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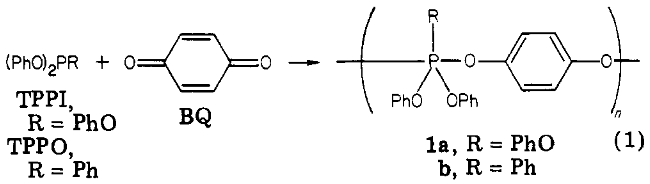
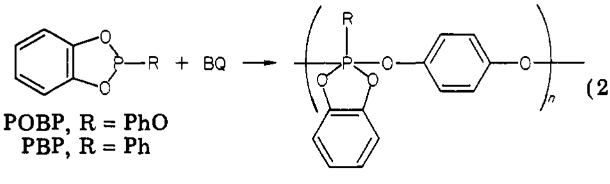
Polyphosphoranylation of *p*-Benzoquinone with Acyclic and Cyclic Phosphorus(III) Compounds Having Aryl and Aryloxy Groups

In a series of studies on the "no-catalyst alternating copolymerization via zwitterion intermediate", we have discovered a new alternating copolymerization in which cyclic phosphorus(III) compounds serve as nucleophilic monomers.[1-15] This communication reports alternating copolymerization between acyclic as well as cyclic phosphorus(III) compounds and *p*-benzoquinone (BQ). The acyclic phosphorus(III) compounds employed were triphenyl phosphite (TPPI) and diphenyl phenylphosphonite (TPPO) and the cyclic ones were 2-phenoxy- and 2-phenyl-4,5-benzo-1,3,2-phospholanes (POBP and PBP, respectively). The copolymerization gave polyphosphorane-type polymers 1 and 2, in which the phosphorus compounds served as nucleophilic monomers and BQ behaved electrophilically (*polyphosphoranylation*).



TPPI, R = PhO
TPPO, R = Ph
BQ
1a, R = PhO
b, R = Ph
(1)



POBP, R = PhO
PBP, R = Ph
2a, R = PhO
b, R = Ph
(2)

Table I
Alternating Copolymerization of *p*-Benzoquinone with Phosphorus(III) Compounds[a]

sample no.	P(III) compound	temp, °C	time, h	polymer yield, %	polymer structure	polymer mol wt[b]
1	TPPI	130	38	32	**1a**	3200
2	TPPI	150	52	68	**1a**	6400
3	TPPO	150	52	62	**1b**	5900
4	POBP	150	48	43	**2a**	3800
5	PBP	150	58	72	**2b**	4100

[a] 3 mmol each of the monomers in 3 mL of benzonitrile. [b] Determined by vapor pressure osmometry in DMF at 55 °C.

The copolymerization of TPPI and BQ was carried out in benzonitrile. At temperatures higher than 130 °C the copolymerization took place without added initiator and alternating copolymer **1a** was obtained after work-up procedures excluding moisture. The product copolymer was a pale grayish powder soluble in polar solvents such as DMF, Me_2SO, and $CHCl_3$ but insoluble in diethyl ether, benzene, and water. Copolymerization results are given in Table I.

The structure of the copolymer was determined by ^{31}P NMR and IR spectroscopy as well as by elemental analysis. The ^{31}P NMR spectrum of the isolated copolymer **1a** shows a broad peak centered at δ -85.6 ppm, indicating that the copolymer is composed of a pentaphenoxyphosphorane-type structure.[16] Furthermore, absorption due to P=O stretching was not found in the IR spectrum. The results of the elemental analysis were in good agreement with the calculated values for 1:1 TPPI-BQ (Table II).

Similarly, copolymerizations of TPPO, POBP, and PBP with BQ were performed at 150 °C and gave phosphorane-type polymers **1b**, **2a**, and **2b** (Tables I and II). These copolymers were not so unstable to moisture in spite of the fact they contain a phosphorane unit which is usually very sensitive to moisture.

In the present copolymerizations, the phosphorus(III) monomers were converted to pentavalent phosphoranes, whereas BQ was reduced to the ether of hydroquinone. Thus, these copolymerizations offer additional examples of "redox copolymerizations".[5,7,9]

The hydrolysis of polymer **1a** took place readily at room temperature with an excess of water in benzonitrile. The ^{1}H-decoupled ^{31}P NMR of the reaction mixture showed several peaks between -15 and -18 ppm. This result is taken to indicate the production of a mixture of triaryl phosphates of several combinations of phenoxy and para-substituted phenoxy groups. Among these, the main product was triphenyl phosphate. These results show that the P-O bond cleavage occurred at all P-OAr, including that of the main chain. In the case of polymer **2b**, elim-

Table II
^{31}P NMR and Elemental Analyses of Alternating Copolymers

sample no.	structure	^{31}P NMR,[a] ppm	formula[b]	anal. calcd[b] C	anal. calcd[b] H	anal. calcd[b] P	anal. found C	anal. found H	anal. found P
2	**1a**	-85.6	$(C_{24}H_{19}O_5P)_n$	68.90	4.58	7.40	68.78	4.31	7.52
3	**1b**	-69.5	$(C_{24}H_{19}O_4P)_n$	71.64	4.76	7.70	71.32	4.81	7.88
4	**2a**	-56.8	$(C_{18}H_{13}O_5P)_n$	63.54	3.85	9.10	63.46	3.78	9.04
5	**2b**	-40.0	$(C_{18}H_{13}O_4P)_n$	66.67	4.04	9.55	66.31	3.85	9.72

[a] ^{31}P NMR spectra were recorded without proton decoupling. Chemical shifts are negative upfield from external 80% H_3PO_4 standard. [b] Calculated for 1:1 composition.

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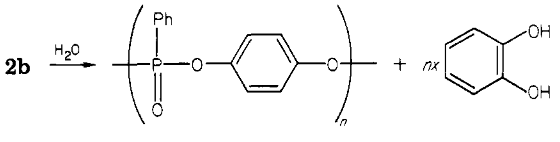
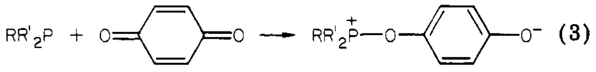
ination of pyrocatechol was a main pathway to polymer **2b′**, whose ^{31}P NMR signal appeared at +15.9 ppm.



2b′

Reactions 3 and 4 are proposed to explain the course of



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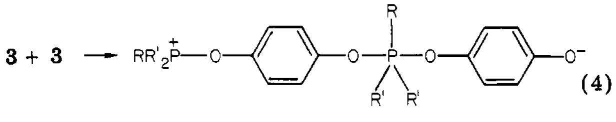

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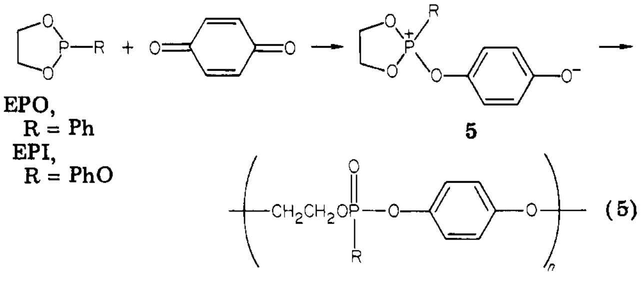
the polyphosphoranylation. The first step probably involves formation of the phosphoniumphenolate-type zwitterion **3**. Two molecules of **3** give dimeric zwitterion **4**. Successive reactions between zwitterions such as **3** and **4** and oligozwitterions lead to macrozwitterions of polyphosphoranes, **1** and **2**. A Japanese patent claiming copolymerization of ethylene phenylphosphonite (EPO) or ethylene phenyl phosphite (EPI) with BQ to produce alternating copolymer **6** was granted in 1971[17] and is similar to the present copolymerization. Sequence 5 was used to



6

explain the reaction of the patent. First, zwitterion **5** is formed which is polymerized to **6**. Propagation consists of opening of the phosphonium ring in **5** by nucleophilic attack of phenoxide anion of other zwitterions according to an Arbuzov-type reaction.[18] The phosphorus(III) monomers employed in the present study prevent the Arbuzov-type reaction involving **3** and hence allow it to undergo the polyphosphoranylation.

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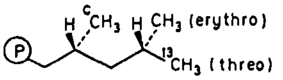
Comment on Proposed Mechanisms for Formation of Isotactic Polypropylene

In a recent paper, Zambelli et al. concluded that metallacyclobutanes are not involved in the δ-$TiCl_3$–$Al(CH_3)_2I$ polymerization of propene.[1] Here, we challenge that mechanistic interpretation.

Zambelli et al. carried out an elegant ^{13}C NMR analysis of the isotactic polypropylene formed from the δ-$TiCl_3$–$Al(^{13}CH_3)_2I$ catalyzed polymerization of propene.[1] They determined that the enriched ^{13}C methyl carbon was located only in the isopropyl end group and predominantly at the threo position relative to ^{c}C. Since neither a chiral carbon atom nor a spiralized chain participates in the first two addition steps, they concluded that the observed steric control must arise from the chirality of the catalytic center. We do not challenge these experimental results or conclusions.



Zambelli et al. point out that these results are in good agreement with a polymerization mechanism involving coordination of propene to a chiral surface M–$^{13}CH_3$ initiator followed by insertion of propene into the M–$^{13}CH_3$ bond.[2] However, Zambelli et al. contended that their results were inconsistent with the metallacyclobutane mechanism proposed by Green et al. in 1978.[3] We challenge this latter contention.

A variation[4] on Green's original mechanism of Zeigler–Natta polymerization involves (a) insertion of a metal into an α-CH bond of a metal alkyl to form a metal–carbene–hydride complex, (b) reaction of an alkene with the metal–carbene unit to produce a metallacyclobutane–hydride intermediate, and (c) reductive elimination of hydride and an alkyl group to produce a chain-lengthened metal alkyl. As Zambelli et al. correctly point out, the simplest version of Green's mechanism cannot account for the failure to observe ^{13}C label incorporated into the isobutyl methylene carbon of the right end group (Scheme I) or for the stereospecific placement of enriched methyls at the right end groups.

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