Polymerization via Zwitterion. 17.[1] Alternating Copolymerization of 2-Phenylimino-1,3-dioxolane with β-Propiolactone

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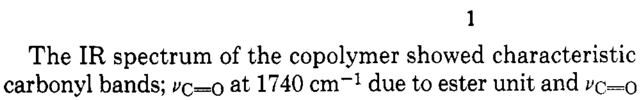
ABSTRACT: This paper describes an alternating copolymerization of 2-phenylimino-1,3-dioxolane (ethylene *N*-phenyliminocarbonate, EIC) with β-propiolactone (BPL). Copolymerization took place at 35 °C without added catalyst. The structure and the composition of copolymer were determined by ^1H-NMR and IR spectroscopy, elemental analysis, as well as alkaline hydrolysis. The copolymerization was reasonably explained by a mechanism involving zwitterion intermediates. The apparent values of monomer reactivity ratio were $\gamma_{EIC} = 0.20$ and $\gamma_{BPL} = 0.00$ at 35 °C in CH_2Cl_2.

Recently we have developed a new type of copolymerizations which take place spontaneously with mixing two monomers of a nucleophilic monomer (M_N) and an electrophilic one (M_E).[2] In these copolymerizations, genetic zwitterion (^+M_N-M_E^-) is formed by the interaction between M_N and M_E, which is involved in both initiation and propagation processes. Thus, alternating copolymers have been obtained in many combinations of M_N and M_E. As M_N we have so far examined cyclic imino ethers,[3] an azetidine,[4] a Schiff base,[5] and cyclic phosphonite, and phosphite.[1,6] We now report an alternating copolymerization of 2-phenylimino-1,3-dioxolane (ethylene *N*-phenyliminocarbonate, EIC) as a new M_N which is successfully combined with β-propiolactone (BPL). Before the present study, cationic and thermally induced homopolymerization of EIC had been reported,[7] and a kinetic study of the EIC polymerization had also been performed.[8]

Results and Discussion

Copolymerization between EIC and BPL took place at 35 °C without added initiator. As the copolymerization proceeded the system became viscous. A usual work-up of the reaction mixture gave a white, gummy-like polymer. Table I shows the results of copolymerizations carried out in four different solvents.

Figure 1 shows a ^1H-NMR spectrum of the copolymer (sample no. 1). Four signals are observed. Peak A at δ 7.15 is due to phenyl protons (5 H), sharp singlet B at δ 4.12 being ascribed to protons of $-OCH_2CH_2O-$ (4 H). Peaks C at δ 3.90 and D at δ 2.50 are assigned to two methylene groups' protons of NCH_2 (2 H) and $C(O)CH_2$ (2 H), respectively. From these ^1H-NMR data the copolymer structure was determined as ester–urethane type **1**, which is a 1:1 alternating copolymer derived from EIC and BPL.



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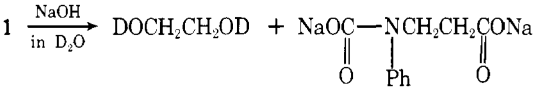
The IR spectrum of the copolymer showed characteristic carbonyl bands; $\nu_{C=O}$ at 1740 cm^{-1} due to ester unit and $\nu_{C=O}$ at 1710 cm^{-1} due to urethane unit (Figure 2). The results of elemental analysis (see Experimental Section) clearly indicate that the copolymer consists of the 1:1 composition of EIC and BPL.

An alkaline hydrolysis experiment of the polymer gave a further strong support to structure **1**. The hydrolysis products were determined from ^1H NMR spectroscopy as a 1:1 mixture of ethylene glycol and carbamic acid derivatives **2** (Figure 3). The reaction mixture was then slightly acidified, heated, and neutralized. By these procedures **2** was converted into *N*-phenyl-β-alanine, which was actually isolated and identified by comparing its IR spectrum with that of the authentic compound.



$$1 \xrightarrow[\text{in } D_2O]{NaOH} DOCH_2CH_2OD + NaOC(=O)-N(Ph)CH_2CH_2C(=O)ONa$$

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$$2 \xrightarrow[\Delta,\ -CO_2]{HCl} PhNHCH_2CH_2CO_2H$$

As seen in Table I the alternating copolymer was produced also in other solvents of chlorobenzene, nitrobenzene, and nitromethane (no. 2–4). Polymer of the highest molecular weight yielded in nitromethane solvent.

The apparent values of monomer reactivity ratio were determined. Copolymerization experiments with low conversion percents were carried out in CH_2Cl_2 at 35 °C for 2 h. The copolymer was isolated and the copolymer composition was determined by ^1H NMR analysis in $CDCl_3$. Figure 4 shows the copolymer composition curve. From these results the apparent copolymerization parameters were obtained according to the curve-fitting method as $\gamma_{EIC} = 0.20$ and $\gamma_{BPL} = 0.00$. These values of monomer reactivity ratio (mrr) are apparent ones, which were determined according to the conventional method. As discussed in the following section, the copolymerization mechanism of the present study is quite specific, which is different from that of usual radical copolymerization. The mrr values, however, are informative to see the alternating tendency of the arrangements of copolymer units.

Copolymerization Mechanism. The present copolymerization can reasonably be explained by the mechanism involving zwitterion according to the general scheme of the intermediates within a "no catalyst copolymerization".[2] First, the reaction of EIC with BPL takes place to give a genetic

Table I
Alternating Copolymerization of EIC with BPL at 35 °C[a]

No.	Solvent	Reaction time, h	Polymer yield, %	Mol wt[d]
1	CH_2Cl_2	48	66[b]	6970
2	PhCl	40	56	4000
3[c]	$PhNO_2$	48	69	8080
4	CH_3NO_2	65	78	13200

[a] EIC = BPL = 3.0 mmol in 0.5 mL of solvent when otherwise noted. The copolymer composition determined by ^1H NMR was in 50/50 EIC and BPL in all cases. [b] Anal. Calcd for the 1.0:1.0 composition of EIC and BPL, $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 60.99; H, 5.45; N, 6.14. [c] The initial monomer feed; EIC = 3.0 mmol, BPL = 1.5 mmol in 0.5 mL of nitrobenzene. [d] Determined by vapor pressure osmometry.

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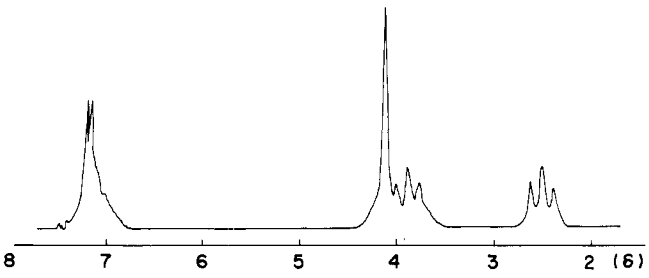


Figure 1. ^1H-NMR spectrum of the EIC-BPL copolymer in $CDCl_3$.

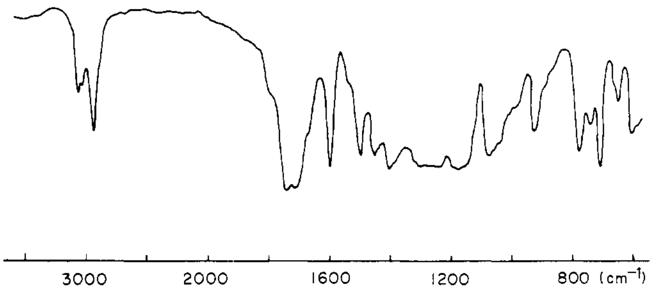


Figure 2. IR spectrum of the EIC-BPL copolymer (KBr).

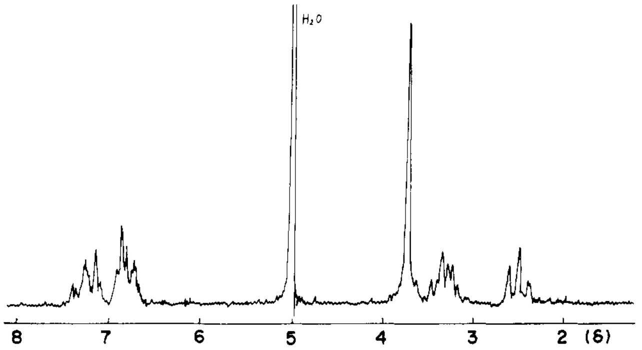
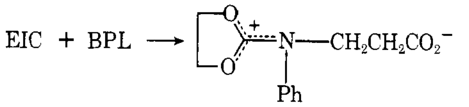


Figure 3. ^1H NMR spectrum of the alkaline hydrolysis system of copolymer in D_2O.

zwitterion **3**, which is a key intermediate for both the initiation and propagation.



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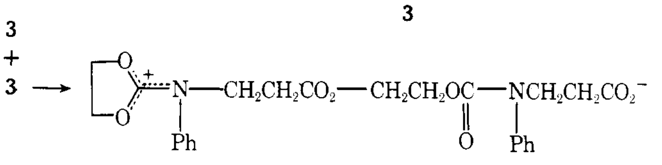

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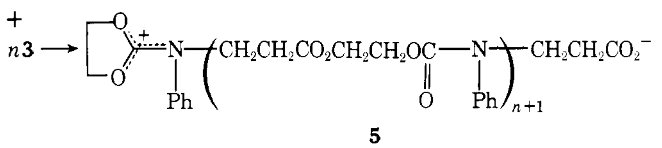

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Then, two molecules of **3** react with each other to form a dimeric zwitterion **4**, the smallest propagating species. Successive attack of **3** onto **4** leads to the formation of a macrozwitterion **5**, which has a structure of alternating copolymer derived from EIC and BPL.

In cases where the concentration of EIC monomer is high the cationic site in zwitterions **3–5** attacks also free EIC monomer to cause the homopropagation of EIC in copolymer. This is due to the higher reactivity (unstability) of the cationic site derived from EIC.

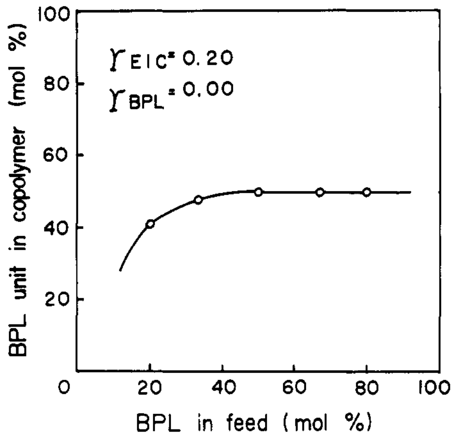

Figure 4. Copolymer composition curve of copolymerization of EIC with BPL (35 °C for 2 h, EIC + BPL = 10 mmol in 1.5 mL of CH_2Cl_2).

Experimental Section

Materials. Solvents, CH_2Cl_2, chlorobenzene, nitrobenzene, and nitromethane, were purified as previously reported.[3c,e] EIC was prepared according to the procedure reported[7] as shown in the following series of reactions. EIC was recrystallized

$$PhN{=}C{=}S \xrightarrow{Cl_2} PhN{=}CCl_2 \xrightarrow{NaOCH_2CH_2ONa} EIC$$

from benzene-ether: mp 73 °C (lit.[7] 73–75 °C), ^1H NMR ($CDCl_3$) δ 7.0 (m, C_6H_5, 5 H) and 4.38 (s, OCH_2CH_2O, 4 H). BPL was purified in a same manner as reported.[3a] *N*-Phenyl-β-alanine was prepared by a Michael addition reaction of aniline to acrylic acid in water: ^1H NMR ($CDCl_3$) δ 8.1 (broad s, NH and OH, 2 H), 7.2–6.5 (m, C_6H_5, 5 H), 3.25 (broad t, NCH_2, 2 H) and 2.46 (t, $CH_2C{=}O$, 2 H); IR, $\nu_{C=O}$ at 1710 cm^{-1}.

Copolymerization. A mixture of EIC and BPL (3.0 mmol of each) in 0.5 mL of solvent was allowed to keep at 35 °C. After a desired time of reaction the mixture was poured into 50 mL of diethyl ether to precipitate copolymer which was dried in vacuo. These results are shown in Table I.

Alkaline Hydrolysis of Copolymer. A solution of copolymer (sample no. 1, 113 mg) in 1.2 mL of 2 N $NaOH$-D_2O was allowed to reflux for 2 h. At the end of reaction the system became homogeneous. The ^1H NMR spectrum at this stage is shown in Figure 3. The reaction system was then weakly acidified with 1 N HCl solution and refluxed for 2 h. The system was neutralized, dried in vacuo, and extracted with chloroform. After evaporation of chloroform 0.33 mg of *N*-phenyl-β-alanine was obtained as viscous oil, which was identified by comparing its IR spectrum with that of the authentic sample.

References and Notes

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