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Communications to the Editor

New Reactive Polymer Carrying a Pendant Oxetane Ring

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Addition reactions[1,2] of oxirane with amine, alcohol, phenol, carboxylic acid, acyl chloride, and an active ester are well-known as is the ring-opening polymerization[3] of oxirane, and pendant epoxide groups in the polymer have been widely used as useful reactive groups for the chemical modification of the polymers. On the other hand, although an enormous number of papers for cationic ring-opening polymerization of oxetane compounds have been reported,[3] the addition reaction of pendant oxetane rings in the polymer with the above reagents has not been investigated previously.

Recently, we reported[4] some new addition reactions of cyclic ethers such as oxirane and oxetane with active esters using quaternary onium salts or crown ether complexes as catalysts. In this paper, we report a new successful addition reaction of the pendant oxetane ring in the polymers with some acyl chlorides and *S*-phenyl thioacetate (PTA) using quaternary onium salts or tertiary amines as catalysts.

(3-Methyl-3-oxetanyl)methyl methacrylate (MOM) [bp 68–69 °C (2 mmHg); lit.[5] bp 66 °C (1 mmHg)] was synthesized in 65% yield by transesterification between 10-fold methyl methacrylate and (3-methyl-3-oxetanyl)methanol using sodium hydroxide (5 mol %) as a catalyst at room temperature for 1.5 h. Poly[(3-methyl-3-oxetanyl)methyl methacrylate] (PMOM) [reduced viscosity was 0.17 dL/g in DMF (0.5 g/dL) at 30 °C] was prepared in 79% yield by radical polymerization of MOM with AIBN (1 mol %) in toluene (1 mol/L) at 60 °C for 5 h and then 80 °C for 3 h under nitrogen.

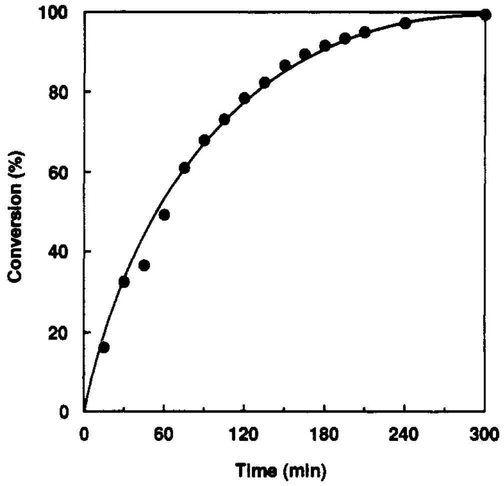

Figure 1. Addition reaction of MOM with BZC: carried out with MOM (4 mmol) and BZC (4 mmol) using TBAB (0.12 mmol) as a catalyst in toluene (2 mL) at 90 °C.

Since MOM can also be classified as a new reactive monomer, an addition reaction of MOM with benzoyl chloride (BZC) was performed in toluene using tetrabutylammonium bromide (TBAB) as a catalyst at 90 °C. As shown in Figure 1, the reaction proceeded very smoothly to give the adduct 3-(benzoyloxy)-2-(chloromethyl)-2-methylpropyl methacrylate[6] (1) in quantitative yield, which was measured by GLC analysis.

On the other hand, corresponding polymers **2a** were obtained with 70 and 86% conversions for 4 and 24 h, respectively, when the addition reaction of PMOM with BZC was carried out using TBAB in toluene at 90 °C (Scheme I). When poly(glycidyl methacrylate) (PGMA) or PMOM was reacted with BZC in DMAc at 90 °C for 4 h, the degrees of conversion were 66 and 67%, respectively. Also the reaction of PMOM with BZC proceeded with high conversions in the presence of tetrabutylphosphonium bromide (TBPB), pyridine, or 4-(*N,N*-dimethylamino)pyridine (DMAP), and then it was found that DMAP has a slightly higher activity than TBAB, TBPB, and pyridine. Reactions with cinnamoyl chloride (CMC)

Table I
Addition Reaction of the Pendant Oxetane Ring with Acyl Chloride or an Active Ester

run no.	cyclic ether (mmol)	reagent (mmol)	catalyst (mmol)	solvent (mL)	temp, °C	time, h	DC,[a] %
1	MOM (4)	BZC (4)	TBAB (0.12)	toluene (2)	90	4	97[b]
2	MOM (4)	BZC (4)	TBAB (0.12)	toluene (2)	90	5	99[b]
3	PMOM (4)	BZC (4)	TBAB (0.12)	toluene (2)	90	4	70[c]
4	PMOM (4)	BZC (4)	TBAB (0.12)	toluene (2)	90	24	86[c]
5	PMOM (4)	BZC (4)	TBAB (0.12)	DMAc (2)	90	4	67[c]
6	PGMA (4)	BZC (4)	TBAB (0.12)	DMAc (2)	90	4	66[c]
7	PMOM (4)	BZC (4)	TBPB (0.12)	toluene (2)	90	4	64[c]
8	PMOM (4)	BZC (4)	pyridine (0.12)	toluene (2)	90	4	70[c]
9	PMOM (4)	BZC (4)	DMAP (0.12)	toluene (2)	90	4	78[c]
10	PMOM (4)	CMC (4)	TBAB (0.12)	toluene (2)	90	4	95[c]
11	PMOM (4)	AC (4)	TBAB (0.12)	toluene (2)	50	4	100[c]
12	PMOM (4)	PTA (12)	TBPB (0.20)	none	120	48	73[c]
13	PMOM (4)	PTA (4)	TBPB (0.12)	NMP (2)	120	48	39[c]

[a] Degree of conversion. [b] Determined by GLC. [c] Determined by ^1H NMR spectrum.

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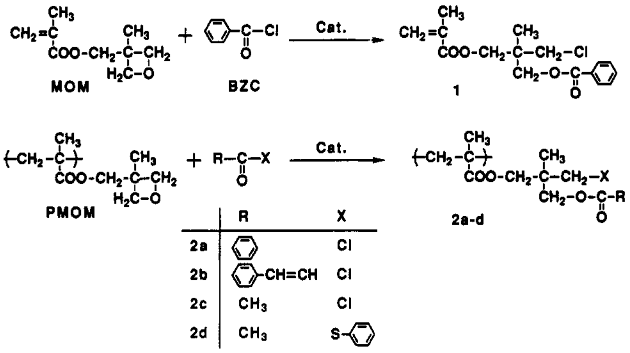
Scheme I



or acetyl chloride (AC) took place in high conversions to give the corresponding polymers (**2b,c**) under similar conditions.

These results suggest that, although the reactivity of the pendant oxetane ring in PMOM was lower than that of MOM because of the steric hindrance of the polymer chain, the reaction of the pendant oxetane ring in the polymer with acyl chlorides proceeded smoothly with high degrees of conversion using quaternary onium salts or tertiary amines as the catalysts. Furthermore, it was found that the reactivity of the pendant oxetane ring in PMOM was mostly the same as that of the pendant oxirane group in PGMA.

An addition reaction of PMOM with PTA was performed without solvent or in *N*-methyl-2-pyrrolidone (NMP) at 120 °C for 48 h. As summarized in Table I, the corresponding polymer (**2d**) was obtained in 65 and 39% conversions, respectively. This indicates that the reactivity of the pendant oxetane ring in PMOM toward an active ester was lower than that of acyl chloride.

From these results, it was concluded that the pendant oxetane ring in the polymer can be used as a new reactive group for the chemical modification of polymers and the synthesis of functional polymers.

References and Notes

(1) Gritter, R. J. *The Chemistry of Ether Linkage*; Patai, S., Ed.; Wiley: New York, 1967; pp 373–443.

(2) Nishikubo, T. *J. Synth. Org. Chem., Jpn.* **1991**, *49*, 218.

(3) For example: Inoue, S.; Aida, T. *Ring Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: London, 1984; Vol. 1, pp 185–298.

(4) Nishikubo, T.; Sato, K. *Chem. Lett.* **1991**, 697.

(5) Luskin, L. S. U.S. Patent 3,105,838, Oct 1, 1963.

(6) Identification of this compound was as follows. IR 1720 (C=O), 1640 cm^{-1} (C=C). ^{1}H NMR (CDCl$_3$): δ 1.20 (s, 3 H, CCH$_3$), 1.95 (dd, 3 H, =CCH$_3$), 3.65 (s, 2 H, CH$_2$Cl), 4.22 (s, 2 H, OCH$_2$), 4.33 (s, 2 H, CH$_2$O), 5.58 (dq, 1 H, cis =CH to methyl group), 6.11 (dq, 1 H, trans =CH to methyl group), 7.3–7.6 and 7.9–8.1 (m, 5 H, aromatic protons).