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Copolymerization of *N*-Phenylmaleimide and Propylene Oxide Initiated with Organozinc Compounds

Copolymerization of cyclic monomer with vinyl monomer has been of considerable interest but difficult because the polymerization reactivity and mechanism of such monomers are generally quite different from each other. Only a few reports have been available including those of the copolymerization via zwitterion,[1,2] though new types of polymers might be produced by copolymerization of these two extremely different types of monomer and new fields of application should be expected.

In a previous paper, it was reported that *N*-phenylmaleimide (*N*-PMI) gave the appreciable yields of poly(*N*-PMI) initiated with organozinc complex of $[Zn(OCH_3)_2(C_2H_5ZnOCH_3)_6]$ (**3** in Table I).[3] This organozinc complex which is synthesized from diethylzinc and methanol has also been known as a polymerization catalyst for epoxides and studied in detail.[4-6]

In Table I the activity of various organozinc initiators on the homopolymerization of *N*-PMI and of propylene oxide (PO) is qualitatively summarized. This table suggests that *N*-PMI and PO may be copolymerized by the initiation system of **3** since the zinc complex gives both homopolymers of *N*-PMI and of PO.

As a preliminary work, the present paper describes the results of copolymerization of *N*-PMI and PO with organozinc compounds.

Table I
Orgnozinc Compounds as Initiators for Homopolymerizations of *N*-PMI and PO

orgnozinc compd	activity for homopolymerization[a] *N*-PMI	activity for homopolymerization[a] PO	ref
$(C_2H_5)_2Zn$ (**1**)	△	×	3, 7
$(C_2H_5ZnOCH_3)_4$ (**2**)	△	×	3, 8, 9
$[Zn(OCH_3)_2(C_2H_5ZnOCH_3)_6]$ (**3**)	○	○	3-6
$(Zn(OCH_3)_2)_n$ (**4**)	△	⊙	3, 9, 10

[a] (⊙) excellently active; (○) fairly active; (△) a little active; (×) inactive.

Table II
Copolymerization of *N*-PMI with PO Initiated with Organozinc Compounds[a]

initiator	polymer yield,[b] g CH_3OH sol.	polymer yield,[b] g CH_3OH insol.
1	0	0.12 (3.1)
2	0	0
3	1.28 (33)	0.73 (19)
4	0.45 (11)	0

[a] Initiator, 0.1 mmol; *N*-PMI, 3 mmol (0.5 g); PO, 59 mmol (3.4 g); in THF; total volume 10 mL; at 80 °C; 24 h. [b] The values in parentheses are yields of polymer in percent calculated from the following equation: yield (%) = [(polymer obtained, g)/(total amount of monomers fed, g)] × 100.

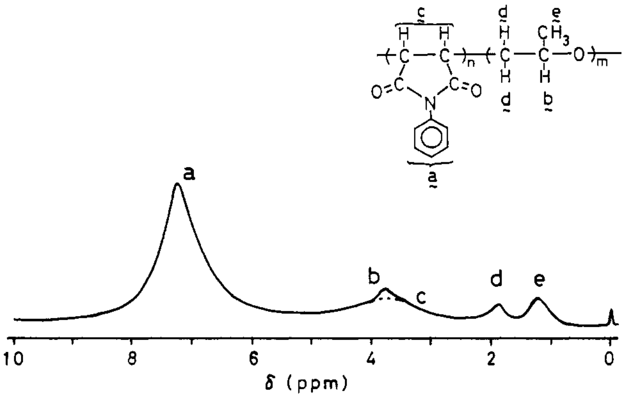

Figure 1. ^1H NMR spectrum of the methanol-insoluble polymer obtained by the copolymerization of *N*-PMI and PO with **3**.

Polymerizations were carried out with purified *N*-PMI and PO in sealed glass ampules under purified nitrogen atmosphere.[11] The reaction was terminated with hydrochloric acid/methanol and the reaction mixture was poured into methanol. The precipitate (methanol-insoluble part) was filtered off and dried under vacuum at 110 °C. The methanol-soluble polymer was collected by evaporation of methanol (precipitant) and extraction with benzene, followed by freeze-drying of the benzene solution.

Results of copolymerization of *N*-PMI (3 mmol) and PO (59 mmol) with organozinc compounds are summarized in Table II. Only **3** gives an appreciable yield of copolymer from *N*-PMI and PO as methanol-insoluble polymer.

Figure 1 shows ^1H NMR[12] of the methanol-insoluble polymer obtained by the copolymerization with **3** in Table II. Absorptions at 1.2 (e), 1.8 (d) and 3.8 ppm (b) are assignable to methyl, methylene and methine groups of PO units in the polymer, respectively. A peak at 7.2 ppm (a) and broad one from 3.0 to 5.3 ppm (c: shown by dotted line with the overlapping signal of methine groups of PO units) are assigned, respectively, to phenyl and methine

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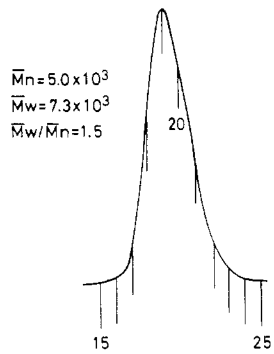

Figure 2. GPC of the methanol-insoluble polymer obtained by the copolymerization of *N*-PMI and PO with **3**.

protons of the polymerized *N*-PMI moiety. This spectrum implies that the polymer consists of both *N*-PMI and PO units. The mole fraction of PO in the polymer was calculated as 20% from the areas of signals a and e.

GPC[13] of the methanol-insoluble polymer obtained gives unimodal molecular weight distribution, as shown in Figure 2. The number-average molecular weight calculated from standardized polystyrene calibration is 5.0×10^3 and the molecular weight distribution ($\bar{M}_w/\bar{M}_n$) is 1.5. Thin layer chromatography (TLC)[14] of the polymer showed only one spot at a different position from those of homopolymers of *N*-PMI and of PO. GPC and TLC measurements suggest that the polymer obtained consists of only one component and is not a mixture of two homopolymers, i.e., a copolymer of *N*-PMI and PO is produced.

^{1}H NMR, GPC, and TLC analyses for the methanol-soluble polymer initiated with **3** revealed that it is a mixture of homopoly(PO) and copolymer of *N*-PMI and PO with high PO content. However, they actually could not be isolated separately.

It was confirmed by means of ^{1}H NMR that no copolymerization takes place with the other organozinc initiators. **1** and **4** only produced homopoly(*N*-PMI) (as the methanol-insoluble part) and homopoly(PO) (as the methanol-soluble part), respectively. The copolymerization in equimolar amount of PO and *N*-PMI (5 mmol each) with **3** also failed to incorporate appreciable amount of PO into the polymer and the mole fraction of PO in the polymer was less than 1% (by ^{1}H NMR).

Copolymerization of *N*-PMI and PO initiated with potassium *tert*-butoxide, which can initiate homopolymerization of both monomers, was carried out in a wide range of feed molar ratio of *N*-PMI to PO. No copolymerization took place but only homopoly(*N*-PMI) was obtained. Grignard reagents, alkyllithium and sodium naphthalenide gave also no copolymer at all but homopoly(*N*-PMI).

In conclusion, only **3** can give rise to the copolymerization of *N*-PMI and PO since the polymer obtained consisted of *N*-PMI and PO units (^{1}H NMR) and possessed only one component (GPC and TLC), though the type of their homopolymerization is quite different from each other. This is the first example of the copolymerization of an N-substituted maleimide with a cyclic ether.

Registry No. (*N*-PMI)(PO) (copolymer), 119770-35-3; Zn(OCH_3)$_2$, 1184-55-0; $C_2H_5ZnOCH_3$, 15860-82-9.

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(11) Purification of monomers are described in ref 3 for *N*-PMI and in ref 6 for PO.

(12) ^{1}H NMR was recorded at 60.0 MHz in deuterated chloroform at 35 °C.

(13) GPC was measured with column series of TSK gel G4000HXL–G3000HXL–G2000HXL (TOSOH Co., Tokyo) using THF as eluent. The exclusion limits of molecular weight: 4×10^5 for G4000HXL; 6×10^4 for G3000HXL; 1×10^4 for G2000HXL.

(14) TLC was performed on a silica gel plate (Merck silica 60) using ethanol/chloroform (8/2 v/v) as a developing solvent. R_f values for obtained copolymer, $0.02 < R_f < 0.28$; for homopoly(PO), $0.83 < R_f < 0.96$; for homopoly(*N*-PMI), $R_f = 0$.

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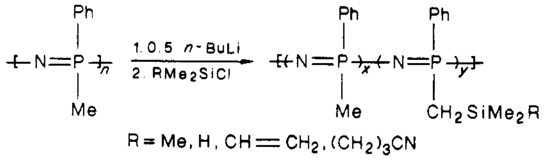
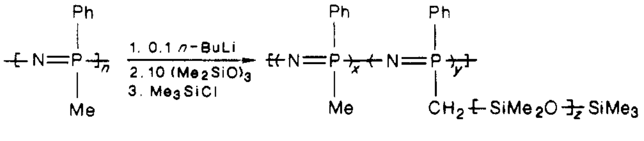
Poly(methylphenylphosphazene)-*graft*-poly(dimethylsiloxane)

Block and graft copolymers of polyphosphazenes are relatively few in number. Recently polystyrene-grafted aryloxy-[1] and alkyl/aryl-substituted[2] polyphosphazenes have been reported, but attempts to prepare copolymers with wholly inorganic silicon–oxygen and phosphorus–nitrogen monomeric units have not been successful.[3] We report here the first polyphosphazene-*graft*-polysiloxane copolymer in which the grafted siloxane chain is attached to the phosphazene backbone by the P–C–Si linkage.

Earlier work in our laboratories has demonstrated that poly(methylphenylphosphazene), $[Me(Ph)P{=}N]_n$, can readily be derivatized by deprotonation-substitution reactions. For example, a series of silylated derivatives[4] have been prepared by sequential treatment of $[Me(Ph)PN]_n$ with n-BuLi and various chlorosilanes, RMe_2SiCl (eq 1).


$$-\!\left[N{=}\underset{Me}{\overset{Ph}{P}}\right]_n \xrightarrow[\text{2. RMe}_2\text{SiCl}]{\text{1. 0.5 }n\text{-BuLi}} \left[\left(N{=}\underset{Me}{\overset{Ph}{P}}\right)_x\left(N{=}\underset{CH_2SiMe_2R}{\overset{Ph}{P}}\right)_y\right] \qquad (1)$$
$R = Me, H, CH{=}CH_2, (CH_2)_3CN$

We have shown that the intermediate polymer anion in these reactions can also be used to prepare inorganic–organic graft copolymers[2] through initiation of addition polymerization of styrene. These reactions indicated that the polyphosphazene anion sites generated from n-BuLi and $[Me(Ph)PN]_n$ could be used to initiate ring opening of $(Me_2SiO)_3$ (eq 2).


$$-\!\left[N{=}\underset{Me}{\overset{Ph}{P}}\right]_n \xrightarrow[\substack{\text{2. 10 (Me}_2\text{SiO)}_3\\ \text{3. Me}_3\text{SiCl}}]{\text{1. 0.1 }n\text{-BuLi}} \left[\left(N{=}\underset{Me}{\overset{Ph}{P}}\right)_x\left(N{=}\underset{CH_2\left[SiMe_2O\right]_zSiMe_3}{\overset{Ph}{P}}\right)_y\right] \qquad (2)$$

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