Cationic Block and Graft Polymerization of 1,3-Dioxolane onto Living Poly(*p*-methoxystyrene)

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ABSTRACT: Cationic block and/or graft copolymerization of 1,3-dioxolane (DOL) onto poly(*p*-methoxystyrene) [poly(*p*-MOS)] was investigated. Block copolymer were obtained by the polymerization of DOL initiated with living poly(*p*-MOS) prepared with an iodine initiator in carbon tetrachloride at 0 ~ -15°C. The successful block copolymerization required the presence of a neutral salt with a less nucleophilic counterion ($\text{ClO}_4^\ominus$, $\text{BF}_4^\ominus$, or $\text{SbF}_6^\ominus$), which activates the living end *via* counterion exchange; in the absence of the salt, the living poly(*p*-MOS) could not polymerize DOL. The blocking reactions were accompanied by the formation of graft copolymers due to the attack of the propagating poly(DOL) chains onto the aromatic rings of poly(*p*-MOS). The $\text{ClO}_4^\ominus$ anion functioned as the best counterion, leading to higher yields of the block copolymer with less graft copolymers. *p*-MOS-DOL graft copolymers were also prepared by the DOL polymerization with an acetyl salt, (AcX ; $\text{X} = \text{ClO}_4^\ominus$, $\text{BF}_4^\ominus$, $\text{SbF}_6^\ominus$), in the presence of a dead poly(*p*-MOS).

KEY WORDS Cationic Polymerization / Living Polymerization / Block Copolymerization / Graft Copolymerization / *p*-Methoxystyrene / 1,3-Dioxolane / Poly(*p*-methoxystyrene-*b*-1,3-dioxolane) / Poly(*p*-methoxystyrene-*g*-1,3-dioxolane) / Exchange of Counterion /

The "living," (strictly speaking, "long-lived"), polymer is formed by the iodine-initiated cationic polymerization of *p*-methoxystyrene (*p*-MOS) which gives a stable carbocation at low temperatures in a nonpolar solvent.¹ Block copolymers have been synthesized by polymerizing isobutyl vinyl ether with the "living" poly(*p*-MOS).²

However, there have been only a few studies on the block copolymers of vinyl and cyclic monomers prepared by cationic polymerization. Yamashita *et al.*³ reported the synthesis of a block terpolymer, poly[styrene-*b*-1,3-dioxolane-*b*-3,3-bis(chloromethyl)oxetane]. Pepper *et al.*⁴ prepared block copolymers by polymerizing aziridines with a dormant polystyryl carbocation at a low temperature. Two reasons are pointed out as to why such block copolymers are difficult to prepare: (a) the "living" cationic polymerization of vinyl monomers is difficult because of the instability of their

propagating carbocations; and (b) although "living" polymers can be prepared in cationic polymerization of cyclic ethers, they cannot add to less basic vinyl monomers because of their low electrophilicity.

The purpose of the present investigation has been the synthesis of block copolymers by polymerizing a cyclic monomer [1,3-dioxolane(DOL)] in the presence of the "living" poly(*p*-MOS). DOL was chosen as a cyclic monomer since it easily polymerizes by a cationic mechanism to form flexible polymers. The graft copolymerization of DOL onto poly(*p*-MOS) was also examined.

EXPERIMENTAL

Materials

p-MOS was synthesized from *p*-methoxyacetophenone.⁵ Guaranteed reagent grade DOL and 3,3-

bis(chloromethyl)oxetane (BCMO) were dried and distilled over calcium hydride (CaH_2) before use. The polystyrene used ($M_n=15000$) was the standard sample for GPC. Iodine (purity > 99.8%) was used without further purification. Acetyl salts (AcX ; $\text{X} = \text{ClO}_4^\ominus, \text{BF}_4^\ominus, \text{SbF}_6^\ominus$) were synthesized by reactions of the corresponding silver salts with acetyl chloride. Carbon tetrachloride (CCl_4) was washed with 10% aqueous sodium hydroxide, dried over calcium chloride overnight and distilled over CaH_2 before use. Bromobenzene was dried and distilled over CaH_2 .

Polymerization Procedures

All polymerizations were carried out under a dry nitrogen atmosphere in a test tube equipped with a three-way stopcock. (i) Polymerization of DOL in the presence of dead poly(*p*-MOS): this reaction was initiated by injecting an initiator solution to a solution of DOL and a dead poly(*p*-MOS) in CCl_4 . The dead poly(*p*-MOS) ($M_n=9000$) was obtained by killing with methanol the "living" poly(*p*-MOS) prepared as below. (ii) Polymerization of DOL initiated by "living" poly(*p*-MOS): *p*-MOS (0.5 M) was polymerized by iodine (10 mM) at 0° or -15°C in CCl_4 to prepare the "living" poly(*p*-MOS). Following completion of the polymerization of *p*-MOS, DOL containing a neutral salt, such as AgSbF_6 , AgBF_4 , or Bu_4NClO_4 , was added to the reaction mixture.

Polymerization was terminated by adding methanol containing a small amount of aqueous ammonia. The conversion of DOL was determined by gas chromatography using bromobenzene as the internal standard. The products were precipitated in a large amount of cold methanol, filtered off, and then dried *in vacuo*.

Characterization of Copolymers

The DOL homopolymer, soluble in methanol, was extracted from the gross polymers with methanol, using a Soxhlet extractor over a period of 24 h. Control experiments showed that a mixture of poly(*p*-MOS) and poly(DOL) could be separated completely into soluble [poly(DOL)] and insoluble [poly(*p*-MOS)] parts in this manner. The composition of copolymers (methanol-insoluble part) was determined by ^1H NMR (JOEL MH60; in CCl_4) from the ratio of the formal protons ($-\text{OCH}_2-$) of poly(DOL) to the aromatic protons of poly(*p*-MOS). The molecular weight distribution

(MWD) of the copolymers was obtained by gel-permeation chromatography (GPC) on a Toyo Soda Model HLC-807 in tetrahydrofuran. The number-average molecular weight (M_n) of copolymers was calculated from GPC curves on the basis of a polystyrene calibration. The thermal behavior of the copolymers was measured by a differential scanning calorimetry (DSC) on a Rigaku Denki Model Thermoflex-8001 under a nitrogen atmosphere. The heat of fusion, ΔH_m (cal g^{-1}), of the polymers was calculated from the DSC peak area by making reference to an indium calibration.

RESULTS AND DISCUSSION

Polymerization of DOL in the Presence of Dead Poly(*p*-MOS)

In order to examine whether the propagating carboxonium ion of DOL attacks the aromatic rings of poly(*p*-MOS) to give a graft copolymer, DOL was polymerized with three acetyl salts (AcX ; $\text{X} = \text{SbF}_6^\ominus, \text{BF}_4^\ominus, \text{ClO}_4^\ominus$) in the presence of poly(*p*-MOS). Extraction with methanol separated the products into soluble and insoluble parts. The methanol-soluble part was a DOL homopolymer since it showed no UV absorption at 254 nm owing to the aromatic ring of poly(*p*-MOS). On the other hand, the methanol-insoluble part was confirmed to contain graft copolymers [poly(*p*-MOS-*g*-DOL)] by the presence of the UV absorption at 254 nm and the ^1H NMR absorption due to the formal units of poly(DOL). By this procedure, the graft copolymer could not be separated from the unreacted poly(*p*-MOS).

Table I summarizes the results of the graft copolymerization. The poly(DOL) content and the grafting efficiency are defined by eq 1 and eq 2, respectively.

The graft copolymers were prepared irrespectively of the type of initiator. The halogenated-metal anions ($\text{SbF}_6^\ominus$ and $\text{BF}_4^\ominus$) as counterions gave poly(DOL) contents and grafting efficiencies higher than the perchlorate anion and the grafting efficiency was higher at 0°C than at -15°C .

Haas *et al.*⁶ reported the formation of graft copolymers on polymerizing styrene with SnCl_4 in the presence of poly(*p*-MOS). They propose that the graft copolymers are prepared by the attack of the polystyryl carbocation on the aromatic ring of poly(*p*-MOS). In the present work, similarly, the

Table 1. Cationic graft copolymerization of DOL onto poly(*p*-MOS) in CCl₄ at 0°C and -15°C^{a,b}

Temp °C	Initiator	DOL content	Grafting efficiency	<i>M_n</i> of polymer	
		%	%	MeOH-insoluble part	MeOH-soluble part
0	AcSbF ₆	69	38	18600	5200
	AcBF ₄	67	36	21900	8800
	AcClO ₄	63	29	21800	8900
-15	AcSbF ₆	63	25	16500	5100
	AcBF ₄	62	25	15900	7900
	AcClO ₄	46	14	11900	7100

^a [DOL]₀, 3.84 M; [poly(*p*-MOS)], 0.50 M (by monomer unit); *M_n*=9000; [C]₀, 10 mM; time, 64 h.^b Conversion (at 64 h): 0°C, 87–90%; -15°C, 93–94%.

$$\text{Poly(DOL) content (\%)} = \frac{\text{Weight of graft-polymerized DOL}}{\text{Weight of poly}(p\text{-MOS}) + \text{Weight of graft-polymerized DOL}} \times 100 \quad (1)$$

$$\text{Grafting efficiency (\%)} = \frac{\text{Weight of graft-polymerized DOL}}{\text{Weight of polymerized DOL}} \times 100 \quad (2)$$

growing carboxonium ion of DOL probably attacks the electron-rich aromatic ring with a methoxy group, yielding graft copolymers.

Polymerization of DOL Initiated by "Living" Poly(*p*-MOS)

The polymerization of DOL initiated by "living" poly(*p*-MOS) will form block copolymers. An attempt to polymerize DOL by the iodine-initiated living poly(*p*-MOS) resulted in a very small reaction rate at 0°C in CCl₄ (Figure 1). Thus, in order to enhance the polymerization activity of the living end, the iodide counterion I₃[⊖] was exchanged with a less nucleophilic counterion (SbF₆[⊖], BF₄[⊖], or ClO₄[⊖]) by adding the corresponding neutral salt (AgSbF₆, AgBF₄, or Bu₄NClO₄, respectively) (Figure 1). Such counterion exchange is known to accelerate the polymerization of vinyl monomers.⁷ Figure 1 shows that the polymerization rate of DOL is indeed increased by the counterion exchange in the order SbF₆[⊖] > ClO₄[⊖] > BF₄[⊖] > I₃[⊖]. Plesch *et al.*⁸ also observed the same order for the polymerization rate of DOL by triethyloxonium salts. DOL did not polymerize by these neutral salts themselves. The polymerization of *p*-MOS with the less nucleophilic counterions (SbF₆[⊖], BF₄[⊖], and ClO₄[⊖]) was accom-

Figure 1. Acceleration of DOL polymerization by addition of a neutral salt: initiator, living poly(*p*-MOS) prepared at [*p*-MOS]₀, 0.50 M and [I₂]₀, 10.0 mM at 0°C or -15°C; [DOL]₀, 3.84 M; solvent, CCl₄. Added neutral salt (10.0 mM): (□) AgSbF₆; (○) Bu₄NClO₄; (△) AgBF₄; (×) none (I₃[⊖] counterion).

panied by frequent chain transfer, with the result that no living polymers were formed. Exchange of the counterion, therefore, is necessary for the formation of the block copolymer.

The methanol-insoluble part of the product had the ¹H NMR absorptions due to the aromatic

protons of poly(*p*-MOS) ($\delta=6.5$ ppm) and the formal protons of poly(DOL) ($\delta=4.6$ ppm), thus confirming the formation of the block and/or graft copolymers. The DOL content in the copolymers, calculated from the formal to aromatic proton ratio, increased with increasing conversion of DOL both at 0°C and -15°C, and in the order $\text{BF}_4^- > \text{ClO}_4^- \approx \text{SbF}_6^- > \text{I}_3^- = 0$ at 0°C, as shown in Figure 2. However, it is not yet conclusive whether the DOL units are incorporated as block or graft since DOL can graft-copolymerize onto dead poly(*p*-MOS) as described in the previous section. Figure 2 also shows the blocking and/or grafting efficiency calculated from eq 2. The efficiency increased with increasing of DOL both at 0°C and -15°C, but was below 50% with any counterion. These results suggest the considerable formation of DOL homopolymer by chain transfer reactions.

As Figure 3 shows, the MWD curve of the methanol-insoluble polymers obtained with ClO_4^- shifted toward the higher MW side and broadened

Figure 3. GPC curves of poly(*p*-MOS-*b/g*-DOL) obtained with ClO_4^- in CCl_4 at 0°C. DOL content: A, 0% (original poly(*p*-MOS)); B, 11%; C, 24%.

Figure 2. Effects of counterions on the DOL content in copolymers and on the block and/or graft efficiency in the polymerization of DOL. Polymerization conditions are the same as in Figure 1. Counterion: (□) SbF_6^- ; (○) ClO_4^- ; (△) BF_4^- ; (×) I_3^- (no salt).

with an increase of the DOL content. The M_n of the insoluble polymers also increased with increasing DOL content when the other counterions were involved (Figure 4). On the other hand, the M_n of the methanol-soluble part [homopoly(DOL)] did not greatly change during the polymerization.

Figure 4. Relationship between the M_n of the methanol-insoluble part and the DOL content in poly(*p*-MOS-*b/g*-DOL) obtained with various counterions. Polymerization conditions are the same as in Figure 1. Counterion: (□) SbF_6^- ; (○) ClO_4^- ; (△) BF_4^- .

Figure 5. DSC curves for *p*-MOS-DOL copolymers and relevant polymers obtained in CCl_4 at 0°C : A—C, block/graft copolymers; D, poly(*p*-MOS); E, poly(DOL); F—H, graft copolymers. DOL content (counterion in synthesis): A, 34% (SbF_6^-); B, 39% (BF_4^-); C, 44% (ClO_4^-); F, 18% (SbF_6^-); G, 30% (BF_4^-); H, 46% (ClO_4^-). The poly(DOL) was prepared with AcClO_4 in CCl_4 at 0°C .

Structure of Copolymers Obtained with Living Poly(*p*-MOS)

Figure 5 shows the DSC curves for the copolymers which contained 30–50% of DOL units. The DSC curves for poly(*p*-MOS), poly(DOL) and graft copolymers obtained from dead poly(*p*-MOS) are also shown for comparison. Two endothermic peaks were observed for the copolymers obtained with the living poly(*p*-MOS) irrespective of counterions. The graft copolymers, however, showed no endothermic peak. In the range of 20 to 80°C , the DSC curve for poly(*p*-MOS) exhibited no thermal change at all, while that for poly(DOL) exhibited two endothermic peaks corresponding to the melting of the polymer. These two endothermic peaks are due to the multi-morphology of crystalline poly(DOL).⁹

In general, block chains in a solid state easily gather together to construct a crystalline structure, whereas graft chains, especially at a low graft content, cannot come together in that they are

distributed separately on a trunk-polymer chain. If this view is valid, then the endothermic peaks of the copolymers obtained with the living poly(*p*-MOS) imply that the copolymers contain poly(DOL) blocks. Thus, the products from the living poly(*p*-MOS) consist of not merely graft copolymers, but also block copolymers.

Figure 6 shows the plots of the heat of fusion (ΔH_m), calculated from the DSC peak area in the range of 20 to 80°C , against the DOL content in the copolymer. The copolymers obtained with the living polymer gave the melting peaks due to the poly(DOL) component even at a low DOL content. ΔH_m increased with increasing DOL content, approaching the value for poly(DOL) (26.8 cal g^{-1}). At low DOL content, a poly(DOL) block, combined to poly(*p*-MOS), is certainly too short to crystallize. The increase in ΔH_m with increasing DOL content suggests an increase in the block-chain length.

A graft chain may also be able to crystallize at a high DOL content, since the number of poly(DOL) branches on a poly(*p*-MOS) chain increases with an increase in the DOL content. Consequently, the graft copolymers as well as the block copolymers showed a large ΔH_m value at a high DOL content.

Figure 6 also indicates qualitatively the effect of counterions on the blocking efficiency. The copolymer obtained with the ClO_4^- counterion gave a large ΔH_m value even at a low DOL content. This means that, with the ClO_4^- counterion, the block

Figure 6. Relationship between the heat of fusion (ΔH_m) and the DOL content for poly(*p*-MOS-*b/g*-DOL) obtained in CCl_4 at 0°C and -15°C . Polymerization conditions are the same as in Figure 1 and Table I. (○, △, □), block/graft copolymers; (●, ▲, ■), graft copolymers. Counterion in synthesis: (□, ■) SbF_6^- ; (○, ●) ClO_4^- ; (△, ▲) BF_4^- .

copolymerization proceeds without formation of a graft copolymer and the resultant copolymer has a crystallizable long block. The formation of long poly(DOL) blocks is consistent with the low graft efficiency of the ClO_4^- counterion in the polymerization of DOL in the presence of dead poly(*p*-MOS) as shown in Table I.

At approximately the same DOL content, the copolymer obtained at 0°C revealed a somewhat smaller ΔH_m than that at -15°C. This may be due to a frequent transfer reaction, or, in other words, the formation of a shorter block at higher temperature.

Cause of Graft Polymerization

The polymerization of DOL initiated by the living poly(*p*-MOS) yielded simultaneously both block and graft copolymers. Two factors are considered to bring about the graft polymerization: (a) the high electron density on the aromatic ring of *p*-MOS owing to its electron-donating methoxy group; and (b) the high reactivity of the propagating carboxonium ion of DOL. In order to clarify the dominant factor, the graft copolymerization of DOL onto polystyrene and of BCMO onto poly(*p*-MOS) were examined. In the former system, the backbone polymer lacks a substituent that may enhance the grafting reaction; in the latter, BCMO probably forms a less reactive carboxonium ion than DOL.

Table II summarizes the results of the graft copolymerization of DOL onto polystyrene initiated with AcSbF_6 or AcClO_4 . Both the poly(DOL) content and the grafting efficiency were smaller than those for the graft copolymerization onto poly(*p*-MOS) shown in Table I. Especially with the ClO_4^- counterion, DOL combined only to a small extent with polystyrene. These results suggest that the propagating carboxonium ion of DOL hardly attacks the aromatic rings of polystyrene which has no electron-donating group.

BCMO was polymerized with three acetyl salts in

Table II. Cationic graft copolymerization of DOL onto polystyrene in CCl_4 at 0°C and -15°C^{a,b}

Temp °C	Initiator	DOL content	Grafting efficiency
		%	%
0	AcSbF_6	27	5
	AcClO_4	10	2
-15	AcSbF_6	26	4
	AcClO_4	2	0.3

^a $[\text{DOL}]_0$, 3.84 M; $[\text{polystyrene}]$, 0.50 M (by monomer unit); $M_n = 15000$; $[\text{C}]_0$, 10 mM; time, 64 h.

^b Conversion (at 64 h): 0°C, 88–89%; -15°C, 89–93%.

Table III. Cationic graft copolymerization of BCMO onto poly(*p*-MOS) in CCl_4 at 0°C and -15°C^a

Temp °C	Initiator	Conversion %	Benzene-insoluble part		Benzene-soluble part	
			$\text{Cl}^+\%$ ^b	BCMO%	$\text{Cl}^+\%$ ^b	BCMO%
0	AcSbF_6	82	44.0	96.0	16.2	35.3
	AcBF_4	76	33.7	73.5	16.4	35.9
	AcClO_4	14	—	—	1.9	4.3
-15	AcSbF_6	91	42.3	92.4	13.3	29.1
	AcBF_4	63	32.6	71.1	8.2	17.9
	AcClO_4	13	—	—	1.2	2.5

^a $[\text{BCMO}]_0$, 0.50 M; $[\text{poly}(p\text{-MOS})]$, 0.50 M (by monomer unit); $M_n = 9000$; $[\text{C}]_0$, 10 mM; time, 64 h.

^b 45.8% for pure poly(BCMO).

the presence of dead poly(*p*-MOS). The products were separated by Soxhlet extraction with benzene. When a mixture of poly(*p*-MOS) and poly(DOL) was extracted, the benzene-soluble and -insoluble parts were confirmed to be poly(*p*-MOS) and poly(BCMO), respectively. As shown in Table III, both benzene-soluble and -insoluble parts contained poly(BCMO) as well as poly(*p*-MOS) components, and hence it was found that the graft copolymer could be prepared with AcSbF₆ and AcBF₄. This shows that even the less reactive oxonium ion derived from BCMO attacks the aromatic ring of poly(*p*-MOS) to give graft copolymers. With the ClO₄[−] counterion, however, the graft polymerization hardly occurred again.

The above results indicate that grafting of the propagating poly(DOL) chain onto poly(*p*-MOS) is caused by the high electron density on the aromatic ring of the latter.

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