cyanine units in these films. In PLCP–QLC blends, the order parameter of merocyanine is higher than that of PLCP alone,[10,16] which is in accord with our hypothesis of $\chi^{(2)}_{zzz}$ arising from aggregates aligned by the mesogenic domains. Better penetration into the mesogenic domains is also achieved by DANS in PLCPs and QLCs as is also borne out by the order parameters[10,18] and increased $\chi^{(2)}_{zzz}$. We also note the possibility that, in these latter samples, intermolecular DANS–merocyanine interactions could be contributing to the observed nonlinearity, as has been found for Langmuir–Blodgett films of closely related molecules.[21]

Two compositions (samples 8 and 18 in Table I) containing the MBANS molecule or the PLCP with dinitrospiropyran groups showed long-term stability of the $\chi^{(2)}_{zzz}$ SHG. In both of these cases the concentration of the high β moiety was large, which may be an important factor in the long-term stabilization of the nonlinearity.

The nonlinearity increases with the strength of the poling field. We showed earlier that for fields of up to 10 kV/cm the $\chi^{(2)}_{zzz}$ term increased approximately quadratically with the field, while the dependence of $\chi^{(2)}_{xxx}$ was linear. Three samples (7, 12, and 16 in Table I) were poled at both 10 and 50 kV/cm. This 5-fold increase in the field caused a further increase of both $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{xxx}$ by about a factor of 10 in all three cases.

In conclusion, we have clearly demonstrated that asymmetric ordering both parallel and perpendicular to the poling field is a widespread phenomenon for dye aggregates in nematic matrices. These films therefore exhibit numerous independent nonzero $\chi^{(2)}$ coefficients, which can be an advantage in applications such as phase-matched SHG in thicker films or electrooptic modulation.[16] Blend compositions that further enhance the perpendicular ordering and its stability have also been found, leading to very large $\chi^{(2)}$ coefficients, close to 10^{-7} esu/cm^3.

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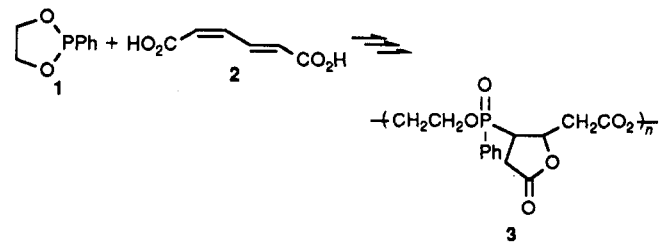
Ring-Opening-Closing Alternating Copolymerization of 2-Phenyl-1,3,2-dioxaphospholane with Muconic Acid

Ring-opening polymerization constitutes an important area in polymerization chemistry, in which various cyclic monomers polymerize via ring opening to produce linear polymers.[1] On the other hand, cyclopolymerization, or ring-forming polymerization, has long been known, in which monomers of a linear structure give polymers of a ring-closed structure.[2] On the basis of a new concept to combine these two modes of polymerization, the present paper reports a novel copolymerization of 2-phenyl-1,3,2-dioxaphospholane (**1**) with *cis,trans*-muconic acid (**2**), where monomers **1** and **2** provide a ring-opened and ring-closed structural unit, respectively, of product copolymer **3** in an alternating arrangement (*ring-opening-closing alternating copolymerization*). During the copolymerization, the phosphorus atom of monomer **1** is oxidized from P(III) to P(V) in **3**, whereas monomer **2** is reduced from unsaturated carbons to saturated carbons in **3** ("oxidation–reduction alternating copolymerization").[3,4]



The reaction of the 1:1 monomer feed ratio proceeded without any added initiator to give an alternating copolymer **3**. A mixture of monomers **1** (0.168 g, 1.0 mmol)

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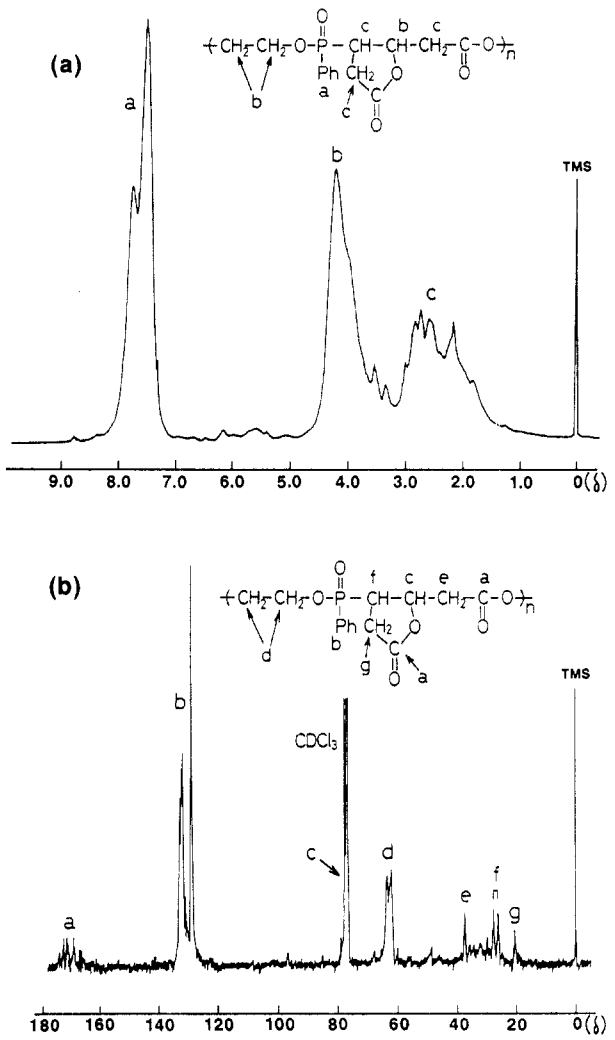


Figure 1. ^1H (250-MHz) (a) and ^{13}C (62.8-MHz) (b) NMR spectra of copolymer **3** (entry 4) in $CDCl_3$.

Table I
Ring-Opening-Closing Alternating Copolymerization of 1 with 2[a]

entry	temp, °C	time, h	yield,[b] %	mol wt[c]
1	35	786	68	1200
2	50	69	56	670
3	100	9	54	1000
4	100	71	59	2000

[a] 1.0 mmol of each monomer in 1.5 mL of DMF. [b] Diethyl ether insoluble part. [c] Determined by GPC in $CHCl_3$ at 40 °C.

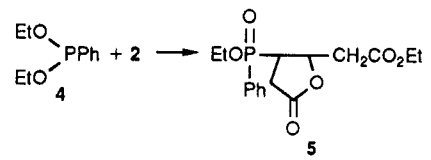
and **2** (0.142 g, 1.0 mmol) in 1.5 mL of *N*,*N*-dimethylformamide (DMF) under argon was placed in a polymerization tube. The tube was then sealed and kept at 100 °C. After 71 h the tube was opened and the reaction mixture was poured into a large amount of diethyl ether to precipitate the polymeric product. The material was isolated by filtration and dried in vacuo to give 0.183 g of a hygroscopic powder (59% yield). The molecular weight was 2000 as determined by gel permeation chromatography (GPC) with $CHCl_3$ at 40 °C with polystyrene standard.

The structure of the material was determined by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopies as well as elemental analysis. Figure 1a shows the 250-MHz ^1H NMR spectrum of the copolymer. A peak around δ 7.5 is due to phenyl protons (5 H), and a large peak centered at δ 4.2 is ascribed to methylene protons of $-OCH_2-$ (4 H) and a methine proton of –CHO– (1 H). Broad peaks at δ 1.5–3.1 are due to methylene protons of $-CCH_2C-$ (4 H) and a methine proton of –PCH– (1 H). In addition, a small broad peak centered at δ 5.6 was ascribed to the OH protons of hydroxyl and carboxylic acid groups in the polymer ends, since the peak disappeared when measured in D_2O. When the integral value of peak a was compared with that of peaks b and c, the content of **1** and **2** in the copolymer was calculated to be 50%. The ^{13}C NMR spectrum (Figure 1b) shows two peaks at δ 20.4 and 37.2 due to two carbons of CCH_2C, peaks at δ 26.8 (J_{CP} = 22.7 Hz) due to the carbon of P–*C*, peaks at δ 62.2 and 63.5 ascribed to two OCH_2 carbons, peaks at δ 128.7–132.6 due to aromatic carbons, and peaks at δ 168.7–172.0 assigned as two carbonyl carbons. A peak due to the carbon of OCH is overlapping with signals due to $CDCl_3$, the peak being observed, however, in DMSO-d_6 solvent at δ 75.6. These ^{13}C NMR data also support the copolymer unit structure of **3**.

The ^{31}P NMR spectrum of the copolymer in $CDCl_3$ showed a broad peak centered at δ +50 (relative to H_3PO_4 external standard). The peak is reasonably assigned to the phosphinate unit of the copolymer. The most characteristic features of the IR spectrum are the strong absorption bands at 1774 cm^{-1} due to the carbonyl group of the five-membered lactone, at 1722 cm^{-1} for the carbonyl of the backbone ester group, at 1208 cm^{-1} for P=O, and at 1026 cm^{-1} for the P O C stretching vibration. Anal. Calcd for $(C_{14}H_{15}O_6P)_n$ (**3**): C, 54.19; H, 4.84. Found: C, 54.10; H, 4.58. These spectroscopic as well as elemental analysis data strongly support copolymer structure **3**.

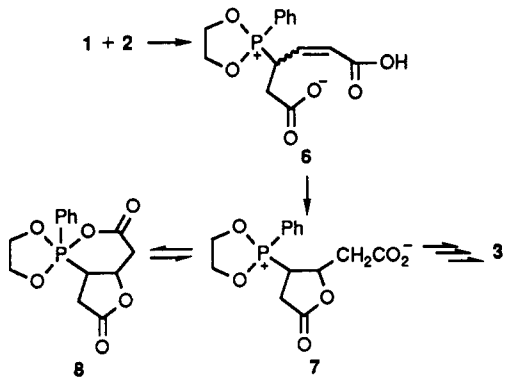
Similarly, the copolymerization of **1** and **2** was performed under other reaction conditions (Table I).

In order to obtain additional information about the copolymer structure, the following model reaction was carried out.

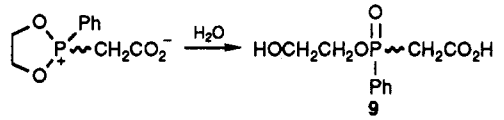


When a mixture of diethyl phenylphosphonite (**4**) as a model of monomer **1** and **2** in DMF was heated at 100 °C for 24 h, adduct **5** was almost quantitatively formed. The structure of **5** was confirmed by NMR and IR spectroscopies. The production of **5** from **4** and **2** also supports the copolymer unit structure **3**.

The following mechanism is assumed to explain the course of the present copolymerization. The first step of the reaction is the formation of a zwitterion by the Michael-type addition of **1** to **2**, followed by a hydrogen-transfer process to give a transient zwitterion **6**. Then, **6** is converted into a key species of genetic zwitterion **7** via a ring-closing process involving an intramolecular Michael-type addition and a hydrogen-transfer process. The next step is the reaction between two molecules of **7**, in which the phosphonium ring of **7** is opened by a nucleophilic attack of the anion from another molecule **7** according to an Arbuzov-type reaction. The propagation proceeds via the successive attack of genetic zwitterions **7** onto dimeric zwitterions to lead to alternating copolymer **3** of a macrozwitterion structure. From the ^{31}P NMR spectral data of the copolymerization system in situ at 60 °C in DMF-d_7, **7** is in equilibrium with a spiro pentacovalent phosphorus compound **8**, since the ^{31}P NMR spectrum showed a small signal at δ –14.9 assignable to **8** together with the main signal due to the copolymer. The spectrum also showed a small signal at δ +0.7, which was ascribed to the phosphorus atom of the terminal phos-



phonium ion of genetic zwitterions and/or macrozwitterions. The terminal groups of the isolated copolymer are probably of carboxylic acid and alcohol structures, the former coming from proton abstraction by the carboxylate group and the latter due to hydrolysis of the phosphonium ring during the isolation process as given by **9**. The small signals at δ 3.54 and 3.40 in the ^{1}H NMR spectrum (Figure 1) may be assigned to the terminal methylene groups $HOCH_2CH_2$–.



In conclusion, the results of this study indicate that the copolymer from the reaction of 2-phenyl-1,3,2-dioxaphospholane (**1**) with *cis,trans*-muconic acid (**2**) consists exclusively of structure **3** and that this unit has been formed according to the ring-opening-closing alternating copolymerization involving oxidation–reduction. The present reaction is the first example of the 1:1 copolymerization in which ring opening of one monomer and ring-closing of the other monomer occur alternatively. More detailed studies of the present copolymerization are now in progress.

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