Polymerization of acrylate monomers induced by chlorodiphenylphosphine and epoxide

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A catalytic amount of chlorodiphenylphosphine induced the polymerization of α,β-unsaturated esters. The polymerization was greatly accelerated by addition of a catalytic amount of epoxide.

(Keywords: α,β-unsaturated esters; chlorodiphenylphosphine; epoxide)

Introduction

The use of phosphorus compounds as comonomer or co-initiator in the polymerization of acrylate monomers is generally attractive for the synthesis of controlled polymers[1-4]. Cyclic phenylphosphonite has been used as an effective comonomer[1-3] for zwitterionic polymerization with α,β-unsaturated carbonyl compounds. In this copolymerization, the phosphite attacks the C=C double bond of the acrylate via Michael-type addition, leading to an initial zwitterion intermediate[2]. On the other hand, non-cyclic phosphorus species, such as tertiary phosphines, behave as co-initiators with trialkylaluminium in the polymerization of methyl methacrylate, in which the formation of syndiotactic poly(methyl methacrylate) is controlled[4]. The interest in trivalent phosphorus species for the polymerization of acrylate monomers is due mainly to the addition reaction of trivalent phosphorus species with C=C double bond of α,β-unsaturated carbonyl compounds[1-4]. We recently found a new Wittig reaction between chlorodiphenylphosphine (CDP) and epoxides[5], which gives β-chloroalkyl diphenylphosphinic esters and olefins. In the same reaction system, unexpectedly, the reaction of CDP with glycidyl methacrylate (GMA) did not give phosphinate but rapidly resulted in polymerization due to addition of CDP. This phenomenon prompted us to investigate the role of two species, i.e. CDP and epoxide, on the polymerization of acrylate monomers. In this paper, we report the polymerization of α,β-unsaturated esters induced by CDP as pre-initiator, with the aid of epoxides.

Experimental

Benzyl methacrylate (BMA), ethyl acrylate (EA) and glycidyl methacrylate (GMA) were purified by the usual method. Cyclohexene oxide (CHO) and styrene oxide (SO) were dried on CaH_2 and distilled before use. CDP was used without further purification.

Typical polymerization was carried out as follows. To the mixture containing EA (0.4 g, 4 mmol), BMA (0.705 g, 4 mmol), CHO (0.02 g, 0.2 mmol) and 1.0 ml of diglyme, CDP (0.044 g, 0.2 mmol) was added by syringe under N_2. Then the mixture was heated to 80°C and kept at that temperature for 6 h. A small amount of chloroform was added to the mixture, and the solution was poured into methanol (100 ml) to precipitate poly(BMA-*co*-EA). A transparent copolymer was recovered by filtration and dried in vacuum at 60°C. Yield: 0.920 g (84%).

Results and discussion

Evidence to prove that CDP–epoxide induces polymerization of acrylate monomers was obtained from the time–conversion relation in the polymerization of BMA in four cases: (a) without catalyst; (b) with β-chlorocyclohexyl diphenylphosphinite (c-Hex-O-PPh_2)[5]; (c) with CDP; and (d) with CDP and CHO. As shown in *Figure 1*, BMA did not convert at all within 6 h in cases (a) and (b). In contrast, the conversion curve of BMA changed drastically after 5 h to produce poly(benzyl methacrylate) (PBMA) when a catalytic amount of CDP was added. Under the same condition, upon adding CHO to BMA containing CDP, the conversion of BMA increased dramatically within the initial time (up to 20% within 15 min). These results indicate that the combination of CDP with CHO greatly enhances the rate of polymerization of BMA. In the bulk condition, the polymerization of BMA and GMA with different amounts of CDP was examined (*Table 1*). BMA was polymerized in both the presence and absence of CHO when a catalytic amount of CDP was added, but the presence of CHO afforded PBMA of higher molecular weight within a relatively short reaction time (entries 2 and 5). When an equivalent amount of CDP was added to the BMA, no polymerization occurred. Addition product **9** was isolated from the equivalent reaction mixture both with and without CHO (entries 3 and 4); the reaction became faster upon adding CHO to the mixture. [Addition product **9**: Analysis: calculated for $C_{23}H_{23}O_3P$: C 72.68; H 6.53; found: C 72.92; H 6.23. ^1H n.m.r. ($CDCl_3$, relative to $SiMe_4$ $\delta = 0$ ppm), $\delta = 1.25$ (d, 3 H, CH_3), 2.2–2.4 (m, 1 H, CH), 2.85–3.15 (m, 2 H, CH_2-P), 4.95 (s, 2 H, OCH_2Ph), 7.3–7.9 (m, 15 H, 3 C_6H_5). ^{31}P n.m.r. ($CDCl_3$, relative to 85% H_3PO_4 $\delta = 0$ ppm), $\delta = +30.87$.] With respect to

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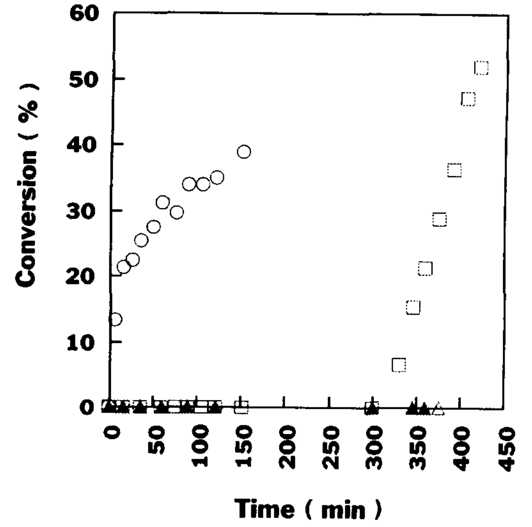


Figure 1 Conversion of BMA *versus* reaction time. The polymerizations were carried out under the following conditions: BMA (4 mmol), diglyme (0.7 ml), phenylacetic ester (0.3 ml) as internal standard; temperature 80°C, N_2. △, Without catalyst; ▲, 0.2 mmol c-Hex-O-PPh_2; □, 0.2 mmol CDP; ○, 0.2 mmol CDP and 0.2 mmol CHO. The conversion of BMA was monitored by g.l.c. analysis

the GMA, addition of an equivalent amount of CDP induced the polymerization of GMA; the polymer produced did not involve the pendent epoxide but had phosphorus groups ($\delta_P = +23$ ppm). On the other hand, the polymerization of GMA occurred quickly upon adding a catalytic amount of CDP, and the gelled poly(glycidyl methacrylate) (PGMA) appeared in the bulk or in a higher concentration of the monomer. These results provide evidence that the combination of CDP and epoxide may produce an effective initiator for the polymerization of acrylate monomers.

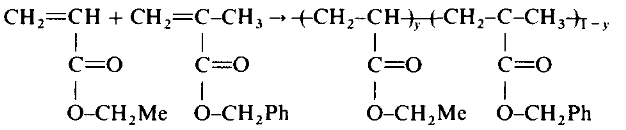
Copolymerization of BMA with EA was also performed by CDP associating with several epoxides. As summarized in *Table 2*, the content (y) of EA residue in the copolymer depended upon the existence of epoxides. The copolymer composition value of y was 0.45, 0.38 and 0.46 with addition of CHO, SO and GMA, respectively; these values are higher than that in the case without epoxide (entry 12). This indicates that the monomer pairs with equivalent ratio could give the corresponding copolymer with nearly quantitative composition distribution with the addition of epoxides. The copolymer (entries 9 and 11) obtained by precipitation ($CHCl_3$ solution to CH_3OH) was transparent and highly soluble in the usual

Table 1 Bulk polymerization of BMA and GMA in the presence of CDP

				Conditions		Polymer	
Entry	Monomer (mmol)	CDP (mmol)	Epoxide (mmol)	Temp. (°C)	Time (h)	M_n ($\times 10^5$)	M_w/M_n
1	BMA 4	0	0	80	4	No polymer	
2	BMA 4	0.2	CHO 0.2	80	0.5	2.09	1.56
3	BMA 2	2	CHO 2	80	8	No polymer	
4	BMA 2	2	0	80	14	No polymer	
5	BMA 4	0.2	0	80	3	0.27	1.76
6	GMA 4	0.2	4	80	0.5	1.42	1.76
7	GMA 2	2	2	80	4.5	1.93	1.77[a]
8	GMA 4	0	4	80	6	No polymer	

[a] $\delta_P = +23$ ppm; the ratio of the residue of CDP to GMA was determined to be 1:2

Table 2 Copolymer of ethyl acrylate and benzyl methacrylate[a]

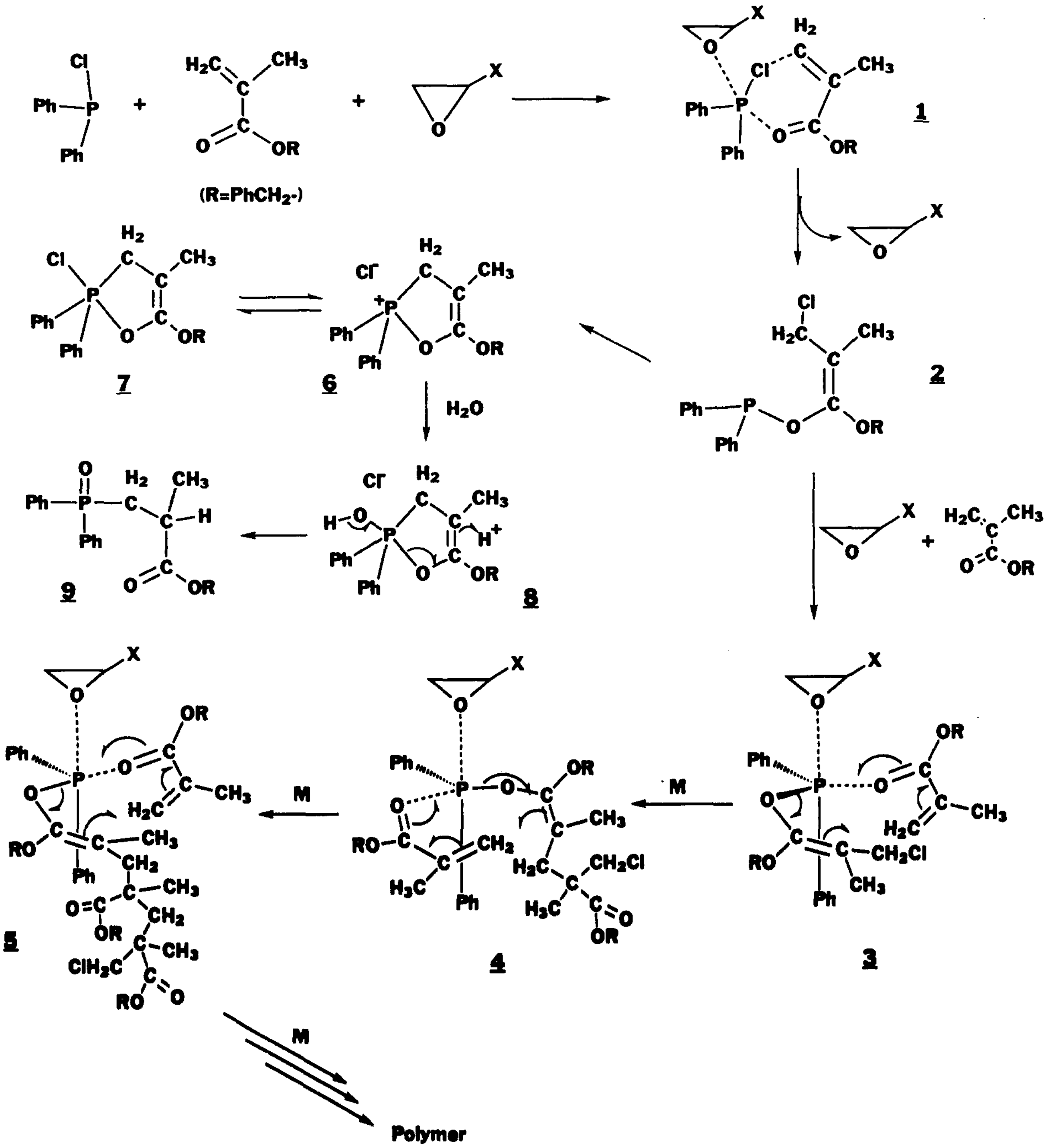


$$CH_2{=}\underset{\substack{| \\ C{=}O \\ | \\ O{-}CH_2Me}}{CH} + CH_2{=}\underset{\substack{| \\ C{=}O \\ | \\ O{-}CH_2Ph}}{C}{-}CH_3 \rightarrow \left(CH_2{-}\underset{\substack{| \\ C{=}O \\ | \\ O{-}CH_2Me}}{CH}\right)_y\left(CH_2{-}\underset{\substack{| \\ C{=}O \\ | \\ O{-}CH_2Ph}}{C}{-}CH_3\right)_{1-y}$$

						Composition[b]	
Entry	CDP (mmol)	Epoxide (mmol)	Yield (%)	M_n ($\times 10^5$)	M_w/M_n	y	$(1-y)$
9	0.2	CHO 0.2	84	1.28	1.5	0.45	0.55
10	0.2	SO 0.2	83	1.35	1.58	0.38	0.62
11	0.2	GMA 0.2	89	0.98	1.51	0.46	0.54
12	0.2	0	82	1.09	1.66	0.30	0.70

[a] Copolymerization was carried out upon adding CDP to the mixture containing EA (4 mmol), BMA (4 mmol) and epoxide in diglyme (1 ml) for 6 h at 80°C under N_2

[b] The composition was determined from the integration values of $-C(O)OCH_2-$ at 4.05 and 4.95 ppm for EA and BMA residues on copolymer, respectively, on ^1H n.m.r. in $CDCl_3$ relative to the internal standard $Si(CH_3)_4$ ($\delta = 0$ ppm)



Scheme 1

organic solvents, including ethyl ether. In addition, the molecular weight distribution was about 1.5 in this copolymerization system.

In addition to epoxides, other cyclic ethers, such as oxetane and oxorane, were employed in the above polymerization; it was found that four-membered oxetane had a catalytic effect like that of the epoxides, but five-membered oxorane did not. This distinction could arise from the different basicity of the oxygen atom[4] in oxirane, oxetane and oxorane. That is, the more basic oxygen may coordinate easily to phosphorus.

Trivalent phosphorus compounds, such as trialkyl or aryl phosphine[6], phosphite[7,8] and phenylphosphonite[1], acted as nucleophiles in their reaction with α,β-unsaturated carbonyl compounds. On the contrary, CDP has a strong electrophilic property and is easily attacked by nucleophilic compounds. Thus, it is hardly conceivable that the phosphorus in CDP undergoes the same reaction route as nucleophilic phosphorus species when reacted with α,β-unsaturated ester. One recent report briefly described[9] that the reaction between CDP and methyl vinyl ketone (α,β-unsaturated ketone) leads to the cyclic, penta-coordinated phosphorus compound oxaphospholene, which is considered as a transient intermediate in a successive reaction. In view of the fact that trivalent phosphorus is readily converted to the penta-coordinated form, we suppose that the preferential formation of an enolate **2** via the six-membered approach consisted of CDP, BMA and epoxide, the enolate **2** acting as a basic initiator in the polymerization system

(*Scheme 1*). The absence of epoxy participation might also induce **2**, but the formation of **2** might be slower compared with the epoxy participation system. The enolate **2** gives a cyclic species of oxaphospholene, **6** or **7**, via an intramolecular route to give product **9**, which was isolated in the mixture of equivalent reaction between CDP and BMA. By another pathway, the enolate **2** favours penta-coordination with acrylate and epoxide to form **3**, by which initiation just occurs to give the next enolate by an increase of one monomer unit. Then the new enolate undergoes the same step forming **4**, from which the propagation progresses. This approach is similar to the concept of the group-transfer polymerization[10] for the organosilicon-initiated enolate system.

Although the true behaviour of the CDP pre-initiator is not clear at present, this method is extremely useful for the controlled polymerization of acrylates. Further investigations, including block polymerization and tacticity, are in progress.

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