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RADICAL/CATION TRANSFORMATION POLYMERIZATION AND ITS APPLICATION TO THE PREPARATION OF BLOCK COPOLYMERS

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ABSTRACT

ESR study on the primary radicals obtained by decomposition of azo-compounds showed that primary radicals with electron donating substituents were transformed to the corresponding cations in the presence of electron acceptors such as $\text{Ph}_2\text{I}^+\text{PF}_6^-$. Accordingly, propagating radicals are transformed to the corresponding cations in the polymerization of *p*-methoxy-styrene (MOS), *n*-butyl vinyl ether (BVE), and *N*-vinylcarbazole (VCZ) with azoinitiators such as AIBN in the presence of electron acceptors such as $\text{Ph}_2\text{I}^+\text{PF}_6^-$. In the case of BVE, the polymer formation was caused by cationic species produced by the transformation of the initiating radical. The polymerizations of MOS and VCZ were ascribed to the transformation of the growing radical to the corresponding cation during the propagation step which was classified as the radical/cation transformation polymerization. Block copolymers of MOS/cyclohexene oxide (CHO) and VCZ/CHO were effectively prepared by the radical/cation transformation polymerization of the appropriate monomers in the presence of AIBN, electron acceptor and CHO. The formation of block copolymers was characterized by turbidimetry, thin-layer chromatography, and solubility tests.

INTRODUCTION

We have performed ESR study on the radical polymerization for a long time [1]. In the course of ESR study on the radical polymerization, we came across the fact that some propagating radicals are easily transformed to the corresponding cations in the presence of electron acceptor. As a result, we considered transformation of the radical to ion might be available for the sequence and structure control in the radical polymerization.

In the reference search, the possibility of the radical-promoted ionic polymerization has been pointed out by Ledwith in 1978 [2]. Crivello *et al.* [3] and Neckers *et al.* [4] succeeded in the polymer formation of cyclic epoxide and vinyl ether by the radical-promoted cationic polymerization. Block polymer formation from telechelic polymer has been reported by Yagci and Schnabel [5]. All papers applied the radical/cation transformation in initiation process to the polymer formation.

Radical polymerization is the most utilized method for the polymer formation of vinyl and diene compounds in industry. Numerous papers have been reported on the polymer formation by the radical polymerization mechanism. Accordingly, the radical polymerization is one of the most well-refined research fields in the polymer synthesis [6-10]. Sequence and structure controls are the most important problems in the polymer syntheses. These controls in the radical polymerization have been desired not only in the industrial points but also in the development in radical chemistry. However, these controls are more difficult in the radical polymerization than in ionic polymerization. Although it seemed to be difficult to control the sequence and the structure of polymer chains, progress in the reaction control has made in the following radical polymerization: 1) Discovery of iniferter by Professor Otsu [11]. 2) Preparation of telechelic polymers using chain transfer reagents and primary radical termination [12]. 3) Living radical polymerization using metal complexes [13] and weakly covalent bond [14].

To our knowledge, no paper has been reported on the radical/ion transformation in the propagation process. We paid attention to the sequence control by the radical/cation transformation of vinyl monomers [15, 16].

In this paper, we will mention radical-promoted cationic polymerizations using azocompounds and the block polymer formation by radical/cation transformation polymerization.

EXPERIMENTAL

Materials

1,1'-Azobis[1,1'-(4-methoxyphenyl)ethane] (ABMPE) was synthesized by the method of Schepple and Seltzer [17]. 2,2'-Azobis(2,2'-phenoxypropane) (ABPOP) was obtained by the method described by Benaring [18]. Commercially available 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. Diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) was prepared according to the reported manner [19]. Commercially available MOS, CHO, and *n*-butyl vinyl ether (BVE) were dried over calcium hydride, and distilled under reduced pressure. *N*-vinylcarbazole (VCZ) was recrystallized from methanol. Methylene dichloride and ethylene dichloride were purified by the general method [20].

Polymerization

A CH_2Cl_2 or $(\text{CH}_2\text{Cl})_2$ solution of a given amount of radical initiator (AIBN, or ABMPE), $\text{Ph}_2\text{I}^+\text{PF}_6^-$, and monomer or monomer mixtures in a glass ampoule was degassed by a freeze-thaw method. After being sealed off under high vacuum, the ampoule was kept at a certain temperature in the dark for a given period of time. The content of the ampoule 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.

Measurements

^1H -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 (M_n and M_w) and molecular weight distributions were roughly estimated by gel permeation chromatography (GPC) on a TOSOH CCP&8010 series high-speed liquid chromatography system equipped with 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.

Thin Layer Chromatography

Thin layer chromatography (TLC) was performed on the 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 micro syringe a spot of each solution was formed on the layer. Gradient elution was performed in the manner as described by Kotaka *et al.* [21]. CCl_4 and tetrahydrofuran (THF) were used as the first solvent and the second one, respectively. The ratio of CCl_4 /THF was 40/18. The sheet was placed into a chamber that contained iodine, making the position of the polymer as brown spots.

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

Radical/Cation Transformation Polymerization of *p*-Methoxystyrene and Vinyl Ether

(a) Influence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$ on the ESR Spectra of Different Radicals

Electron transfer reaction from propagating radicals of vinyl monomers to acceptors depends on the redox potentials of the radicals and acceptors. It is known that radicals with an electron-donating substituent are easier to transfer an electron to acceptors than those with an electron-accepting substituent. Accordingly, the propagating radicals of MOS and VCZ that have an electron-donating 4-methoxyphenyl and carbazole substituent, respectively, might be easier to transfer electrons to acceptors than radicals generated from AIBN that has an electron-accepting nitril substituent. This was confirmed by ESR experiments. The influences of $\text{Ph}_2\text{I}^+\text{PF}_6^-$ on ESR spectra of the propagating radical of MOS and the primary radical of AIBN are shown in Figure 1.

With the addition of $\text{Ph}_2\text{I}^+\text{PF}_6^-$, the ESR spectrum of the primary radical obtained from AIBN did not change. This result suggests that $(\text{CH}_3)_2\text{C}^-\text{CN}$ having an electron-accepting substituent did not perform an electron-transfer reaction to $\text{Ph}_2\text{I}^+\text{PF}_6^-$. On the other hand, the ESR spectrum of the propagating radical of MOS, which was clearly detected in radical polymerization of MOS, almost disappeared in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$. This means that the polyMOS propagating radical having an electron-donating substituent underwent the electron transfer reaction to $\text{Ph}_2\text{I}^+\text{PF}_6^-$ to form the corresponding carbocation.

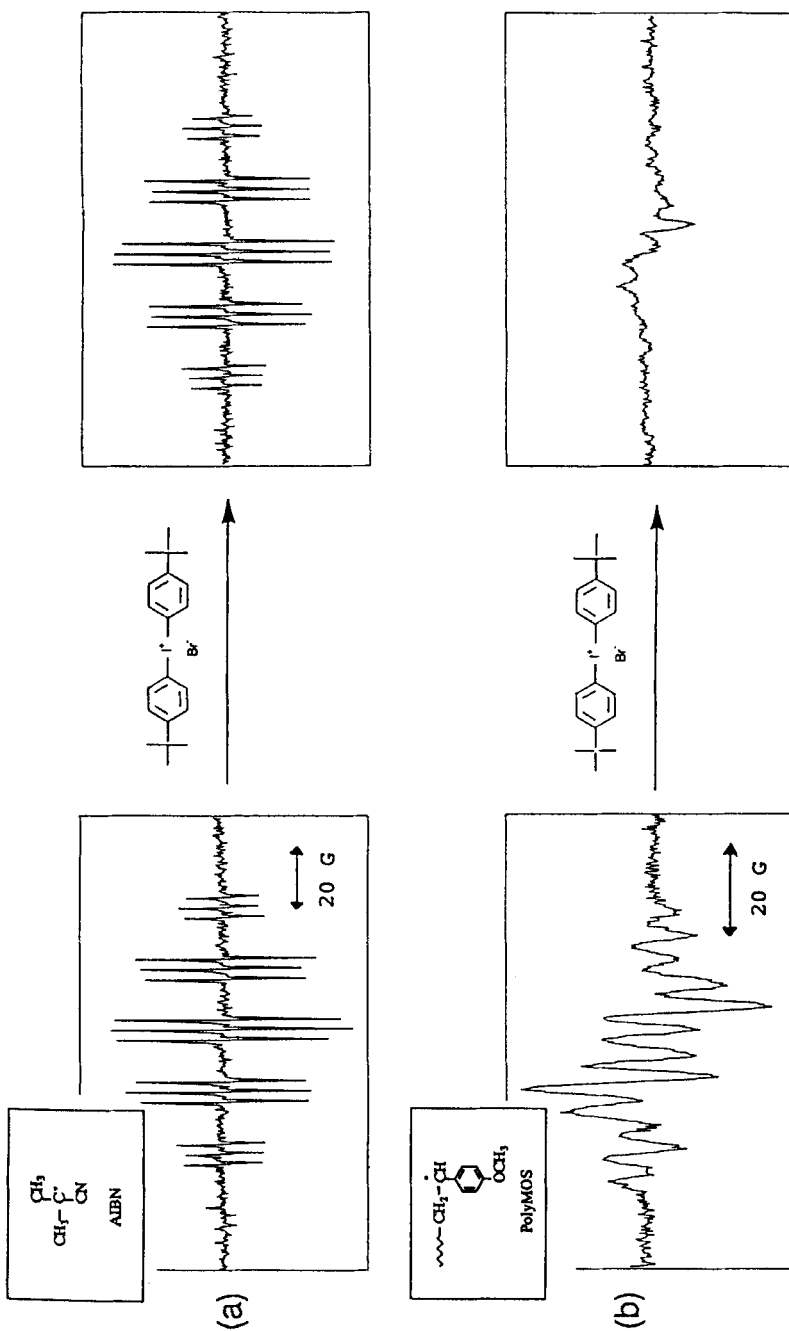


Figure 1. ESR spectra of primary radical obtained by decomposition of AIBN (a) and propagating radical of p-methoxy styrene (b) in the absence and presence of an acceptor under irradiation of an ultra-high pressure mercury lamp at 20°C.

TABLE 1. Cationic Polymerization of *n*-Butyl Vinylether (BVE), *p*-Methoxystyrene (MOS) and Cyclohexene Oxide (CHO) Promoted by Free Radical Initiators^{a)}

Monomer	Radical Initiator	concn (mol/l)	Ph ₂ I ⁺ PF ₆ ⁻ (mol/l)	Time (min)	conv. (%)	M _w × 10 ⁻⁴
BVE	none	0	6 × 10 ⁻³	80	5	1.08
	AIBN	6 × 10 ⁻³	0	80	0	
	AIBN	6 × 10 ⁻³	6 × 10 ⁻³	80	62	0.85
	ABMPE	6 × 10 ⁻³	0	80	0	
	ABMPE	6 × 10 ⁻³	6 × 10 ⁻³	80	68	0.95
	ABPOP	6 × 10 ⁻³	0	80	0	
	ABPOP	6 × 10 ⁻³	6 × 10 ⁻³	80	63	1.11
MOS	none	0	1.2 × 10 ⁻²	120	4	3.40
	AIBN	6 × 10 ⁻³	0	120	10	2.26
	AIBN	6 × 10 ⁻³	1.2 × 10 ⁻²	120	74	4.23
	ABMPE	6 × 10 ⁻³	0	120	4	4.81
	ABMPE	6 × 10 ⁻³	1.2 × 10 ⁻²	120	34	3.24
	ABPOP	6 × 10 ⁻³	0	120	2	6.01
	ABPOP	6 × 10 ⁻³	1.2 × 10 ⁻²	120	64	4.46
CHO	none	0	1.2 × 10 ⁻²	120	~1	
	AIBN	6 × 10 ⁻³	0	120	0	
	AIBN	6 × 10 ⁻³	1.2 × 10 ⁻²	120	~1	
	ABMPE	1.2 × 10 ⁻²	0	24 ^{b)}	0	
	ABMPE	1.2 × 10 ⁻²	2.4 × 10 ⁻²	24 ^{b)}	30	1.74
	No	0	2.4 × 10 ⁻²	24 ^{b)}	6	2.52

^{a)}Solvent: (CH₂)₂Cl₂; polymerization time: 80°C; monomer/(CH₂)₂Cl₂ = 1:3 (v);

^{b)}At 100°C in hours.

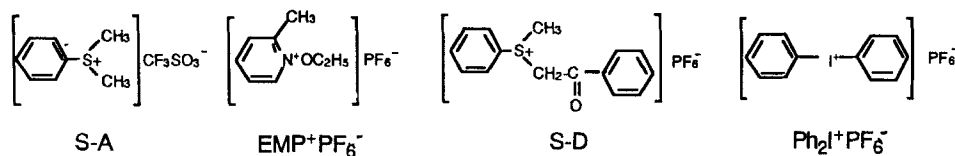
(b) Radical Promoted Cationic Polymerization

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 Ph₂I⁺PF₆⁻. In the presence of Ph₂I⁺PF₆⁻, however, high polymer was obtained in much higher yield from MOS and BVE by polymerization with AIBN, ABPOP, or ABMPE. CHO was polymerized to high polymer with ABMPE in the

presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$ and did not polymerize with AIBN even in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$.

Polymerizations of MOS, BVE, and CHO with $\text{Ph}_2\text{I}^+\text{PF}_6^-$ 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 [22], the polymer formation from these monomers shows that cationic polymerizations were performed with ABMPE in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$. 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 $\text{Ph}_2\text{I}^+\text{PF}_6^-$. The fact that CHO did not polymerize with AIBN, even in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$, is in agreement with the ESR observation in which no electron transfer reaction took place from $(\text{CH}_3)_2\text{C}^-\text{CN}$ to $\text{Ph}_2\text{I}^+\text{PF}_6^-$. However, the finding that BVE was polymerized in a high yield by AIBN in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$ is inconsistent with the explanation, because BVE does 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 the additional reaction of $(\text{CH}_3)_2\text{CCN}$ to BVE, to $\text{Ph}_2\text{I}^+\text{PF}_6^-$.

MOS was initiated to form high polymer by AIBN, and not by $\text{Ph}_2\text{I}^+\text{PF}_6^-$. When the polymerization of MOS was performed with AIBN in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$, the polymer formation from MOS was remarkably promoted, which indicates that polyMOS radicals initiated by AIBN were transformed into polyMOS cations by $\text{Ph}_2\text{I}^+\text{PF}_6^-$ 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 1. The polymerization of MOS with ABMPE and ABPOP was remarkably promoted in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$. This is also explained by radical/cation transformation of initiating radical and/or propagating radical in the propagation process.



Radical/Cation Transformation Polymerization of *N*-vinylcarbazole

The polymerization of VCZ in dichloromethane could be initiated by many kinds of electron-acceptors such as, sulfonium (S-A, S-D), pyridinium ($\text{EMP}^+\text{PF}_6^-$), and iodonium ($\text{Ph}_2\text{I}^+\text{PF}_6^-$). However, in the presence of CHO the polymerization

TABLE 2. Polymerization of *N*-Vinylcarbazole (VCZ) Initiated by Acceptor Itself Effect of Basic Compound on the Polymerization Rate ^a

Acceptor		CHO (M)	Temperature (°C)	Time (h)	Yield (%)
Name	E _p (V) ^b				
none		0	60	2	0.5
S-A	-1.64	0	60	2	13
			60	2	1
			60	2	63
EMP ⁺ PF ₆ ⁻	-0.91	0	60	2	1.5
		1.66	60	2	81
		1.66	60	2	2
S-D	-0.63	0	60	2	100
		1.66	60	2	
		1.66	60	2	
Ph ₂ I ⁺ PF ₆ ⁻	-0.20	0	25	at instance	
		1.66	60	2	2

^a Solvent: CH₂Cl₂; [VCZ] = 1.66 (mol/l). ^bHalf wave reduction potential vs. SCE [24-26].

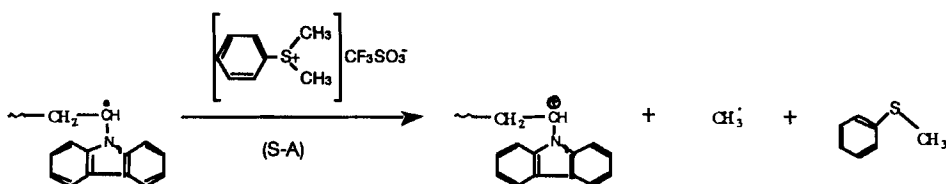
TABLE 3. Polymerization of *N*-Vinylcarbazole (VCZ) and Trioxane (TXN) Initiated by AIBN and/or S-A ^a

No.	AIBN (M)	S-A (M)	conv (%)	M _w × 10 ⁻⁴
1	6 × 10 ⁻³	0	5	3.89
2	6 × 10 ⁻³	1.2 × 10 ⁻²	13	3.02
3	0	1.2 × 10 ⁻²	1	2.75
4	6 × 10 ⁻³	1.2 × 10 ⁻²	0	

^aSolvent, (CH₂Cl₂)₂; polymerization temperature, 60°C; polymerization time, 4 hours; [VCZ] = [TXN] = 1.66 (M).

of VCZ almost did not occur (Table 2). This might be due to the solvation effect of basic compounds towards electron-acceptors [23]. Increased solvation leads to a more 'difficult' reduction of the electron-acceptor corresponding to a higher negative potential.

It is noteworthy that though almost no polymerization of VCZ occurred when initiated by S-A itself in the presence of trioxane (TXN), the polymerization of VCZ could take place in high rate when initiated by AIBN and S-A system. In



Scheme 1

spite of the fact that the radical polymerization of VCZ could take place by AIBN, a significant acceleration in the polymerization rate of VCZ was certainly found when initiated by AIBN in the presence of S-A (Table 3).

It is considered that the propagating radical of VCZ initiated by AIBN could be oxidized into propagating cation by S-A (Scheme 1) and the propagating cation of VCZ thus produced initiate the cationic polymerization of VCZ. This resulted in an acceleration in the polymerization rate of VCZ. These are understandable from the fact that electron transfer reaction from a propagating radical of VCZ to electron-acceptors is easier than from VCZ monomers.

From these results, it seems that the polymerization of VCZ can be controlled by making good use of the different reactivity towards electron-acceptors between VCZ and its propagating radical by selection of environment conditions such as the basicity of solvent and/or monomers.

Preparation of Block Copolymers

(a) Block Copolymer of MOS and CHO

Attention was paid to the findings that MOS is polymerized with an AIBN/ $\text{Ph}_2\text{I}^+\text{PF}_6^-$ 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 [22]. 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 $\text{Ph}_2\text{I}^+\text{PF}_6^-$ as shown in the Scheme 2. Results of the polymerization of the mixture of CHO and MOS are shown in Table 4 along with those of the control experiments.

The polymer was scarcely formed by the polymerization of a mixture of CHO and MOS with $\text{Ph}_2\text{I}^+\text{PF}_6^-$, and polyMOS was obtained in low yield by the polymerization with AIBN. The polymer was isolated in higher yield by the polym-

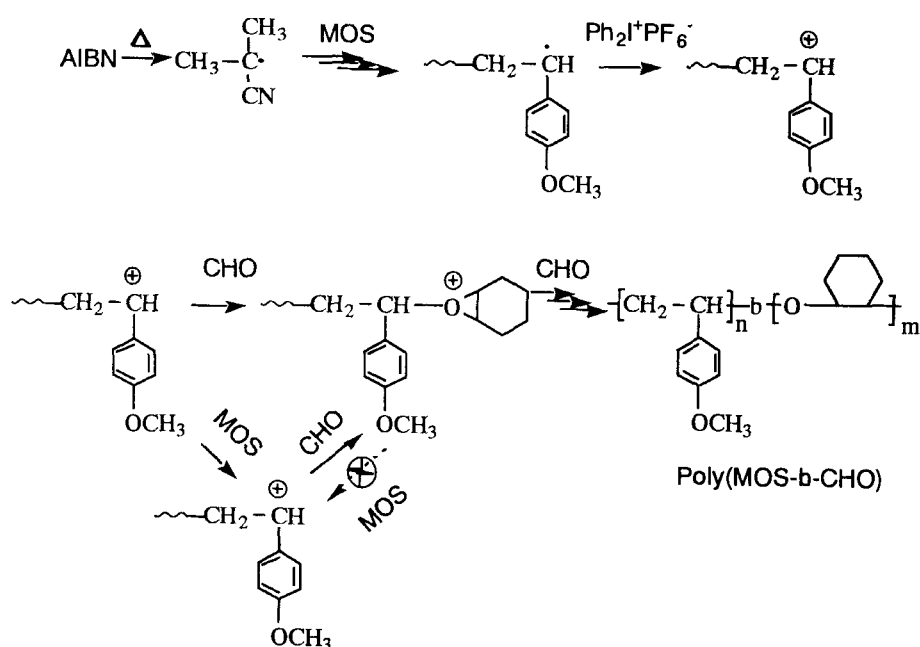


TABLE 4. Block Copolymerization of *p*-Methoxystyrene (MOS) and Cyclohexene Oxide (CHO) Initiated by AIBN and/or $\text{Ph}_2\text{I}^+\text{PF}_6^-$ ^a

MOS (mol/l)	CHO (mol/l)	AIBN (mol/l)	$\text{Ph}_2\text{I}^+\text{PF}_6^-$ (mol/l)	Yield (%)	$M_w \times 10^{-4}$	PMOS/PCHO (unit ratio)
1.9	2.5	6×10^{-3}	0	10	2.26	
1.9	2.5	0	1.2×10^{-2}	1		
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	0	6×10^{-3}	1.2×10^{-2}	74	4.23	

^aSolvent: CH_2Cl_2 ; polymerization temperature: 80°C ; polymerization time: 2 hours.

erization of the mixture with AIBN in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$. The NMR spectrum of the polymer obtained from a 1:1.3 mixture of monomers have both MOS and CHO units whose ratio is 1:0.8.

(b) Block Copolymer of VCZ and CHO

The polymerization results are shown in Table 5 along with those of control experiments.

TABLE 5. Block Copolymerization of *N*-Vinylcarbazole (VCZ) and Cyclohexene Oxide (CHO) Initiated by AIBN and $\text{Ph}_2\text{I}^+\text{PF}_6^-$ a)

VCZ (mol/l)	CHO (mol/l)	AIBN (mol/l)	$\text{Ph}_2\text{I}^+\text{PF}_6^-$ (mol/l)	Yield (%)	$M_w \times 10^{-4}$	PVCZ /PCHO (unit ratio)
1.5	3.0	1.2×10^{-2}	0	45	12.1	1 : 0
1.5	3.0	1.2×10^{-2}	2.4×10^{-3}	67	9.39	1 : 1.0
1.5	3.0	1.2×10^{-2}	4.8×10^{-3}	74	5.00	1 : 1.5
1.5	3.0	1.2×10^{-2}	9.6×10^{-3}	85	4.70	1 : 1.8
1.5	3.0	0	9.6×10^{-3}	4	3.12	
0	3.0	1.2×10^{-2}	1.2×10^{-2}	1		

a) Solvent: $(\text{CH}_2)_2\text{Cl}_2$; polymerization temperature: 65°C ; polymerization time: 4 hours.

When the polymerization of the mixture of VCZ and CHO was initiated by AIBN and $\text{Ph}_2\text{I}^+\text{PF}_6^-$ system, the polymer yield and the content of CHO unit in the polymer were increased with increasing concentration of $\text{Ph}_2\text{I}^+\text{PF}_6^-$. Since CHO can not be initiated by AIBN, and scarcely initiated by $\text{Ph}_2\text{I}^+\text{PF}_6^-$ itself, the polymerization of CHO must be initiated by the propagating cation of VCZ that was produced by the electron transfer reaction from the corresponding propagating radical of VCZ to $\text{Ph}_2\text{I}^+\text{PF}_6^-$. The VCZ unit in the polymer must be formed by the radical polymerization of VCZ because the cation polymerization of CHO was preferred at the monomer ratio of 2:1 CHO to VCZ [16] and the radical polymerization of VCZ could take place easily as shown in Table 5. This proposition is also supported by the block copolymer formation of VCZ and CHO [16].

Characterization of Block Copolymers

The formations of block polymers were confirmed by extraction separation, ^1H NMR, TLC, turbidimetric titration, and solubility [15, 16]. The characterization of PMOS-*b*-PCHO block copolymer are given here.

Some homopolymers may be produced (for example) by back-biting reactions of heterocyclic monomers in the course of polymerization along with the formation of the block copolymer. PolyCHO was separable 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. The 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

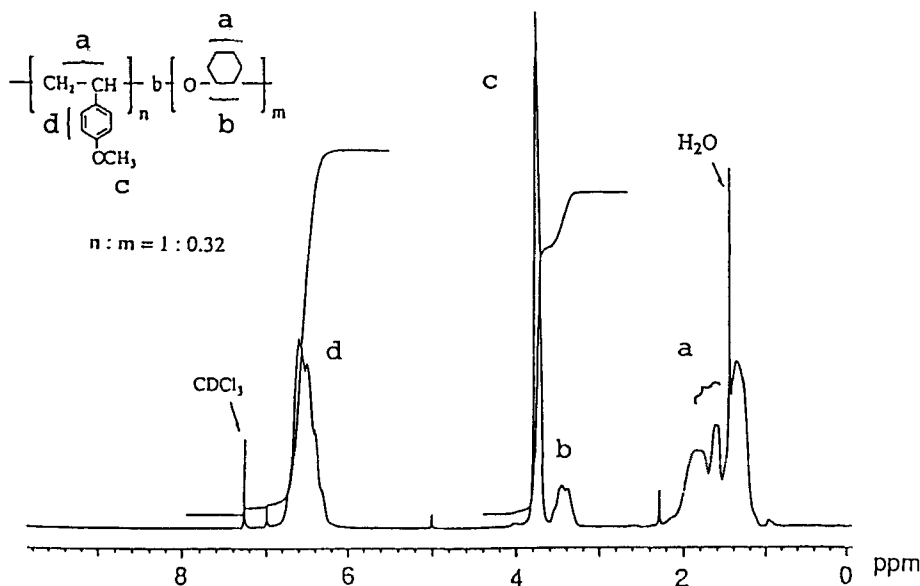


Figure 2. $^1\text{H-NMR}$ spectrum of poly(MOS-*b*-CHO) after extraction with hexane.

from the hexane-insoluble fraction was attempted by organic solvents such as *n*-butanone [27], which dissolves 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 block copolymer. The NMR spectrum of the hexane-insoluble part is shown in Figure 2, which gives the MOS to CHO unit ratio in the purified polymer of 1:0.32. This result, along with other examples, are shown in Table 6. 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.

In order to get more information on the block copolymer formation, characterization of the hexane-insoluble part (80%) was performed using turbidimetric titration. The turbidimetric titration curves of the hexane-insoluble fraction, polyCHO, polyMOS, and a mixture of these homopolymers (having the same composition as the hexane insoluble fractions) are shown in Figure 3. 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

TABLE 6. Block Copolymerization of *p*-Methoxystyrene (MOS) and Cyclohexene Oxide (CHO) Initiated by AIBN and $\text{Ph}_2\text{I}^+\text{PF}_6^-$ —Effects of Polymerization Conditions^{a)}

No.	MOS/CHO (molar ratio)	$[\text{M}_0]$ (mol/l)	AIBN (mM)	Ph_2I^+ (mM)	Time (h)	Conv (%)	$\text{M}_n \times 10^{-4}$	PMOS/PCHO (unit ratio)
1	1:1.3	2.0	6	12	2	24	1.28 (1.85)	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; $[\text{M}_0] = [\text{MOS}] + [\text{CHO}]$.

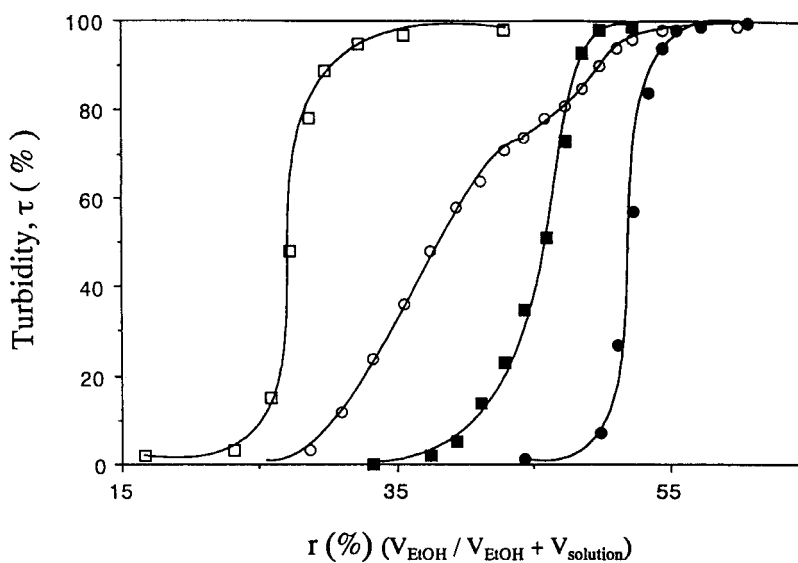


Figure 3. Turbidity plots of the solutions of block polymers, homopolymers, and blend of homopolymers, detected at 400nm: polymer concentration: 0.1% (wt); solvent: 75% (vol) benzene + 25% (vol) butanone; non-solvent: ethanol; molar ratio of polyMOS vs polyCHO of the block copolymer and the blend sample: 1:0.3; (□) polyCHO; (●) polyMOS; (○) polyMOS-blend-polyCHO, and (■) poly(MOS-b-CHO).

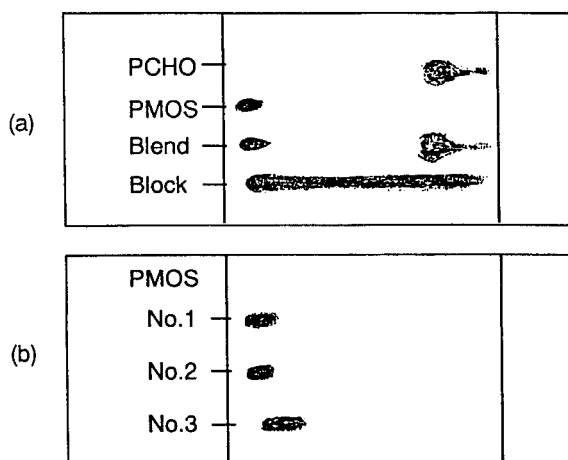


Figure 4. Thin-layer chromatogram obtained for (a) homopolymer, block copolymer, and their blend sample of CHO and MOS; (b) homopolymers of MOS with different molecular weights. No. 1: 2.06×10^4 ; No. 2: 1.39×10^4 ; No. 3: 0.38×10^4 .

of the homopolymers, and the shape of the curve is similar to those of homopolymers. The turbidimetric behavior of the mixture of homopolymers gradually changed in two steps, which is quite different from that of the hexane-insoluble fractions. These findings support the fact 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 small to be detected by the turbidimetric titration. This result is concordant with the solubility experiments in butanone in which the block copolymer showed a blue turbidity, and the blend sample of homopolymer (of molecular weight 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 [28]. The chromatographic behavior of the hexane-insoluble fraction is shown in Figure 4 along with those of polyCHO, polyMOS, and a mixture of the homopolymers. From a comparison of all data for the hexane-insoluble fraction with those for polyCHO, polyMOS homopolymers, and their blend, it is concluded that the hexane-insoluble fraction is mostly block copolymer. The reason 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.

The formation of poly(VCZ-b-CHO) was confirmed by a similar method [16].

CONCLUSION

We have found a new route to control radical polymerization by transformation the propagating radical into the corresponding cation with electron acceptors in the radical polymerization process of vinyl monomers. Many kinds of block copolymers with radically polymerized segments and cationically polymerized segments were prepared by this one shot method. Studies on the factors effecting the radical/cation transformation and the conditions for preparation of block copolymers with other monomers are now in progress.

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