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Polymerization of macromers

2. Group transfer polymerization of methacrylate-terminated polystyrene macromer

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SUMMARY

The possibility of group transfer polymerization of methyl methacrylate-terminated polystyrene macromer (MA-PSt) was explored by using 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene and tris(dimethylamino)sulfonium difluorotrimethylsilicate as initiator and catalyst, respectively. The results obtained at the polymerization temperature of 0°C were undesirable. However, the oligomerization at -78°C gave almost quantitatively oligo(MA-PSt) of which the degree of polymerization was in good agreement with the mole ratio of macromer to initiator. The GPC curve of oligo(MA-PSt) was sharp and symmetrical. In addition, it was shown by the copolymerization with methyl methacrylate that the polymerizability of the macromer was markedly enhanced in the presence of methyl methacrylate comonomer.

INTRODUCTION

Many polymer chemists who concern themselves with synthetic method for control of polymer architecture have deeply been interested in living polymerization. Recently, a new type of living polymerization, termed group transfer polymerization, was developed (1-3) by du Pont's group (1,2). This new addition polymerization of acrylic monomers by special initiator and catalyst has extensively utilized for preparing various types of well-controlled polymers such as functional polymers (4-7), block polymers (5,6) as well as usual polymers with narrow molecular weight distribution. More recently, Pugh and Percec (8) synthesized reactive polymethacrylates containing pendant styrene groups by group transfer homo- and copolymerization of *p*-vinylbenzyl methacrylate, making use of features of the unique polymerization process. Moreover, many reports (9) on this polymerization process have been presented at the New York ACS Meeting (April 1986). Also, we (10) have been able to prepare styrene-terminated poly(methyl methacrylate) macromer with high functionality and narrow molecular weight distribution, employing the new method.

In the course of conducting study on well-controlled polymer synthesis, the authors have been much interested in the group transfer polymerization as methodology to polymerize macromers bearing acrylic end-group(s). First of all, the group transfer polymerization of methyl methacrylate-terminated polystyrene macromer was studied. The present paper reports on some first results on the polymerization of the macromer in tetrahydrofuran using alkyl silyl ketene acetal as initiator, and the detailed discussion on the results will be described in a forthcoming paper.

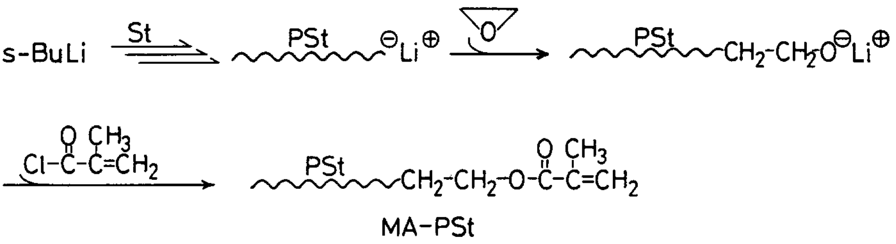
EXPERIMENTAL

Materials

An alkyl silyl ketene acetal (SKA) used as an initiator was 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene which was prepared according to a literature procedure (11). Catalyst, tris(dimethylamino)sulfonium difluorotrimethylsilicate ($TASF_2SiMe_3$, from Aldrich Chemical Co., Inc.) was used as received. Methyl methacrylate (MMA, from Nakarai Chemicals, LTD, JAPAN) was purified first by the usual method and finally according to the method of MacGrath *et al* . (12) in which triethylalminum was used. Tetrahydrofuran (THF) as polymerization solvent was purified by distillation *in vacuo* in the presence of sodium salts of the benzophenone dianion.

Synthesis and Characterization of Macromer

Methacrylate-terminated polystyrene macromer (MA-PSt) was prepared by a method similar to that described by Schulz and Milkovich (13), *i.e.*,



The macromer obtained was purified by several reprecipitations from a benzene-methanol and characterized by a method described elsewhere (14). The characterization results are summerized below:

Molecular weight (Mn) = 3.8×10^3
Molecular weight dispersity (Mw/Mn) = 1.04
Functionality (C=C/molecule) = 96 %

Polymerization Procedure

The initiator and catalyst were degassed in ampules with break-seals on a high vacuum line (10^{-5} torr) for 24 h, dissolved in THF *in situ*, and stocked as 0.1-4 mmol/L solutions.

An example for preparation of a solution of MA-PSt in THF is as follows. MA-PSt (4 g), freshly ground CaH_2 (*ca.* 1 g) and a magnetic stirring bar were placed in a 100 mL round bottomed flask equipped with a break-seal and a joint for attachment to the vacuum manifold. The flask was attached on the high vacuum line, degassed for several hours, and the macromer was dissolved in benzene (*ca.* 20 mL) which was distilled just before use in the presence of sodium-benzophenone complex. The solution was stirred at ambient temperature for a few days* while shielding from light, freeze-dried for 24 h, and THF (60 mL) was distilled into the flask, and then the flask was sealed off from the vacuum line. The THF solution of MA-PSt containing CaH_2 powder was carefully** filtered with a fine sintered-glass filter by break-seal techniques. The clear solution was divided into small ampules (with break-seals) for the group transfer polymerization.

The group transfer polymerization of MA-PSt was carried out at 0°C or -78°C by using the same apparatus as described previously (15).

(* It was confirmed that the functionality of MA-PSt did not decrease for the period of a few days; ** It was found that the group transfer polymerization did not occur if the solution contained a minute amount of CaH_2 after the filtration.)

Measurements

Gel permeation chromatography (GPC) was performed at a column oven temperature of 38°C on a Toyo Soda HLC-802A equipped with three types of detectors, *i.e.*, UV (UV-8 model II), RI (RI-6), and LALLS (LS-8) detectors. Columns used were TSKgel-GMHs or -G2000H_8 and -G3000H_8 which were calibrated with polystyene standards***. THF was used as the eluent and the flow rate was 1 mL/min.
(***The polystyrene standards are not ideal ones for poly(MA-PSt); therefore, the molecular weights in Tables 1 and 2 are apparent values.)

RESULTS AND DISCUSSION

Group transfer polymerization of MA-PSt macromer was carried out in THF using SKA and TASF SiMe as initiator and catalyst, respectively. The results are summerized in Table 1. In general, the extent of conversion of MA-PSt to poly(MA-PSt) increases as the mole ratio of [MA-PSt]/[I] is decreased and as the polymerization temperature is lowered.

Table 1

Group Transfer Polymerization of MA-PSt [a]

Expt	MA-PSt	SKA [b]	$[M_1]$/	Temp	Time	Conv.[c]	Poly(MA-PSt)		
	$[M_1]$	$[I^{b)}]$	$[I^{b)}]$				mol. wt. x 10^{-4}		$(DP)^{d)}_{GPC}$
	(mmol/L)	(mmol/L)		(°C)	(h)	(%)	calcd	GPC	
H- 1	8.42	1.68	5.01	0	4	71	1.3	(0.8, 1.8)[e]	(2.1, 4.7)[e]
H- 2	8.42	1.68	5.01	0	20	72	1.4	(0.8, 1.9)[e]	(2.1, 5.0)[e]
H- 3	8.42	1.68	5.01	0	52	71	1.3	(0.8, 1.9)[e]	(2.1, 5.0)[e]
H- 4	9.25	0.894	10.3	0	24	8	—	2.0	5.3
H- 5	8.30	0.412	20.1	0	24	trace	—	—	—
H- 6	6.15	1.21	5.08	-78	2	71	1.3	1.9	5.0
H- 7	6.15	1.21	5.08	-78	24	99	1.9	2.0 (2.2)[f]	5.3
H- 8	9.06	0.930	9.74	-78	0.5	23	0.9	1.6	4.2
H- 9	9.06	0.930	9.74	-78	24	67	2.5	3.0	7.9
H-10	10.5	0.532	19.7	-78	24	trace	—	—	—

[a] Solvent, THF.
[b] Initiator, 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene; catalyst, $TASF_2SiMe_3$; $[TASF_2SiMe_3]/[\ I\ ] \approx 0.2$.
[c] Corrected by the purity of MA-PSt.
[d] Degree of polymerization estimated from GPC.
[e] Poly(MA-PSt) has bimodal peaks.
[f] Determined by a LALLS detector.

In the polymerization at 0°C, however, satisfactory results could not be obtained even at a low level of the ratio of [MA-PSt]/[I] of about 5. That is, the conversion of the macromer was saturated at *ca.* 71% as shown in Table 1 and the peak of poly(MA-PSt) in the GPC curve was bimodal as illustrated in Figure 1.

On the other hand, MA-PSt is polymerized quantitatively under the conditions of Expt H-7 ([MA-PSt]/[I] = 5.08; temperature, -78°C; time, 24 h). The GPC curve of oligo(MA-PSt) thus obtained was sharp and symmetrical except for the small peak of unpolymerized MA-PSt, as can be seen in Figure 2. Furthermore, the molecular weight (by GPC) of oligo(MA-PSt) was consistent with calculated one and the degree of polymerization of oligo(MA-PSt) was in good agreement with the mole ratio of macromer to initiator. These findings indicate that well-defined oligo(MA-PSt), star-shaped polystyrene having five branches at least, can be prepared by the group transfer polymerization of MA-PSt macromer.

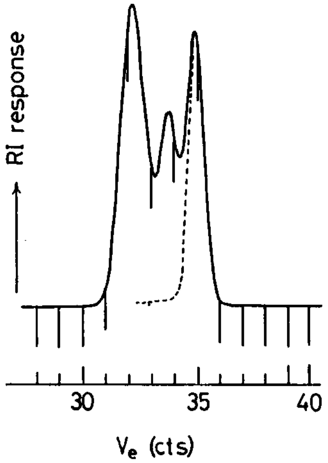


Figure 1. GPC curve of the recovered polymer in Expt H-2. (dotted line curve, unpolymerized MA-PSt)

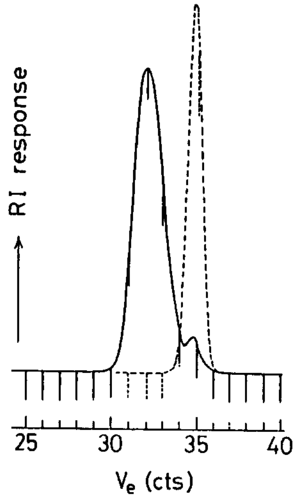


Figure 2. GPC traces of MA-PSt macromer (---) and oligo(MA-PSt) (—) obtained in Expt H-7.

In order to check further the polymerizability of MA-PSt macromer in the group transfer polymerization, we performed the polymerization in the presence of MMA, *i.e.*, the copolymerization with MMA, using the same initiator and catalyst as in the homopolymerization. Table 2 shows polymerization conditions and the results of the copolymerization. In conclusion, the extent of conversion of MA-PSt is greatly heightened in the copolymerization with MMA. Even though the polymerization temperature was 0°C, MA-PSt was copolymerized quantitatively to give poly(MA•PSt-*co*-MMA) of which molecular weight was consistent with calculated one. In addition, the rate of copolymerization was so fast that the copolymerization completed within 20 min as shown in Figure 3. Also, in spite of [MA-PSt]/[I] = 20.5, about half amount of MA-PSt was converted to poly(MA•PSt-*co*-MMA) at -78°C. As a notable feature of this copolymerization, it can be noted that the molecular weight distribution of poly(MA•PSt-*co*-MMA) prepared by the group transfer copolymerization is very narrow compared to that prepared by radical copolymerization under the condition of similar monomer feed ratio (Figure 4). These results suggest that the group transfer copolymerization has a

Table 2

Group Transfer Copolymerization of MA-PSt with MMA[a)]

Expt	MA-PSt $[M_1]$ (mmol/L)	MMA $[M_2]$ (mmol/L)	$[M_1]/[I]$	$[M_2]/[I]$	Temp (°C)	Time (h)	Conv. of M_1 (%)	Copolymer mol. wt. x 10^{-4} calcd	GPC
C-1	5.88	162	4.94	136	0	0.3	96	3.2	3.1
C-2	6.52	179	5.02	138	0	8	96	3.3	3.1
C-3	6.52	179	5.02	138	0	24	97	3.3	3.2
C-4	9.32	51	19.2	106	0	48	9	8.4	2.2
C-5	10.2	175	20.5	352	-78	24	49	11	7.2

a) Solvent, initiator, catalyst, mole ratio of initiator to catalyst, and explanatory notes are the same as in Table 1.

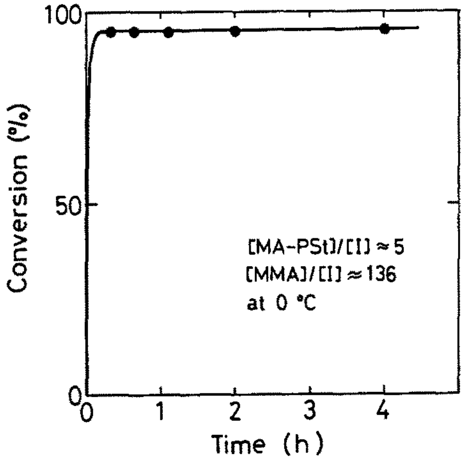


Figure 3. Time-conversion curve for group transfer copolymerization of MA-PSt with MMA.

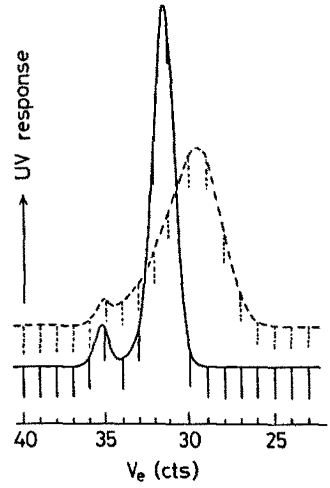


Figure 4. Molecular weight distributions of poly(MA•PSt-*co*-MMA)s obtained by radical (---) and group transfer (——) copolymerizations.

bright prospect of preparing well-controlled graft copolymers and they have prompted us to study further the group transfer copolymerization of other methacrylate-ended macromers such as poly(tetrahydrofuran) and poly(ethylene oxide) macromers as well as MA-PSt. Details on the copolymerizations will be reported elsewhere in the near furture.

REFERENCES

1. O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham and T. V. RajanBabu, J. Am. Chem. Soc. **105**, 5706 (1983); Polym. Prepr. **24** (2), 52 (1983).
2. W. R. Hertler, D. Y. Sogah, O. W. Webster and B. M. Trost, Macromolecules **17**, 1417 (1984).
3. F. Bandermann and H.-D. Speikamp, Makromol. Chem., Rapid Commun. **6**, 335 (1985).
4. D. Y. Sogah and O. W. Webster, J. Polym. Sci., Polym. Lett. Ed. **21**, 927 (1983); Polym. Prepr. **24** (2), 54 (1983).
5. O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham and T. V. RajanBabu, J. Macromol. Sci.-Chem. **A21** (8&9), 943 (1984).
6. D. Y. Sogah, W. R. Hertler and O. W. Webster, Polym. Prepr. **25** (2), 3 (1984).
7. W. Kreuder and O. W. Webster, Makromol. Chem., Rapid Commun. **7**, 5 (1986).
8. C. Pugh and V. Percec, Polym. Bull. **14**, 109 (1985).
9. O. W. Webster; D. Y. Sogah; W. R. Hertler; W. R. Farnham and D. Y. Sogah; F. Bandermann, H. D. Sitz and H. D. Speikamp; P. Mai and A. Mueller, Polym. Prepr. **27** (1), pp 161-170 (1986).
10. R. Asami, Y. Kondo and M. Takaki, Polym. Prepr. **27** (1), 186 (1986).
11. C. Ainsworth, F. Chem and Yu-Neng Kuo, J. Organomet. Chem. **46**, 59 (1972).
12. R. D. Allen, T. E. Long and J. E. McGrath, Polym. Bull. **15**, 127 (1986).
13. G. O. Schulz and R. Milkovich, J. Appl. Polym. Sci. **27**, 4773 (1982).
14. M. Takaki, R. Asami, S. Tanaka, H. Hayashi and T. E. Hogen-Esch, to be published.
15. M. Takaki, R. Asami, M. Mizuno, Macromolecules **10**, 845 (1977).

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