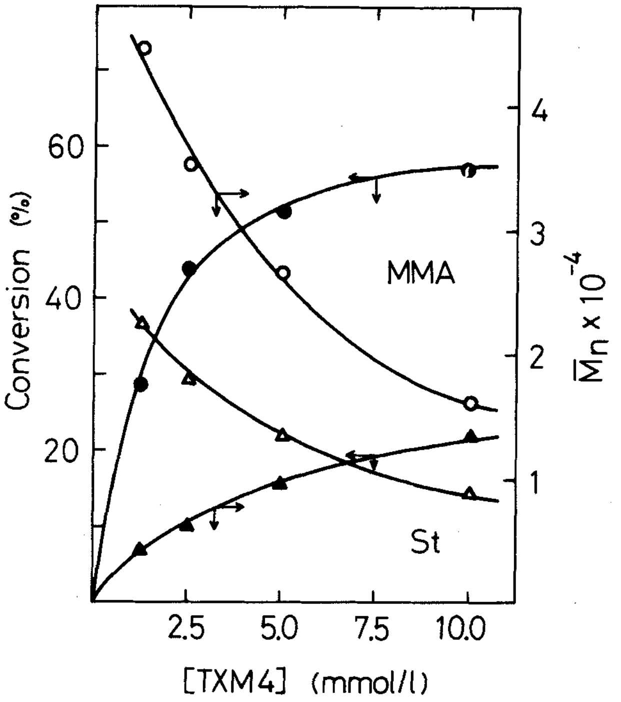

FIG. 9. Conversion at constant polymerization time (MMA, 4 h; St, 12 h) and $\overline{M}_n$ as functions of [TXM4] for the polymerization of St and MMA initiated by telechelic isopropyl xanthate-terminated poly(methyl methacrylate) (TXM4) at 30°C.

hand, $\overline{M}_n$ of the polymer increased with decreasing macroinitiator concentration. The ratio of $\overline{M}_n$ of the polymer obtained to that of TXS2, $(\overline{M}_n/\overline{M}_{n,\mathrm{I}})$, ranges from 3.8 to 24.7 for MMA, while the block polymerization of MA showed a very large range, from 10.7 to 49.8, in comparison with the chain-extension styrene polymerization, which ranged from 2.9 to 14.5 under the same experimental conditions.

The GPC curves (Fig. 10, D-F) contain two peaks, indicating a bimodal molecular weight distribution for the polymer obtained from MMA polymerization. The peak of the high molecular weight fraction is assigned based on GPC peak area of the St-block-MMA polymer, because the peak of the low molecular weight fraction was in agreement with the GPC peak position of

TABLE 4. Effect of Macroinitiator Concentrations on Conversion at Constant Time and Molecular Weight of Polymer Obtained for the Photopolymerization of Vinyl Monomers[a]

Monomer:	Methyl acrylate		Methyl methacrylate		Styrene	
Time, h:	2.5		4.0		12.0	
[TXS2], mmol/L	Yield,[b] %	$\bar{M}_n/\bar{M}_{n,\mathrm{I}}$	Yield,[b] %	$\bar{M}_n/\bar{M}_{n,\mathrm{I}}$	Yield,[b] %	$\bar{M}_n/\bar{M}_{n,\mathrm{I}}$
1.25	55.2	49.8	20.3	24.7	4.9	14.5
2.5	67.5	30.2	28.4	19.5	8.0	9.5
5.0	75.8	26.8	34.0	13.0	15.6	7.2
10.0	77.2	17.8	39.2	7.3	19.0	5.2
20.0	79.3	10.7	43.2	3.8	25.6	2.9

[a] Initiated by TXS2, telechelic isopropyl xanthate-terminated polystyrene, in benzene at 30°C, [M] = 5.0 mol/L.

[b] Yield of monomer polymerized.

the starting materials. The low peak area decreased with a decreasing molar ratio of TXS2 to MMA monomer in the feed, and the low peak is almost not observed when [TXS2]/[M] = 0.1% is used (Fig. 10, Curve F).

The GPC curves have only one peak for any TXS2 concentration even if [TXS2]/[M] = 10.0% is used in the block polymerization of MA (Fig. 10, Curves A-C), in contrast to the polymerization of MMA. The peak migrated from the position of the lower peak toward higher molecular weight with decreasing macroinitiator concentration. Accordingly, at lower TXS2 concentration, a block of larger molecular weight is formed.

The change of GPC pattern with [TXS2] in the chain-extended polystyrene showed a similar tendency for ST-block-MA copolymer, but the region of migration to higher molecular weight for the former was relatively narrow.

These results indicate that the reactivity between monomer and TXS2 depended significantly on the monomer species. We may speculate on the way in which the degree of reaction of TXS2 affects the parameters for the primary radical termination and the chain-transfer constant. Indeed, these parameters for BX showed a significant difference for St and MMA monomers in the previous paper.

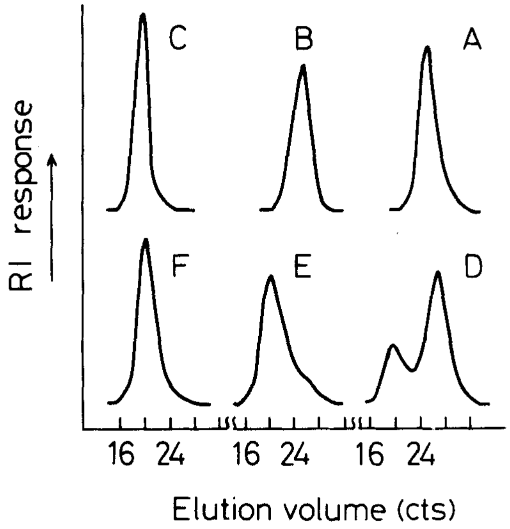

FIG. 10. GPC curves of polymers obtained in the polymerization of MA (A-C) and MMA (D-F) with TXS2. Mol% of xanthate unit in TXS2 per monomer: A and D, 10.0; B, 1.0; E, 0.5; C and F, 0.1.

Table 5 summarizes the isopropyl xanthate contents for chain-extended polystyrene and St-block-MA polymers; these always had a single GPC peak. The chain-extended polystyrene, a telechelic functional polymer, also contains two terminal isopropyl xanthate groups which can again be initiated for block polymerization. Conversions of St-block-MA copolymers were higher than 90%, and N_x depended on the macroinitiator concentration. For the comparatively low concentration, 2.5 mmol/L, N_x was as low as 1.2, which corresponds to the survival of 61% of the initial isopropyl xanthate groups. Thus, the block copolymer can be also utilized as a macroinitiator for block polymerization of a third monomer, though it is unsatisfactory in comparison with the chain-extended polystyrene.

In order to design a block copolymer, it is important to select a suitable concentration of the macroinitiator for each of the monomers in the block polymerization using TXP.

TABLE 5. Effect of Macroinitiator Concentrations on Number of Xanthate Terminal Groups per Polymer Molecule (N_X)

Monomer	Styrene			Methyl acrylate		
[TXS2], mmol/L	$\bar{M}_n \times 10^{-4}$	X, mmol/g	N_X	$\bar{M}_n \times 10^{-4}$	X, mmol/g	N_X
1.25	2.45	0.078	1.91	8.41	0.011	0.93
2.5	1.61	0.120	1.93	5.10	0.024	1.22
5.0	1.22	0.161	1.96	4.53	0.033	1.49
10.0	0.87	0.228	2.01	3.01	0.057	1.72
20.0	0.49	0.414	2.03	1.80	0.106	1.91

REFERENCES

[1] K. Noma, M. Niwa, T. Yoshida, and S. Nesumi, *Kobunshi Ronbunshu, 34,* 97 (1977).

[2] M. Niwa, T. Matsumoto, Y. Shimada, and Y. Matsui, *Sci. Eng. Rev. Doshisha Univ., 26,* 219 (1986).

[3] M. Niwa, T. Matsumoto, and H. Izumi, *J. Macromol. Sci.–Chem., A24*(5), 567 (1987).

[4] M. Niwa, T. Hayashi, and T. Matsumoto, *Ibid., A23,* 433 (1986).

[5] M. Niwa and K. Noma, *Sci. Eng. Rev. Doshisha Univ., 11,* 105 (1970).

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

[7] T. Otsu, A. Kuriyama, and M. Yoshida, *Kobunshi Ronbunshu, 40,* 583 (1983).

Received February 17, 1987