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Spacer-Modified Polymeric Catalysts Containing Phosphonium Salts for Regioselective Addition Reaction of Epoxy Compounds with Active Esters

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ABSTRACT: The catalytic activity of insoluble polymer-supported catalysts with alkylene spacer chains between polystyrene backbones and quaternary phosphonium salts (catalysts **1**-**19**) was examined for regioselective addition of epoxy compounds (**22a**-**c**) with active esters (**23a**,**b**). The activity was strongly affected by the structure of onium salts, the degree of ring substitution (DRS), the degree of cross-linking (DC), the length of the alkylene spacer chain, and the reaction solvents. The chloride-containing catalysts exhibited higher activity than the bromide-containing catalysts. The catalysts with low DRS had a higher activity than those with high DRS. The catalysts with low DC also had a higher activity than those with high DC. The activity of the spacer-modified catalysts was higher than that of catalysts with no spacer chains. It was found that suitable combination of catalyst and solvent gave a higher activity than low molecular weight catalysts such as tetrabutylammonium bromide (**20**) or chloride (**21**). Furthermore, catalysts with suitable DRS and alkylene spacer can be reused for at least 10 runs.

Introduction

Epoxy compounds with high reactivity are highly useful materials for synthetic organic chemistry and polymer synthesis. It has been reported[1] that quaternary onium halides have a higher catalytic activity than tertiary amines for the addition reaction of epoxy compounds with carboxylic acids. Nishikubo et al.[2] have used some quaternary ammonium and phosphonium halides not only as phase-transfer catalysts for modifications of polymers containing pendant chloromethyl groups but also as catalysts[3] for the addition of pendant epoxide groups of polymers with various carboxylic acids.

About 10 years ago, Funahashi reported[4] on the addition of epoxy compounds with phenyl esters using tertiary amine or potassium *tert*-butoxide as catalysts. However, this reaction was carried out at relatively elevated temperatures. We found recently that the reaction of pendant epoxide groups of polymers with various active esters[5] proceeded smoothly in the presence of quaternary onium halides to give the corresponding adducts under relatively mild reaction conditions. Similar reactions of epoxy compounds with acyl halides,[6] alkyl halides,[7,8] carbon dioxide,[9,10] β-butyrolactone,[11] and diphenyl carbonate[4a,12] have also been conducted by using quaternary onium halides as catalysts.

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Table I
Characterization of Polystyrene Bead Containing Pendant Quaternary Phosphonium Salts

cat.	Ⓟ—Q⁺X⁻	DC[a] of bead, %	halogen in bead, mequiv/g	DRS[b] of bead, %
1	$-CH_2P^+(Bu)_3Cl^-$	2	0.62	10
2	$-CH_2P^+(Bu)_3Cl^-$	2	1.38	20
3	$-CH_2P^+(Bu)_3Cl^-$	2	1.65	30
4	$-CH_2P^+(Bu)_3Cl^-$	2	1.68	40
5	$-(CH_2)_4P^+(Bu)_3Cl^-$	2	0.65	10
6	$-(CH_2)_4P^+(Bu)_3Cl^-$	2	1.46	33
7	$-(CH_2)_7P^+(Bu)_3Cl^-$	2	0.65	9
8	$-(CH_2)_7P^+(Bu)_3Cl^-$	2	1.44	33
9	$-(CH_2)_4P^+(Bu)_3Br^-$	2	0.65	10
10	$-(CH_2)_4P^+(Bu)_3Br^-$	10	0.98	17
11	$-(CH_2)_4P^+(Bu)_3Br^-$	2	1.09	19
12	$-(CH_2)_4P^+(Bu)_3Br^-$	2	1.46	33
13	$-CH_2O(CH_2)_3P^+(Bu)_3Br^-$	2	1.08	19
14	$-CH_2O(CH_2)_3P^+(Bu)_3Br^-$	2	1.49	40
15	$-(CH_2)_7P^+(Bu)_3Br^-$	2	0.65	9
16	$-(CH_2)_7P^+(Bu)_3Br^-$	10	0.99	16
17	$-(CH_2)_7P^+(Bu)_3Br^-$	2	0.99	17
18	$-(CH_2)_7P^+(Bu)_3Br^-$	2	1.44	33
19	$-(CH_2)_7P^+(Oct)_3Br^-$	2	0.81	16

[a] Degree of cross-linking. [b] Degree of ring substitution.

On the other hand, insoluble polymer-supported phase-transfer catalysts containing pendant quaternary onium halides, which were first utilized by Regen,[13] have been extensively investigated by Montanari et al., Ford et al., and Tomoi et al.[14-16]

In an earlier article,[17] we established an essentially new catalytic process of insoluble polystyrene beads containing pendant quaternary onium halides for the regioselective addition of epoxy compounds with active esters and proposed a new reaction mechanism on the basis of our kinetic study. However, the activity of the insoluble catalysts was lower than that of low molecular weight catalysts such as tetrabutylammonium bromide and chloride.

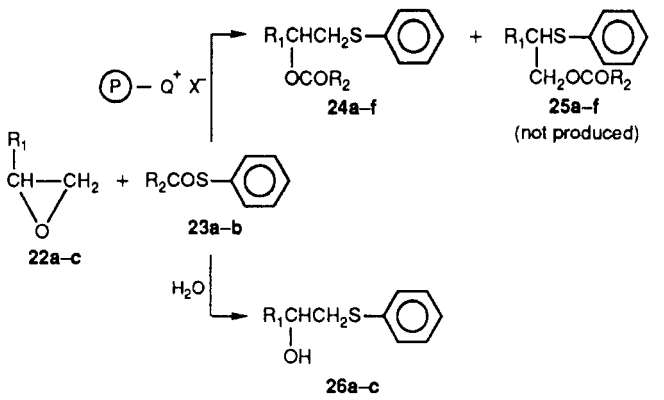
In this article, we describe the high activity of insoluble polystyrene catalysts in which onium halides were attached to the phenyl group via spacer chains. The effects of spacer chains, the degree of loading of the onium halide, the degree of cross-linking of the beads, and the kind of counteranion of the onium halides on the reaction of epoxy compounds with active esters were further evaluated.

Experimental Section

Materials. Characteristics of the cross-linked polystyrene beads containing quaternary phosphonium halides (catalysts **1–19**), which were prepared previously[16] as polymer-supported phase-transfer catalysts, are summarized in Table I. Tetrabutylammonium bromide (**20**) was recrystallized twice from ethyl acetate. Tetrabutylammonium chloride (**21**) was used without further purification. Phenyl glycidyl ether (**22a**), methyl glycidyl ether (**22b**), butyl glycidyl ether (**22c**), and reaction solvents were used after distillation on CaH_2. *S*-Phenyl thioacetate (**23a**) and *S*-phenyl thiobenzoate (**23b**) were prepared by the reaction of thiophenol with the corresponding acid chlorides and purified by two distillations as reported previously.[18]

Measurement of the Rate of Regioselective Addition Reaction. Appropriate amounts of epoxy compound, active ester, reaction solvent, and *p*-dichlorobenzene (internal standard for GLC) were charged into the reaction flasks, thermostatically kept at a fixed temperature with stirring under nitrogen. To the mixtures was added the catalyst at zero time. The reaction mixtures were periodically analyzed by a GLC method (Shimadzu Model GC-9AM gas chromatograph with a 3 mm × 2.6 m column packed with 3% Silicone OV-101 on Shimalite W) as reported previously.[17]

Scheme I[a]



[a] **22a**: $R_1 = C_6H_5OCH_2$. **22b**: $R_1 = CH_3OCH_2$. **22c**: $R_1 = C_4H_9OCH_2$. **23a**: $R_2 = CH_3$. **23b**: $R_2 = C_6H_5$. **24a**: $R_1 = C_6H_5OCH_2$; $R_2 = CH_3$. **24b**: $R_1 = CH_3OCH_2$; $R_2 = CH_3$. **24c**: $R_1 = C_4H_9OCH_2$; $R_2 = CH_3$. **24d**: $R_1 = C_6H_5OCH_2$; $R_2 = C_6H_5$. **24e**: $R_1 = CH_3OCH_2$; $R_2 = C_6H_5$. **24f**: $R_1 = C_4H_9OCH_2$; $R_2 = C_6H_5$. **26a**: $R_1 = C_6H_5OCH_2$. **26b**: $R_1 = CH_3OCH_2$. **26c**: $R_1 = C_4H_9OCH_2$.

Table II
Results of the Addition Reaction of 22a with 23b Using Polymer-Supported Catalyst[a]

cat.	counteranion	DRS[b] of cat., %	yield of adduct,[c] % 24b	26a
1	Cl	10	18.2	11.4
2	Cl	20	12.8	7.8
3	Cl	30	9.5	6.9
4	Cl	40	8.0	7.8
5	Cl	10	91.8	5.3
6	Cl	33	87.9	7.3
7	Cl	9	92.4	6.7
8	Cl	33	89.8	5.1
9	Br	10	63.2	5.2
12	Br	33	39.3	3.7
15	Br	9	65.7	4.8
18	Br	33	52.2	5.4

[a] The reaction was carried out with 4 mmol of **22a** and 4 mmol of **23b** by using 0.2 mmol of the catalyst, cross-linked with 2 mol % of DVB, in 2 mL of chlorobenzene at 90 °C for 24 h. [b] Degree of ring substitution. [c] Determined by GLC.

Results and Discussion

Catalytic Activity of Spacer-Modified Polymeric Onium Salt. It has been reported[5c,17] that the reaction of epoxy compounds such as **22a**, **22b**, and **22c** with active esters such as **23a** and **23b** proceeded regioselectively to give the corresponding adducts (**24a–f**) with small amounts of hydrolysis byproducts (**26a–c**) by using polymer-supported catalysts containing pendant benzyltrialkylammonium or -phosphonium salts and did not produce isomers **25a–f** (Scheme I).

Here, the activities of various new insoluble catalysts having alkylene spacer chains between the phenyl groups of polystyrene and quaternary phosphonium salts (see Table I) are evaluated as to the regioselective addition of the epoxy compounds with the active esters.

As summarized in Table II, when the reaction of **22a** with **23b** was carried out by using 5 mol % of the catalyst containing Cl anion at 90 °C for 24 h, catalyst **1** with a low degree of ring substitution (DRS) showed a higher activity than catalysts **2–4** with relatively high DRS, and the activity decreased gradually with increasing DRS. Furthermore, catalysts **5–8** with a tetra- or heptamethylene spacer seemed to have very high activity.

Catalysts **5–8** having Cl^- as the counteranion showed higher activities than the corresponding catalysts **9**, **12**, **15**, and **18** with Br^- anion.

Table III
Catalytic Activity of Polystyrene Bead Containing Pendant Quaternary Phosphonium Salt for the Addition Reaction of 22a with 23a[a]

cat.	spacer chain	DRS[b] of cat., %	counteranion	yield of adduct,[c] % 24a	yield of adduct,[c] % 26a	k_{obsd}, $\times 10^{-4}$ s^{-1}
1	CH_2	10	Cl	10.0	5.2	0.17
3	CH_2	30	Cl	10.5	5.3	0.16
5	$(CH_2)_4$	10	Cl	91.2	4.4	3.46
6	$(CH_2)_4$	33	Cl	85.3	7.5	2.15
7	$(CH_2)_7$	9	Cl	92.7 (92.9)[d]	4.7 (5.6)[d]	4.77 (6.41)[d]
8	$(CH_2)_7$	33	Cl	88.0	5.8	3.06
9	$(CH_2)_4$	10	Br	50.1	5.2	0.58
10[e]	$(CH_2)_4$	17	Br	16.0	4.5	0.15
11	$(CH_2)_4$	19	Br	43.0	5.1	0.43
12	$(CH_2)_4$	33	Br	37.0	5.0	0.30
13	$CH_2O(CH_2)_3$	19	Br	35.1	6.8	0.32
14	$CH_2O(CH_2)_3$	40	Br	21.8	5.2	0.19
15	$(CH_2)_7$	9	Br	47.0	5.2	0.49
16[e]	$(CH_2)_7$	16	Br	17.3	4.4	0.14
17	$(CH_2)_7$	17	Br	41.6	4.6	0.40
18	$(CH_2)_7$	33	Br	35.4	6.1	0.33
19	$(CH_2)_7$	16	Br	64.3	5.5	0.84
20			Br	57.6	5.2	0.65
21			Cl	93.9 (93.0)[d]	4.6 (4.0)[d]	5.23 (5.12)[d]

[a] The reaction was carried out with 4 mmol of **22a** and 4 mmol of **23a** by using 0.04 mmol of catalyst, cross-linked with 2 mol % of DVB, in 2 mL of chlorobenzene at 90 °C for 5 h. [b] Degree of ring substitution. [c] Determined by GLC. [d] The reaction was carried out in toluene. [e] Cross-linked with 10 mol % of DVB.

Table IV
Solvent Effect for the Addition Reaction of 22a with 23a Using Polymer-Supported Catalyst 6[a]

solvent	b	c	k_{obsd}, $\times 10^{-4}$ s^{-1}
DMSO	4.30	46.7	0.21
DMF	3.86	37.0	0.78
diglyme	1.97		0.53
chlorobenzene	1.54	5.62	0.49
anisole	1.20	4.33	0.91
toluene	0.37	2.38	2.38

[a] The reaction was carried out with 4 mmol of **22a** and 4 mmol of **23a** by using 0.04 mmol of catalyst **6** in 2 mL of the solvent at 80 °C. [b] Dipole moment.[21] [c] Dielectric constant for the pure liquid at 25 °C.[23]

Table V
Rates of the Addition Reactions of Various Epoxy Compounds with Active Esters[a]

epoxy compd	active ester	k_{obsd}, $\times 10^{-4}$ s^{-1}
22a	**23a**	7.80
22b	**23a**	1.38
22c	**23a**	0.96
22a	**23b**	2.17
22b	**23b**	0.13
22c	**23b**	very slow

[a] The reaction was carried out with 4 mmol of epoxy compound and 4 mmol of active ester by using 0.12 mmol of catalyst **6** in 2 mL of chlorobenzene at 90 °C.

When the reaction of **22a** with **23a** was performed under the same conditions, a difference in activity among these polymer-supported catalysts is not clearly understood, because the reaction with each catalyst proceeded very smoothly with high conversion.

These results indicate qualitatively that the activity of the insoluble catalysts was strongly affected by the degree of loading of the onium salt, the introduction of alkylene spacers between the polymer skeleton and the active site, and the kind of counteranion of the onium salt.

As summarized in Table III, detailed activities of polymer-supported catalysts **1**–**19** were evaluated from the observed pseudo-first-order rate constants, k_{obsd}, and yields of the main reaction product **24a** and of byproduct **26a** were given for the reaction of **22a** with **23a** in the presence of 1 mol % of the catalyst in chlorobenzene at 90 °C for 5 h. Low molecular weight catalyst **21** has a higher activity than the polymer-supported phosphonium salts, and catalysts **7** and **8** with a heptamethylene spacer showed the highest catalytic activity among the insoluble catalysts with Cl^- anion. Catalysts **5** and **6** with a tetramethylene chain also showed a higher activity than catalysts **1** and **3** with no spacer chains. Furthermore, the catalysts with low DRS such as **1**, **5**, and **7** were found to have a higher activity than the corresponding catalysts with high DRS such as **3**, **6**, and **8**, respectively.

On the other hand, when the catalytic activities among the bromide-containing catalysts were compared, catalysts **9** and **15** with low DRS showed a higher activity than catalysts **10**–**12** and **16**–**18** with high DRS, respectively. It was also found that the activities of catalysts **10** and **16** with a high degree of cross-linking (DC) were lower than those of catalysts **11** and **17** with a low DC, because the degree of swelling of the former catalyst beads was lower than that of the latter catalyst beads. The activities of catalysts **13** and **14** with a methyleneoxytrimethylene chain were also lower than those of catalysts **11** and **12** with a tetramethylene spacer.

It has been reported that[17] the catalyst having pendant benzyltributylphosphonium salt has a higher activity than the catalyst having pendant benzyltrioctylphosphonium salt in the reaction of the epoxy compounds with the active esters. However, catalyst **19** containing bulky and hydrophobic octyl groups showed a higher activity than catalyst **17** having butyl groups and low molecular weight catalyst **20**.

Table III also indicates that the polymer-supported quaternary phosphonium salts with Cl^- anion have a higher catalytic activity than the corresponding polymer-supported onium salts with Br^-. This is attributed to the high nucleophilicity of Cl^- anion in aprotic solvents compared with Br^-.[19] The spacer-modified catalysts have a higher activity than the catalysts without alkylene spacers. It appears that the alkylene spacer must decrease steric hindrance of the polymer support and increase hydrophobicity of the phosphonium salt, resulting in the enhanced reactivity of the halide ion.

Table VI
Activity of the Reused Polymer-Supported Catalyst 7[a,b]

	cycle no.													
	1	2	3	4	5	6	7	8[c]	9	10	11	12	13	14
yield of **24a**[d]	88.2	82.1	83.3	80.3	74.8	75.5	69.4	83.9	77.2	81.8	57.3	41.2	11.0	0.5
yield of **26a**[d]	11.6	14.9	15.3	16.1	19.8	17.3	22.9	14.1	17.0	11.8	16.5	15.6	11.6	2.7

[a] The reaction was carried out with 4 mmol of **22a** and 4 mmol of **23a** by using 0.07 mmol of catalyst 7 in diglyme (2 mol/L) at 90 °C for 24 h. [b] The recovered catalyst was washed twice in boiling methanol for 2 h and boiling acetone for 2 h, filtered, and dried in vacuo at 40 °C for 18 h. [c] The catalyst was further dried for 16 days in a desiccator and then reused. [d] Determined by GLC.

The low-DRS catalysts have a higher activity than the high-DRS catalysts. That is, the former catalysts have a higher hydrophobicity and less steric hindrance than the latter catalysts. Therefore, it seems that the spacer-modified polymeric catalyst with high hydrophobicity and small steric hindrance has a high activity, because the epoxy compounds and the active esters were attracted to the catalyst by appreciable hydrophobic interaction.

The catalyst with a low DC has a higher activity than the catalyst with a high DC, because low-DC beads swell more in the solvent than do high-DC beads.[20]

The activity of the catalyst with an oxygen-containing spacer chain was lower than that of the catalysts having an alkylene spacer chain. It seems that oxygen in the spacer chain decreased the hydrophobicity of the catalyst.

The effect of solvent on the reaction of **22a** and **23a** was examined in the presence of catalyst **6** (Table IV). The rate was faster in nonpolar solvents[21] than in polar solvents except in the case of DMF. A similar high reactivity of the bromide ion in nonpolar solvents has been reported for the reaction of *n*-octyl methanesulfonate with $C_{16}H_{33}P^+(C_4H_9)_3Br^-$ under anhydrous homogeneous conditions[19] and can be explained by the idea that the halide ion is more poorly solvated by the nonpolar solvents.[22] Such a less solvated, reactive halide ion in toluene is likely to facilitate the addition of **22a** with **23a**.

The activity of catalyst **7** and **21** was reexamined in toluene at 90 °C (see Table III). Interestingly enough, spacer-modified catalyst **7** showed a higher activity than low molecular weight catalyst **21** in toluene, although it has been reported[5c] that catalyst **21** is the best catalyst for the reaction of epoxy compounds with active esters. This result means that suitable combination of the polymer-supported catalyst and the reaction solvent gives an even higher activity than do low molecular weight catalysts having high activity on the reaction of epoxy compounds with active esters.

The reactivity of the epoxy compounds and the active esters used was estimated from the rates in the presence of catalyst **6** in chlorobenzene at 90 °C (Table V). This indicates that the reactivity of epoxy compounds increased in the order **22c** < **22b** < **22a**, while active ester **23a** had a higher reactivity than **23b**.

The stability of catalyst **7** having 9 mol % of DRS was evaluated on the reaction of **22a** with **23a** in diglyme at 90 °C for 24 h (Table VI). This result indicates that catalyst **7** can be reused for at least 10 runs. In addition, it was found that the water and other impurities adsorbed to the catalyst beads strongly depressed activity, because fully dried beads (run no. 8) were restored to high catalytic activity. This result is a very important and long-awaited finding in the field of organic syntheses using polymer-supported catalyst systems. That is, the spacer-modified polymeric catalyst with suitable DRS and DC has very high activity and excellent stability.

Kinetics of the Addition Reaction of an Epoxy Compound with an Active Ester. The addition of equivalent amounts of **22a** with **23a** was carried out by using 1 mol % of catalyst **6** in chlorobenzene at various temperatures. As shown in Figure 1, the observed rate of reaction obeyed first-order kinetics at 60–100 °C. This result indicates that the reaction rate is proportional to the epoxy concentration or the ester concentration.

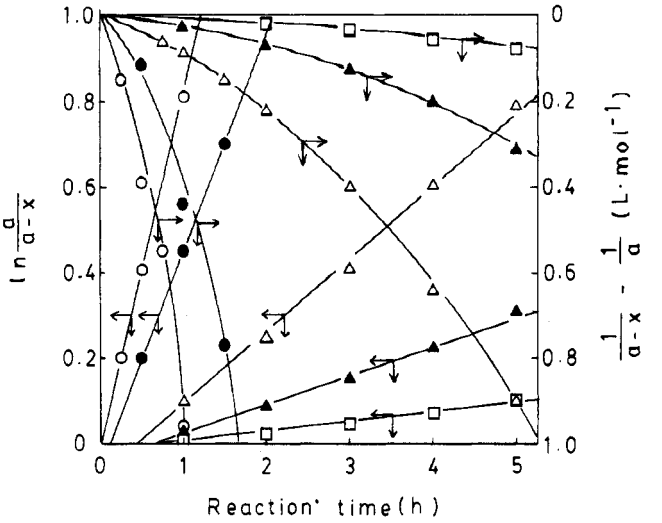


Figure 1. Rate of the reaction of **22a** (4 mmol) with **23a** (4 mmol) in the presence of catalyst **6** (1 mol %) in chlorobenzene (2 mL) at various temperatures: (□) at 60 °C, (▲) at 70 °C, (△) at 80 °C, (●) at 90 °C, (○) at 100 °C.

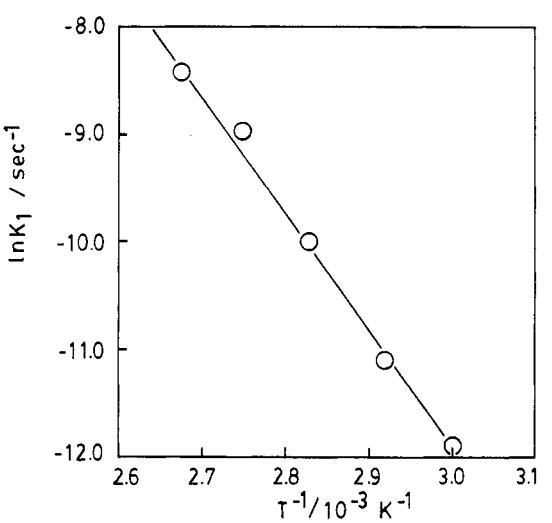


Figure 2. Arrhenius plots of the observed pseudo-first-order rate constant on the reaction of **22a** with **23a** by using catalyst **6**.

The Arrhenius plots based on the above-observed pseudo-first-order rate constant, k_1, of the reaction are shown in Figure 2, and the apparent activation energy of the reaction was estimated as 87.4 kJ/mol.

The rate was also determined at various concentrations of catalyst **6** in chlorobenzene at 70 °C and was found to follow first-order kinetics. As shown in Figure 3, the correlation between the observed pseudo-first-or-

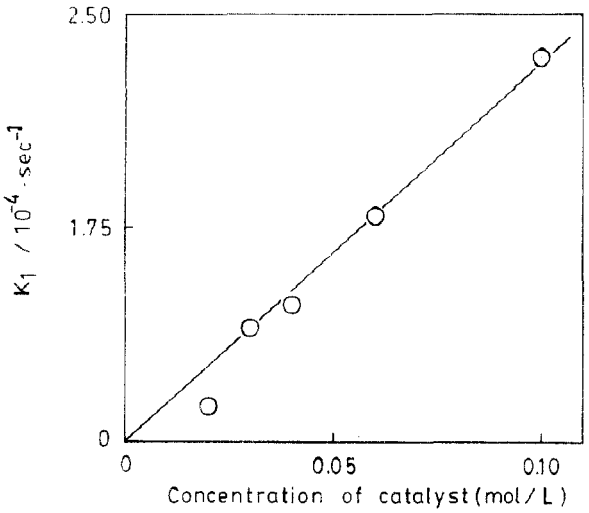


Figure 3. Correlation between the observed pseudo-first-order rate constant and the catalyst concentration: Carried out with **22a** (4 mmol) and **23a** (4 mmol) by using catalyst **6** in chlorobenzene (2 mL) at 70 °C.

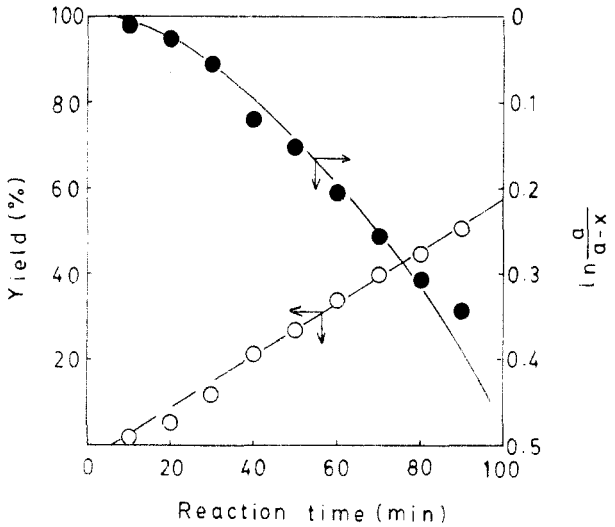


Figure 4. Zero-order dependence of the reaction in excess amounts of epoxy compound: Carried out with **22a** (10 mmol) and **23a** (1 mmol) by using catalyst **6** (0.04 mmol) in chlorobenzene (2 mL) at 70 °C: a, $[\mathbf{23a}]_{initial}$; x, $[\mathbf{23a}]_{decreased}$.

der rate constant, k_1, and the catalyst concentration makes a straight line passing through the origin. This means that the reaction rate is proportional to the catalyst concentration.

As shown in Figure 4, when the reaction of **23a** with 10 times the amount of **22a** was carried out using 4 mol % (to **23a**) of catalyst **6** in chlorobenzene at 70 °C, the observed rate was found to be linearly related to the yield of adduct **24a** and did not conform to the first-order kinetics. That is, the rate of reaction was zero order with respect to the ester concentration.

On the other hand, as shown in Figure 5, when the reaction of **22a** with 10 times the amount of **23a** was conducted in the presence of 4 mol % (to **22a**) of catalyst **6** in toluene at 80 °C, the observed rate obeyed first-order kinetics and did not make a straight line to the yield of adduct **24a**. Furthermore, the observed pseudo-first-order rate constants of the reaction plotted against the epoxy concentrations show a straight line passing through the origin (Figure 6). This means that the rate of reaction was related to the epoxide concentration. Similar kinetic data have also been obtained[5d] in the reaction of epoxy compounds with active esters by using low molecular weight quaternary onium salts as the catalysts.

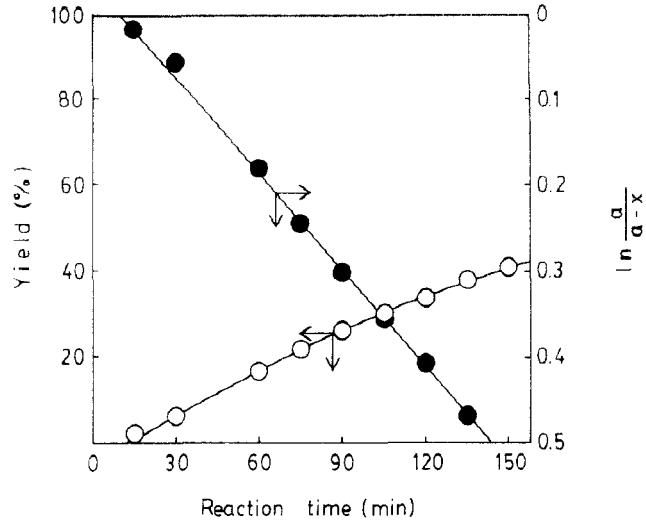


Figure 5. First-order dependence of the reaction in excess amounts of active ester: Carried out with **22a** (1 mmol) and **23a** (10 mmol) by using catalyst **6** (0.04 mmol) in toluene at 80 °C: a, $[\mathbf{22a}]_{initial}$; x, $[\mathbf{22a}]_{decreased}$.

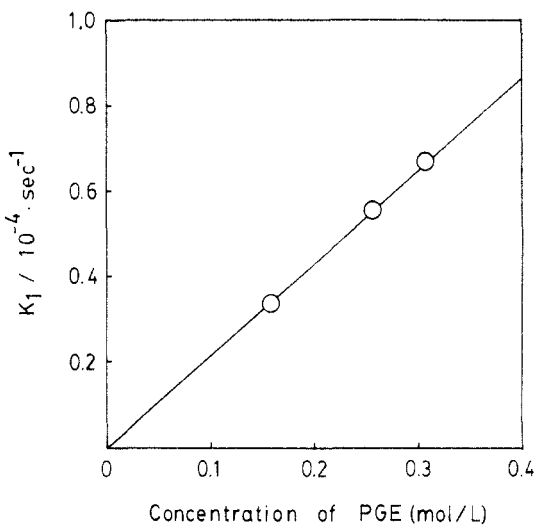


Figure 6. Correlation between the observed pseudo-first-order rate constant and the epoxy concentration: Carried out with **23a** (10 mmol) and catalyst **6** (0.04 mmol) in toluene (2 mL) at 80 °C.

From these results, it has been concluded that the rate of addition reaction of the epoxy compound and the active ester with use of the spacer-modified catalyst was proportional to the product of the epoxide concentration and the catalyst concentration.

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Registry No. 22a, 122-60-1; **22b**, 930-37-0; **22c**, 2426-08-6; **23a**, 934-87-2; **23b**, 884-09-3; **24a**, 120915-43-7; **24b**, 127333-32-8; **26a**, 84137-77-9; DMSO, 67-68-5; DMF, 68-12-2; diglyme, 111-96-6; chlorobenzene, 108-90-7; anisole, 100-66-3; toluene, 108-88-3.

Simultaneous X-ray/DSC Study of Mesomorphism in Polymers with a Semiflexible Mesogen

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ABSTRACT: In order to investigate the limits of macromolecular chain flexibility tolerated by the nematic state, a new group of polyethers has recently been synthesized, where not only the spacer but also the mesogen provide a degree of flexibility. This is achieved by introducing a rotationally mobile ethylene group linking the two phenyl rings in the 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE). These "mesogens" are separated by flexible $-O(CH_2)_nO-$ spacers, where n is either a single value (homopolymers) or has two different values (copolymers). Results of X-ray diffraction studies of MBPE polymers using the simultaneous X-ray diffraction and DSC technique (XDDSC) conclusively prove the existence of the nematic phase in most homopolymers and all copolymers. Depending on the polymer, the phase is either mono- or enantiotropic. While in a few cases the phase is thermodynamically stable, in most cases it is metastable. The weak first-order transition below the I–N transition temperature appears not to be the nematic–smectic transition as previously suspected, and its nature is still being investigated. Current X-ray evidence shows further that the molecular packing density in the nematic phase is considerably higher for polymers with even spacers than it is in polymers with odd spacers.

Introduction

The beneficial effect of liquid crystallinity in the processing of polymers with superior mechanical properties is now well established. However, in order to facilitate processing of main-chain nematogenic polymers, the introduction of flexible spacers into the chain has been experimented with extensively. In order to investigate still further the limits of flexibility tolerated by the nematic state, a new group of polyethers has recently been synthesized,[1-4] where not only the spacer but also the mesogen provide a degree of flexibility. This is achieved by introducing a rotationally mobile ethylene group linking the two phenyl rings in the 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE). Both homo- and copolymers were prepared, the latter containing spacers of two[1-3] or three[4] different lengths in a random sequence.

Original studies by DSC and optical microscopy suggested that the polymers exhibit liquid-crystal phases, presumed nematic and possibly also smectic. Presently we show results of X-ray diffraction studies of MBPE polymers using the simultaneous X-ray diffraction and DSC technique (XDDSC).[5] The results conclusively prove the existence of the nematic phase in most homopolymers and all copolymers. Depending on the polymer, the

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