2354 *Macromolecules* **1996,** *29,* 2354−2358

Radical/Cation Transformation Polymerization and Its Application to the Preparation of Block Copolymers of *p*-Methoxystyrene and Cyclohexene Oxide

Hai-Qing Guo, Atsushi Kajiwara, Yotaro Morishima, and Mikiharu Kamachi*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Received July 27, 1995; Revised Manuscript Received December 11, 1995[⊗]

ABSTRACT: *p*-Methoxystyrene (MOS) and *n*-butyl vinyl ether (BVE) were polymerized to high polymer by azo initiators in the presence of $Ph_2I^+PF_6^-$. The polymer formation shows that the transformation of propagating radical into propagating cation took place in the polymerization process of MOS and BVE. ESR study of the model radicals supports the fact that the transformation of the radical to the corresponding cation occurred in the presence of an electron-transfer reagent. Block copolymers of MOS and cyclohexene oxide (CHO) were effectively prepared by the radical polymerization of MOS in the presence of $Ph_2I^+PF_6^-$ and CHO. The block copolymerization is ascribable to the transformation of growing ends from radical to cationic species during the propagation step.

Introduction

Radical polymerization is the most utilized method in polymer formation from vinyl and diene compounds in industry. Accordingly, a lot of papers and patents have been reported on the radical polymerization of vinyl and diene compounds, and well-refined systematization has been performed on the polymerization process.[1,2] Sequence control and structure control are the most interesting fields in polymer formation by radical polymerization.[3−5] However, these controls of polymer chain are much more difficult in radical polymerization than in ionic polymerization because bimolecular termination takes place in competition with the propagation of growing ends in radical polymerization. Several methods, such as polymerization with iniferter,[6] living polymerization in the presence of metal complexes,[7] or polymerization with nitroxyl radicals,[8] have been found for the sequence control of polymer chain by radical polymerization.

Reaction control of radical polymerization from other points is expected to develop new routes in polymer synthesis. Radical-promoted cationic polymerization has been reported so far.[9] In the course of ESR studies on the radical end of polymers,[10] we also found that propagating radical is effectively transformed into the corresponding cation in the polymerization process of vinyl compounds by radical polymerization in the presence of an electron-transfer reagent. This transformation reaction was confirmed by the preparation of block copolymers of *p*-methoxystyrene (MOS) and cyclohexene oxide (CHO) by the polymerization system of AIBN, MOS, $Ph_2I^+PF_6^-$, and CHO. To our knowledge, however, no paper on the preparation of block copolymers by this transformation reaction of propagating radicals has been reported so far. In this paper, we shall present clear evidence of the transformation of free radical to the corresponding cation and its application to block polymer formation.

Experimental Section

Measurements. ^{1}H-NMR spectra were measured on a JEOL JNM-GX 270 spectrometer as $CDCl_3$ solutions. ESR spectra were recorded on a JEOL JES RE2X spectrometer at X-band utilizing 100 kHz field modulation and a microwave power of 1 mW.

Number- and weight-average molecular weights ($\overline{M_n}$ and $\overline{M_w}$) and molecular weight distribution were roughly estimated by gel permeation chromatography (GPC) on a TOSOH CCP&8010 series high-speed liquid chromatograph system equipped with a TSK gel column, using tetrahydrofuran as solvent at a flow rate of 0.8 mL/min. Molecular weights were calibrated by standard polystyrene. TOSOH UV-8010 and TOSOH RI-8012 detectors were used.

Materials. 1,1′-Azobis[1,1′-(4-methoxyphenyl)ethane] (ABMPE) was synthesized by the method of Schepple and Seltzer.[11] 2,2′-Azobis(2,2′-phenoxypropane) (ABPOP) was obtained by the method described by Benaring.[12] Commercially available 2,2′-azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. Diphenyliodonium hexafluorophosphate ($PH_2I^+PF_6^-$) was prepared according to the reported manner.[13] Commercially available MOS, CHO, and *n*-butyl vinyl ether (BVE) were dried over calcium hydride and distilled under reduced pressure. Methylene dichloride was purified by the method described in a reference book.[14]

Polymerization. A CH_2Cl_2 solution of a given amount of azo initiator (AIBN, ABMPE, or ABPOP), $Ph_2I^+PF_6^-$, and monomer (BVE, MOS, CHO, or a mixture of MOS and CHO) in a glass ampule was degassed by a freeze−thaw method. Being sealed off under high vacuum, the ampule was kept at 80 °C in the dark for a given period of time. The content of the ampule was poured into an excess of methanol containing a small amount of ammonia. Precipitates were filtered, dried in vacuum, and weighed. Polymers isolated as precipitates were again dissolved in CH_2Cl_2 and purified by reprecipitation with methanol. In the polymerization of a mixture of CHO and MOS, the polymer was separated into a hexane-insoluble fraction and a hexane-soluble fraction (polyCHO) with hexane extraction, and the hexane-insoluble fraction was characterized by turbidimetry, thin layer chromatography, and NMR spectroscopy.

Thin Layer Chromatography. Thin layer chromatography was performed on silica gel applied on a plastic sheet with 0.20 mm thickness. Samples for the tests were prepared by dissolving 40 mg of each sample in 10 mL of chloroform. With the aid of a microsyringe, a spot of each solution was formed on the layer. Gradient elutions were performed in the manner as described by Kotaka et al.[15] The first solvent was CCl_4, and the second solvent was tetrahydrofuran. The ratio of CCl_4/THF was 40/18. The sheet was placed into a chamber which contained iodine, making the position of the polymer as brown spots.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

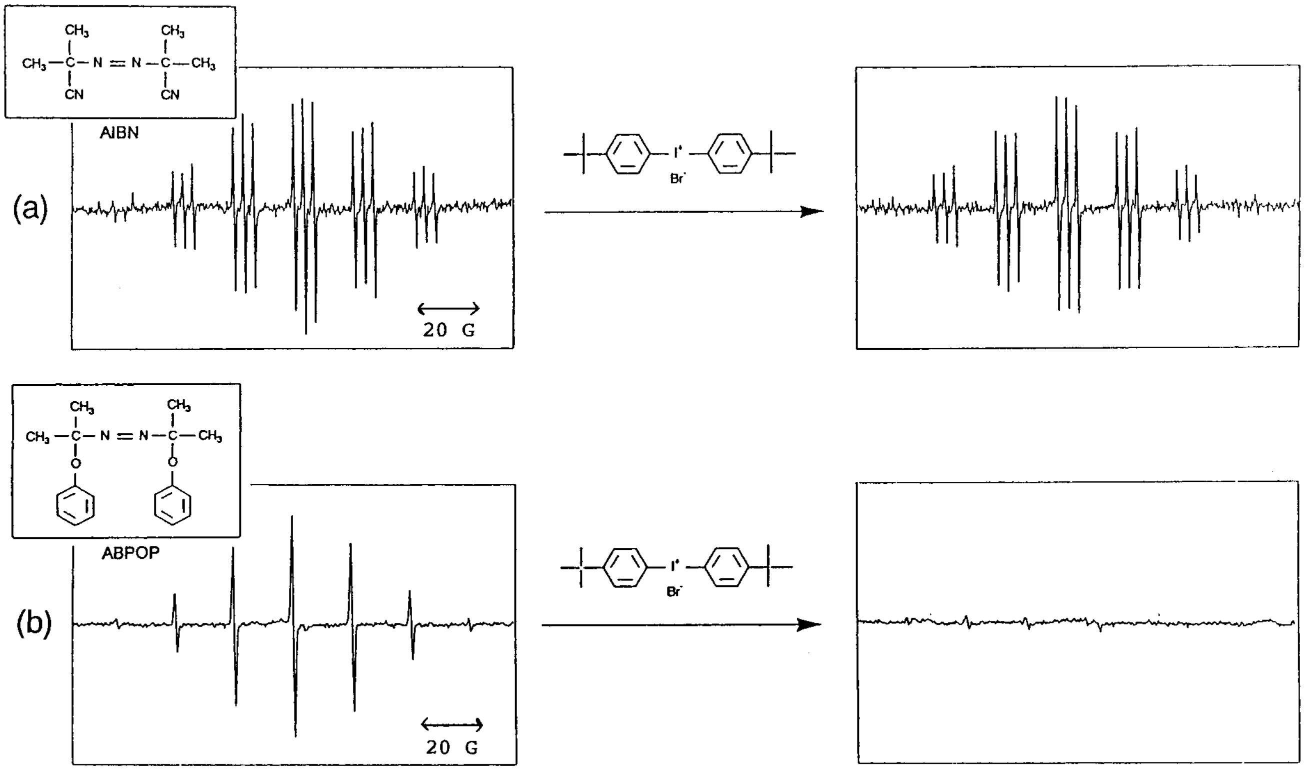


Figure 1. ESR spectra of primary radicals obtained by decomposition of AIBN (a) and ABPOP (b) in the absence and presence of an acceptor under irradiation of an ultra-high-pressure mercury lamp at 20 °C.

Turbidimetry. Turbidimetry was performed by using transmittance of the polymer solution at 400 nm on a Shimadzu UV-2100 spectrometer. The change in turbidity on addition of ethanol to a 0.1 wt % solution of polymer in benzene (3)/butanone (1) was followed.

Results and Discussion

Influence of Ph$_2$I$^+$PF$_6^-$ on ESR Spectra of Primary Radicals. The influence of PH$_2$I$^+$PF$_6^-$ on ESR spectra of primary radicals obtained by photodecomposition of AIBN and ABPOP is shown in Figure 1. On addition of Ph$_2$I$^+$PF$_6^-$, the ESR spectrum of the primary radical obtained from AIBN did not change while that of primary radical produced from ABPOP almost disappeared. This result suggests that $(CH_3)_2C^{\bullet}$-CN having an electron-accepting substituent did not perform an electron-transfer reaction to Ph$_2$I$^+$PF$_6^-$ and that $(CH_3)_2C^{\bullet}$-(OC_6H_5) having an electron-donating substituent underwent the electron-transfer reaction to form the corresponding carbocation, $(CH_3)_2C^+$-(OC_6H_5), whose formation was confirmed by the fact that vinyl ethers and CHO, which cannot be polymerized by radical initiators, were polymerized in high conversion by ABPOP in the presence of Ph$_2$I$^+$PF$_6^-$.

The ESR spectrum of the propagating radical of MOS was also clearly detected in radical polymerization of MOS, while it was only very weakly detected in the presence of Ph$_2$I$^+$PF$_6^-$. This finding also shows the occurrence of electron transfer reaction from propagating radical of MOS to Ph$_2$I$^+$PF$_6^+$. The change in ESR spectra is shown in Figure 2.

Radical/Cation Transformation Polymerization. Polymerizations of MOS, BVE, or CHO were performed with AIBN, ABMPE, and ABPOP. Results shown in Table 1 indicate that polymer was obtained from MOS and no polymer was obtained from BVE and CHO in the absence of Ph$_2$I$^+$PF$_6^-$. In the presence of Ph$_2$I$^+$PF$_6^-$, however, high polymer was obtained in much higher

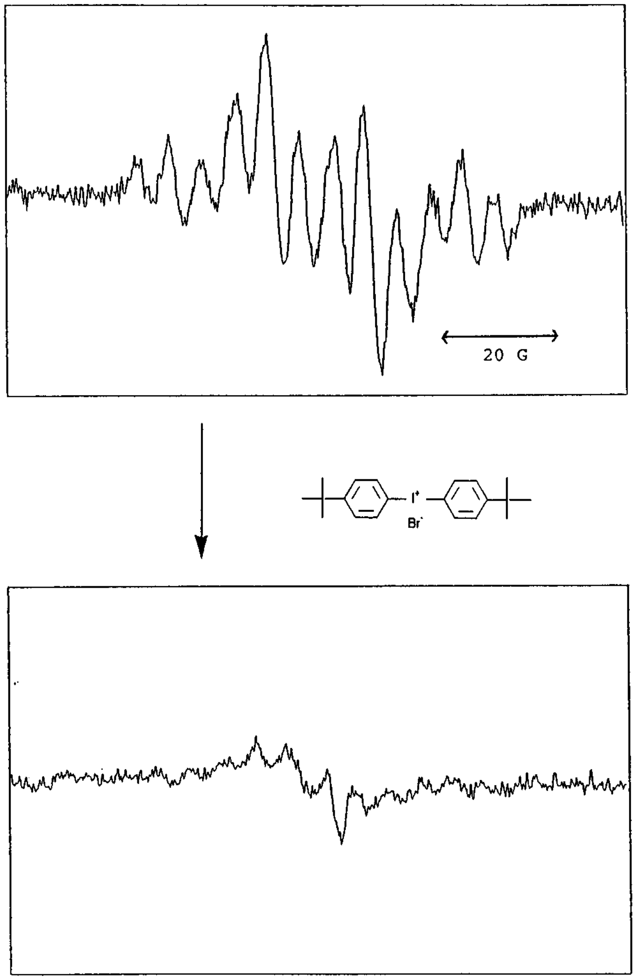


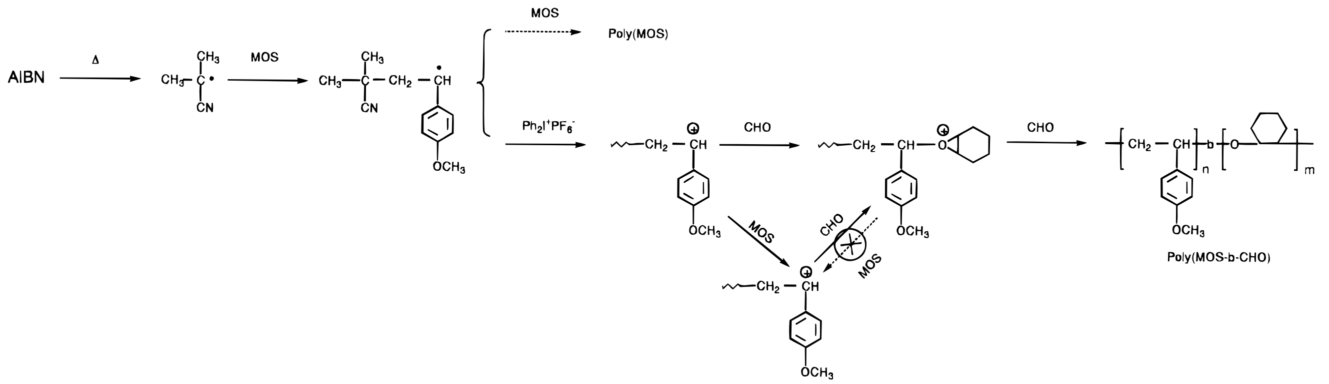
Figure 2. ESR spectra of propagating radical of *p*-methoxystyrene in the absence and presence of an acceptor under irradiation of an ultra-high-pressure mercury lamp at 20 °C.

Table 1. Cationic Polymerization of *n*-Butyl Vinyl Ether (BVE), *p*-Methoxystyrene (MOS), and Cyclohexene Oxide (CHO) Promoted by Free Radical Initiators[a]

monomer	radical initiator	concn (M)	$Ph_2I^+PF_6^-$ (M)	temp[b] (°C)	time (min)	conv (%)	$\overline{M}_w \times 10^{-4}$
BVE	none	0	6×10^{-3}	80	80	5	1.08
	AIBN	6×10^{-3}	0	80	80	0	
	AIBN	6×10^{-3}	6×10^{-3}	80	80	62	0.85
	ABMPE	6×10^{-3}	0	80	80	0	
	ABMPE	6×10^{-3}	6×10^{-3}	80	80	68	0.95
	ABPOP	6×10^{-3}	0	80	80	0	
	ABPOP	6×10^{-3}	6×10^{-3}	80	80	63	1.11
MOS	none	0	1.2×10^{-2}	80	120	4	3.40
	AIBN	6×10^{-3}	0	80	120	10	2.26
	AIBN	6×10^{-3}	1.2×10^{-2}	80	120	74	4.23
	ABMPE	6×10^{-3}	0	80	120	4	4.81
	ABMPE	6×10^{-3}	1.2×10^{-2}	80	120	34	3.24
	ABPOP	6×10^{-3}	0	80	120	2	6.01
	ABPOP	6×10^{-3}	1.2×10^{-2}	80	120	64	4.46
CHO	none	0	1.2×10^{-2}	80	120	~1	
	AIBN	6×10^{-3}	0	80	120	0	
	AIBN	6×10^{-3}	1.2×10^{-2}	80	120	~1	
	ABMPE	1.2×10^{-2}	0	100	24 (h)	0	
	ABMPE	1.2×10^{-2}	2.4×10^{-2}	100	24 (h)	30	1.74
	none	0	2.4×10^{-2}	100	24 (h)	6	2.52

[a] Solvent, $(CH_2)_2Cl_2$; monomer/$(CH_2)_2Cl_2$ = 1:3 (vol). [b] Oil bath temperature.

Scheme 1



yield from MOS and BVE by polymerization with AIBN, ABPOP, or ABMPE. CHO was polymerized to high polymer with ABMPE in the presence of $Ph_2I^+PF_6^-$ and did not polymerize with AIBN even in the presence of $Ph_2I^+PF_6^-$.

Polymerizations of MOS, BVE, and CHO with $Ph_2I^+PF_6^-$ were performed as control experiments, which indicate that only a few polymers were obtained by the polymerizations. Since BVE and CHO do not polymerize to high polymer by radical initiators,[16] the polymer formation from these monomers shows that cationic polymerizations were performed with ABMPE in the presence of $Ph_2I^+PF_6^-$. The polymer formation can be reasonably explained by the polymerization with carbocation formed by the electron-transfer reaction from primary radicals having electron-donating substituents to $Ph_2I^+PF_6^-$. The fact that CHO did not polymerize with AIBN even in the presence of $Ph_2I^+PF_6^-$ is in agreement with the ESR observation in which no electron-transfer reaction took place from $(CH_3)_2C^{\bullet}$-CN to $Ph_2I^+PF_6^-$. However, the finding that BVE was polymerized in high yield by AIBN in the presence of $Ph_2I^+PF_6^-$ is inconsistent with the explanation because BVE dose not polymerize with radical initiators. The formation of cationic-initiating species in the presence of BVE may be reasonably attributed to the electron-transfer reaction of an initiating radical, which can be formed by addition reaction of $(CH_3)_2^{\bullet}$-CN to BVE, to $Ph_2I^+PF_6^-$.

MOS was initiated to form high polymer by AIBN and not by $Ph_2I^+PF_6^-$. When the polymerization of MOS was performed with AIBN in the presence of $Ph_2I^+PF_6^-$, the polymer formation from MOS was remarkably promoted, which indicates that polyMOS radicals initiated by AIBN were transformed into polyMOS cations by $Ph_2I^+PF_6^-$ before they disappeared by the bimolecular termination such as the coupling reaction. The transformation of the propagating species from radical to cation is consistent with change in the ESR spectrum as shown in Figure 2. The polymerization of MOS with ABMPE and ABPOP was remarkably promoted in the presence of $Ph_2I^+PF_6^-$. This is also explained by radical/cation transformation of initiating radical and/or propagating radical in the propagation process.

Block Copolymers of MOS and CHO. We paid attention to the findings that MOS is polymerized with an AIBN/$Ph_2I^+PF_6^-$ initiating system and that CHO is not polymerized with the initiating system. It has been known that the propagating cation of MOS initiates the polymerization of CHO and the propagating oxonium ion of CHO does not initiate the polymerization of MOS.[16] Accordingly, it can be expected that block copolymers of MOS and CHO can be prepared by the polymerization of a mixture of CHO and MOS with AIBN in the presence of $Ph_2I^+PF_6^-$ as shown in Scheme 1. Results of the polymerization of the mixture of CHO and MOS are shown in Table 2 along with those of the control experiments.

Table 2. Block Copolymerization of *p*-Methoxystyrene (MOS) and Cyclohexene Oxide (CHO) Initiated by AIBN and $Ph_2I^+PF_6^-$ [a]

MOS (M)	CHO (M)	AIBN (M)	$Ph_2I^+PF_6^-$ (M)	conv (%)	$\overline{M}_w \times 10^{-4}$	PMOS/PCHO (molar ratio, unit)
1.9	0	6×10^{-3}	0	10	2.26	
1.9	0	0	1.2×10^{-2}	4	3.40	
1.9	0	6×10^{-3}	1.2×10^{-2}	74	4.23	
1.9	2.5	6×10^{-3}	1.2×10^{-2}	24	1.75	1:0.8
0	2.5	6×10^{-3}	1.2×10^{-2}	1		
1.9	2.5	0	1.2×10^{-2}	$\sim$1		

[a] Solvent, CH_2Cl_2; polymerization temperature, 80 °C; polymerization time, 2 h.

Table 3. Cationic Copolymerization of 4-Methoxystyrene (MOS) and Cyclohexene Oxide (CHO) Initiated by $SnCl_4$ [a]

MOS/CHO (molar ratio)	time (min)	yield (%)	PMOS/PCHO (molar ratio, unit)	$\overline{M}_w \times 10^{-4}$
1:0	10	100	1:0	28.0
7:1	140	4	1:8	1.29
1:1	140	20	0:1	1.85

[a] Solvent, dichloroethane; $[SnCl_4] = 6 \times 10^{-3}$ (M); [MOS] + [CHO] = 2.0 (M); polymerization temperature, 0 °C.

Polymer was scarcely formed by the polymerization of a mixture of CHO and MOS with $Ph_2I^+PF_6^-$, and polyMOS was obtained in low yield by the polymerization with AIBN. Polymer was isolated in higher yield by the polymerization of the mixture with AIBN in the presence of $Ph_2I^+PF_6^-$. The NMR spectrum of the polymer obtained from a 1:1.3 mixture of monomers has both MOS and CHO units whose ratio is 1:0.8.

In order to understand the block copolymer formation, cationic polymerizations of MOS, CHO, and their mixtures were performed using $SnCl_4$ as an initiator (Table 3). MOS polymerized to high polymer very rapidly in the absence of CHO, but the polymerization of MOS was retarded in the presence of CHO. MOS was hardly polymerized to high polymer at the ratio of 7:1 MOS to CHO. When the monomer ratio was 1:1, most of the obtained polymer was the homopolymer of CHO. These results indicate that the initiating and propagating cations preferably attack CHO rather than MOS. The preparation of block polymer, which has a long MOS sequence, is quite difficult from typical cationic polymerization of a mixture of MOS and CHO. Accordingly, it can be concluded that the MOS sequence in the block copolymers obtained from the mixture of MOS and CHO with AIBN in the presence of $PH_2I^+PF_6^-$ is mainly due to the radical polymerization as shown in Scheme 1.

Characterization of Block Copolymer. In the transformation polymerization, a considerable amount of homopolymers is expected to be produced by proton-transfer reaction in the course of the polymerization along with the formation of the block copolymer. PolyCHO was able to be separated from block copolymer by hexane extraction using a Soxhlet extractor. The extraction time was determined by control experiments using a mixture of polyCHO and polyMOS. About 20% of the polymer was separated by the extraction as a hexane-soluble part. NMR spectrum of the hexane soluble part was almost the same as that of polyCHO, and only 5% of the MOS unit was included in the fraction. Separation of polyMOS from the hexane-insoluble fraction was attempted by organic solvents such as *n*-butanone[18] which dissolve polyMOS and not polyCHO. However the separation was not successful because the solubility of polyMOS and poly(MOS-*b*-CHO) in these solvents is very similar. The hexane-insoluble fraction was used for the characterization of the formation of block copolymer. NMR spectrum of the hexane-insoluble part is shown in Figure 3, which shows that the unit ratio of MOS to CHO in the purified polymer is 1:0.32. This result along with other examples is shown in Table 4. The yield and composition of block copolymers of MOS and CHO could be adjusted by selection of polymerization conditions, such as the monomer ratio, concentrations of radical initiator, acceptor, and/or monomers, and so on.

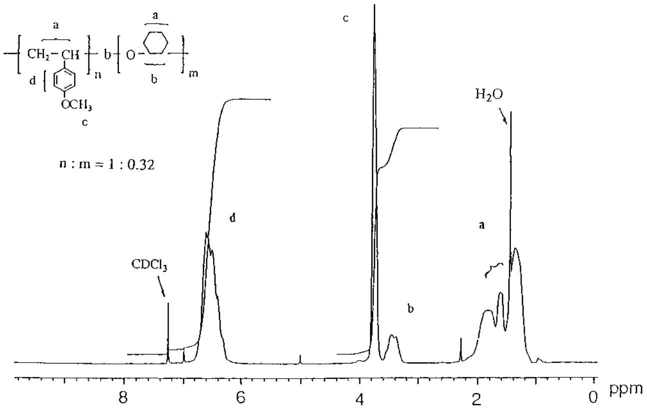


Figure 3. ^{1}H-NMR spectrum of poly(MOS-*b*-CHO) after extraction with hexane.

In order to get more information on the block copolymer formation, characterization of the hexane-insoluble part (80%) was performed using turbidimetric titration[19] and thin layer chromatography (TLC).[15] The turbidimetric titration curves of the hexane-insoluble fraction (no. 1 of Table 4), polyCHO, polyMOS, and a mixture of these homopolymers having the same composition as the hexane-insoluble fraction are shown in Figure 4. The turbidity appeared much sooner in polyCHO than in polyMOS in the solvent–precipitant system. The turbidimetric curve of the hexane-insoluble part is between the curves of the homopolymers, and the shape of the curve is similar to those of homopolymers. The turbidimetric behavior of the mixture of homopolymers gradually increased in two steps, which is quite different from that of the hexane-insoluble fraction. These findings support that the hexane-insoluble fraction is mainly composed of a block copolymer of MOS and CHO and that the amount of polyMOS homopolymers in the hexane-insoluble fraction is too little to be detected by the turbidimetric titration. This result is concordant with other solubility experiments in butanone, in which the block copolymer showed a blue turbid, and the blend

Table 4. Block Copolymerization of *p*-Methoxystyrene (MOS) and Cyclohexene Oxide (CHO) Initiated by AIBN and $Ph_2I^+PF_6^-$—Effects of Polymerization Conditions[a]

no.	MOS/CHO (molar ratio)	$[M_0]$ (M)	AIBN (mM)	Ph_2I^+ (mM)	time (h)	conv (%)	$\overline{M}_w \times 10^{-4}$	PMOS/PCHO (molar ratio, unit)
1	1:1.3	2.0	6	12	2	24	1.28 (1.58)	1:0.8 (1:0.32)
2	1:1.0	5.7	12	24	13	40	1.59 (1.85)	1:0.9 (1:0.40)
3	1:0.5	neat	24	72	13	84	1.25 (1.61)	1:0.6 (1:0.27)

[a] Solvent, CH_2Cl_2; polymerization temperature, 80 °C; data in parentheses, after extraction separation with *n*-hexane; $[M_0]$ = [MOS] + [CHO].

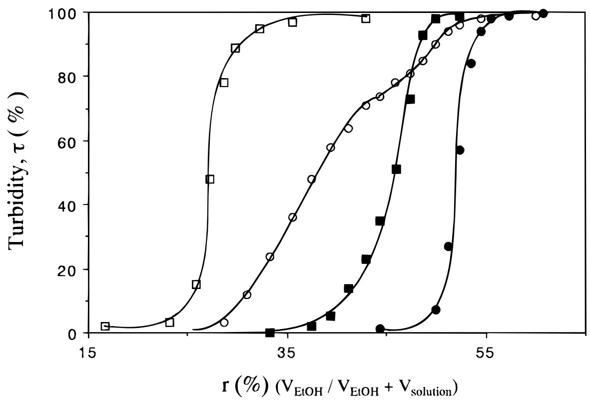


Figure 4. Turbidity plots of the solutions of block copolymer, homopolymers, and blend of homopolymers, detected at 400 nm: polymer concentration, 0.1% (wt); solvent, 75% (vol) benzene + 25% (vol) butanone; nonsolvent, ethanol; mole ratio of polyMOS vs polyCHO of the block copolymer and the blend sample, 1:0.3; (□) polyCHO, (●) polyMOS, (○) polyMOS−blend−polyCHO, and (■) poly(MOS-*b*-CHO).

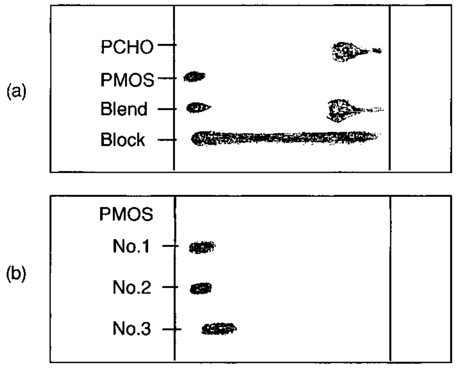


Figure 5. Thin-layer chromatogram obtained for (a) homopolymer, block copolymer, and their blend sample of CHO and MOS and (b) homopolymers of MOS with different molecular weights: no. 1, 2.06 × 10^4; no. 2, 1.39 × 10^4; and no. 3, 0.38 × 10^4.

sample of homopolymer whose molecular weight is almost the same as the hexane-insoluble fraction showed a phase separation with the liquid phase transparent.

TLC was used to get further information on the preparation of block copolymer.[15] The chromatographic behavior of the hexane-insoluble fraction (no. 1 of Table 4) is shown in Figure 5 along with those of polyCHO, polyMOS, and a mixture of the homopolymers. It is concluded from comparison of all data for the hexane-insoluble fraction with those for polyCHO, polyMOS homopolymers, and their blend that the hexane-insoluble fraction is mostly block copolymer. The reason why polyMOS is negligibly small in yield is probably due to the fact that the rate of the electron-transfer reaction is much faster than the bimolecular termination rate.

In conclusion, we have found a new method for the radical/cation transformation polymerization and succeeded in preparation of block copolymers by the transformation reaction from a free radical to a cationic mechanism.

References and Notes

(1) Odian, G. *Principles of Polymerization*, 3rd ed.; John-Wiley & Sons: New York, 1991.

(2) Bamford, C. H. Radical Polymerization. *Encyclopedia of Polymer Science and Engineering*; John-Wiley & Sons: New York, 1990; Vol. 13, p 708.

(3) (a) Hirooka, M.; Yabuuchi, H.; Morita, S.; Kawasumi, S.; Nakaguchi, K. *J. Polym. Sci., B* **1967**, *5*, 47. (b) Hirooka, M.; Yabuuchi, H.; Iseki, J.; Nakai, Y. *J. Polym. Sci., A-1* **1968**, *6*, 1381.

(4) Barton, J.; Borsig, E. *Complexes in Free Radical Polymerization*; Elsevier: Amsterdam, 1988.

(5) Kamachi, M. *Adv. Polym. Sci.* **1981**, *38*, 56.

(6) (a) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127. (b) Otsu, T.; Yoshida, M.; Tazaki, T. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 133. (c) Otsu, T.; Kuriyama, A. *Polym. J.* **1985**, *17*, 97.

(7) (a) Mardare, D.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1994**, *15*, 37. (b) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638. (c) Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 645. (d) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.

(8) (a) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1982**, *15*, 909. (b) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Patent 4,581,429, March 27, 1985. (c) Rizzardo, E. *Chem. Aust.* **1987**, *54*, 32. (d) Druliner, J. D. *Macromolecules* **1991**, *24*, 6079. (e) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987. (f) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316. (g) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185. (h) Hawker, C. j.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993.

(9) Examples for radical-promoted cationic polymerizations: (a) Bottcher, A.; Hasebe, K.; Hizal, G.; Stelberg, P.; Yagci, Y.; Schnabel, W. *Polymer* **1991**, *32*, 2289. (b) Sundell, P.-E.; Jönsson, S.; Hult, A. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1525. (c) Timpe, H.-J.; Rajendran, A. G. *Eur. Polym. J.* **1991**, *27*, 77. (d) Yagci, Y.; Borbely, J.; Schnabel, W. *Eur. Polym. J.* **1989**, *25*, 129. (e) Timpe, H.-J. *Pure Appl. Chem.* **1988**, *60*, 1033. (f) Ledwith, A. *Makromol. Chem., Suppl.* **1979**, *3*, 348. (g) Ledwith, A. *Polymer* **1978**, *19*, 1217. (h) Abdul-Rasoul, F. A. M.; Ledwith, A.; Yagci, Y. *Polymer* **1978**, *19*, 1219. (i) Pappas, S. P.; Pappas, B. C.; Gatechair, L. R. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 77. (j) Pappas, S. P.; Jilek, J. H. *Photogr. Sci. Eng.* **1979**, *23*, 140. (k) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977. (l) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, 16, 2441. (m) Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307.

(10) (a) Kuwae, Y.; Kamachi, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2474. (b) Kuwae, Y.; Kamachi, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2325.

(11) Schepple, S. E.; Seltzer, S. *J. Am. Chem. Soc.* **1968**, *90*, 358.

(12) Benaring, E. *Ann. Chem.* **1960**, *631*, 1.

(13) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977.

(14) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

(15) (a) Kotaka, T.; Uda, T.; Tanaka, T.; Inagaki, H. *Makromol. Chem.* **1975**, *176*, 1273. (b) Inagaki, H. Thin-Layer Chromatography. In *Fractionation of Synthetic Polymers*; Tung, L. H., Ed.; Marcel Dekker: New York, 1977.

(16) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; John-Wiley: New York, 1982.

(17) Battcher, A.; Hasebe, K.; Hizal, G.; Stelberg, P.; Yagci, Y.; Schnabel, W. *Polymer* **1991**, *32*, 2289.

(18) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley Interscience: New York, 1989; Chapter VIII.

(19) Dawkins, J. V. Characterization and Solution Properties of Block Copolymers. In *Block Copolymers*; Allpor, D. C., Janes, W. H., Eds.; Applied Science Publishers Ltd.: London, 1973; p 546.

MA951096Y