The time dependence of the parameter ϵ is then

$$\epsilon(\tau) = k_t/k_pM_0f(\tau) \tag{9}$$

The time dependence of P becomes

$$P = \int_0^t k_pM\,dt' = (k_pM_0/k_t)\int_0^\tau f(\tau')\,d\tau' = (k_pM_0/k_t)F(\tau) \tag{10}$$

and the distribution function of the number of chains in terms of the time τ at which the chains were terminated is

$$N(\tau) = \epsilon(\tau)\exp\left[-\int_0^\tau \epsilon(\tau')\,(dP/d\tau')\,d\tau'\right] = \epsilon(\tau)\exp(-\tau) \tag{11}$$

Of special interest is the result to be obtained when the polymerization is allowed to run its course, i.e., $\tau \rightarrow \infty$. In that case

$$(M/M_0)_\infty = \exp(-X) \tag{12}$$

$$\frac{\bar{P}_w}{\bar{P}_n} = \frac{\int_0^\infty P^2N(\tau)\,d\tau \int_0^\infty N(\tau)\,d\tau}{\left[\int_0^\infty PN(\tau)\,d\tau\right]^2} = \frac{\int_0^\infty [F^2(\tau)e^{-\tau}/f(\tau)]\,d\tau \int_0^\infty [e^{-\tau}/f(\tau)]\,d\tau}{\left\{\int_0^\infty [F(\tau)e^{-\tau}/f(\tau)]\,d\tau\right\}^2} \tag{13}$$

Relation 13 may be transformed[3] to

$$\frac{\bar{P}_w}{\bar{P}_n} = (1 - e^{-X})\left[1 + \frac{2}{\left\{\int_0^X (1 - e^{X'})\,\frac{dX'}{X'}\right\}^2} \times \int_0^X\left\{\int_0^{X''}(e^{X'} - 1)\,\frac{dX'}{X'}\right\}\frac{dX''}{X''}\right] \tag{14}$$

and from this formulation it can be easily shown that $\bar{P}_w/\bar{P}_n \rightarrow 2$ as $X \rightarrow 0$, while $\bar{P}_w/\bar{P}_n \rightarrow 1$ as $X \rightarrow \infty$. Some typical values of $\bar{P}_w/\bar{P}_n$ are 1.70, 1.47, 1.21, and 1.09 for X = 0.5, 1, 2, and 3. The chain length distribution will, of course, be further narrowed if the polymerization is interrupted before it has run its course.

Since X may be obtained from eq 12, we may compare $\bar{P}_w/\bar{P}_n$ computed from eq 13 or eq 14 with experimental values. If the width of the experimentally determined chain length distribution is larger than the computed value, the cause may be the inadequacy of two assumptions on which the above analysis is based, i.e., chain initiation may not be simultaneous and chain transfer may not be entirely absent.

Acknowledgment. This work was supported by the National Science Foundation Grant No. DMR 77-05210, Polymer Program. The author wishes to acknowledge also NSF support for attendance at the Brazilian–U.S. Polymer Seminar, Rio de Janeiro, Nov. 28–Dec. 1, 1978, which provided the stimulus for this study, and Mr. Steven Izen's computation of $\bar{P}_w/\bar{P}_n$ from eq 14.

References and Notes

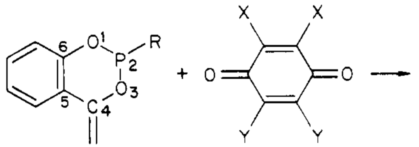
(1) J. P. Kennedy, private communication.
(2) H. Morawetz, "Macromolecules in Solution", 2nd ed., Wiley, New York, 1975, pp 12–14.
(3) I am indebted to Professor C. S. Morawetz for this transformation.

Polymerization via Zwitterion. 21. Alternating Copolymerizations of Cyclic Acyl Phosphonite and Phosphite with *p*-Benzoquinones

TAKEO SAEGUSA,* TAKATOSHI KOBAYASHI, TAK-YUEN CHOW, and SHIRO KOBAYASHI

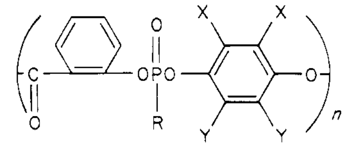
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.
Received October 10, 1978

In a series of our studies on the "No Catalyst Copolymerizations via Zwitterion Intermediates", we have found various combinations of nucleophilic (M_N) and electrophilic monomers (M_E) which gave rise to alternating copolymers from M_N and M_E.[1] As phosphorus-containing M_N monomes, ethylene phenyl phosphonite (EPO) and ethylene phenyl phosphite (EPI) were studied recently.[2] In this paper, we describe new phosphorus monomers of 2-phenyl-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (salicylyl phenyl phosphonite, SPO) and 2-phenoxy-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (salicylyl phenyl phosphite, SPI) which behave as M_N. They were combined with *p*-benzoquinone and its substituted derivatives as M_E. These copolymerizations took place without added catalyst and produced 1:1 alternating copolymers **2** consisting of ester group and phosphonate or phosphite in the main chains (eq 1). These cyclic acyl phosphorus compounds are interesting monomers in relating with cyclic acyloxyphosphoranes.[3] Both classes of compounds contain reactive POC(O)– group.



SPO, R = Ph
SPI, R = OPh

1a, X = Y = H
b, X = Y = Cl
c, X = Y = Me
d, X = Cl; Y = CN



(1)

2a, R = Ph; X = Y = H
b, R = Ph; X = Y = Cl
c, R = Ph; X = Y = Me
d, R = Ph; X = Cl; Y = CN
e, R = OPh; X = Y = H

Experimental Section

Reagents. SPO was prepared by a similar method of EPO[4] from dichlorophenylphosphine and salicylic acid in the presence of triethylamine in benzene and purified by recrystallization from chloroform (white solid, mp 40.5 °C). SPI was synthesized from triphenyl phosphite and salicylic acid and purified by fractional distillation, $bp_{0.2}$ 132–4 °C (lit.[5] $bp_{0.2}$ 135–7 °C). Commerically available *p*-quinones were used. All solvents were purified by distillation by the usual methods.

Polymerization Procedure. To 3 mL of solvent containing 3 mmol of *p*-quinone 3 mmol of SPO (or SPI) was added at room temperature under nitrogen, and the tube was sealed. Then, the mixture was kept at a desired temperature. After the reaction, the reaction mixture was poured into a large amount of diethyl ether to precipitate the copolymer. The resulting copolymer was dried in vacuo to give white powder.

Results and Discussion

Copolymerization of SPO with *p*-Benzoquinones. The copolymer obtained from SPO and *p*-benzoquinone

0024-9297/79/2212-0533$01.00/0

Table I
Alternating Copolymerization of Cyclic Acyl Phosphorus Compounds with *p*-Benzoquinones[a]

no.	M_N	M_E	solvent	temp, °C	time, h	copolymer yield, %	mol wt[b]
1	SPO	1a	$CHCl_3$	90	36	67	4120
2	SPO	1a	$CHCl_3$	rt[c]	47	48	2060
3	SPO	1b	$CHCl_3$	90	40	38	3220
4	SPO	1b	$CHCl_3$	rt[c]	170	53	1260
5	SPO	1c	$CHCl_3$	90	32	46	3240
6	SPO	1d	$CHCl_3$	90	47	45	2370
7	SPO	1d	$CHCl_3$	rt[c]	480	32	1360
8	SPI	1a	CH_3CN	90	21	38	2530
9	SPI	1a	PhCN	130	38	52	3640

[a] 3 mmol of each monomer in 3 mL of solvent. [b] Determined by vapor pressure osmometry in $CHCl_3$. [c] At room temperature.

Table II
Results of ^{31}P NMR and Elemental Analyses of 1:1 Alternating Copolymers

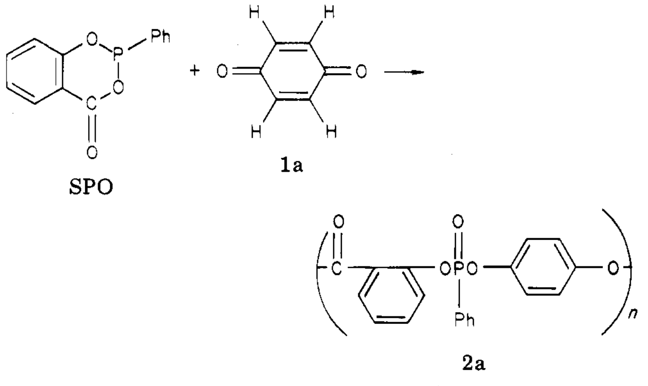
sample no.	$\delta(^{31}P)$, ppm[a]	formula	anal. calcd[b] C	H	P	N	Cl	anal. found C	H	P	N	Cl
1	+12.1	$(C_{19}H_{13}O_5P)_n$	64.78	3.72	8.79			64.56	3.68	8.82		
3	+12.6	$(C_{19}H_9O_5PCl_4)_n$	46.57	1.85	6.32		28.93	46.43	1.85	6.33		28.76
5	+11.8	$(C_{23}H_{21}O_5P)_n$	67.64	5.18	7.58			67.58	5.22	7.47		
6	+12.8	$(C_{21}H_9O_5PN_2Cl_2)_n$	53.53	1.93	6.57	2.97	15.05	53.48	1.93	6.72	2.88	15.14
8	−17.8	$(C_{19}H_{13}O_6P)_n$	61.96	3.56	8.41			61.68	3.64	8.38		

[a] Chemical shift is positive to the downfield relative to external 80% H_3PO_4 standard. [b] For the 1:1 compositions of copolymers.

(*p*-BQ) is soluble in polar solvents such as DMF, acetonitrile, chloroform, and methanol but insoluble in benzene, diethyl ether, and water. Table I shows the results.

The structure of the copolymer was determined by IR, ^{31}P NMR spectroscopy, and elemental analysis. The IR spectrum of the copolymer shows strong absorption bands at 1270 cm^{-1} due to $\nu_{P=O}$ and at 1740 cm^{-1} due to the ester group. The ^{31}P NMR spectrum of the copolymer showed only one signal at +12.1 ppm (Table II). The assignment of the chemical shift of ^{31}P NMR was established by the comparison with that of triphenyl phosphonate. These spectral data strongly indicate that the copolymer is composed of the triphenyl phosphonate ester structure **2a**. The results of the elemental analysis (Table II) were in good agreement with the calculated values of the 1:1 composition. This copolymerization took place even at room temperature to give the white powder (Table I, run no. 2).

Similarly, copolymerizations were performed between SPO and *p*-benzoquinone derivatives **1b–d**. The copolymer structures were determined as 1:1 alternating ones **2b–d**. Characteristic absorptions of the IR spectrum of **2b**, for example, are $\nu_{C=O}$ at 1750 cm^{-1} and $\nu_{P=O}$ at 1280 cm^{-1}. Copolymer from SPO and **1d** shows an additional characteristic absorption at 2230 cm^{-1} due to $\nu_{C\equiv N}$. The chemical shifts of ^{31}P NMR show little difference among these copolymers (Table II). The elemental analyses (Table II) are also in agreement with the 1:1 composition of the two monomer units. The solubilities of the copolymers were similar to the solubility of **2a**. These copolymerizations also took place at room temperature.

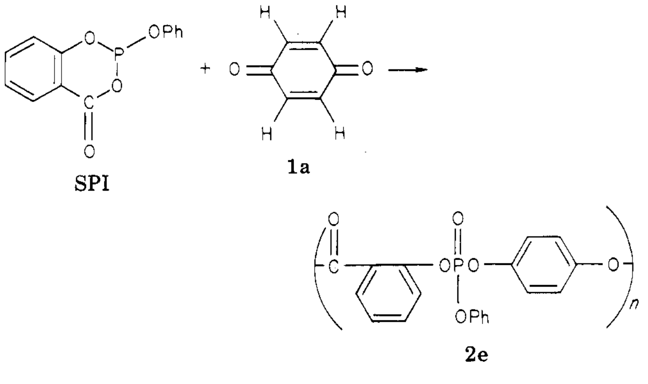


SPO

1a

2a

Copolymerization of SPI with *p*-Benzoquinones. Among the combinations of SPI with four quinones, the one with *p*-BQ **1a** was only possible by heating to produce a 1:1 alternating copolymer (Table I, run no. 8 and 9). At room temperature the copolymerization did not occur. SPI–*p*-benzoquinones **1b–d** systems did not give the copolymers even by heating at 130 °C. The IR spectrum shows strong absorption bands at 1740 cm^{-1} due to $\nu_{C=O}$ and at 1290 cm^{-1} due to $\nu_{P=O}$. The ^{31}P NMR spectrum of the copolymer (Table II) shows a broad singlet at −17.8 ppm which was similar to that of triphenyl phosphate. The result of the elemental analysis shows the 1:1 composition of the two kinds of units (Table II). All the above data strongly support the following phosphate ester structure.

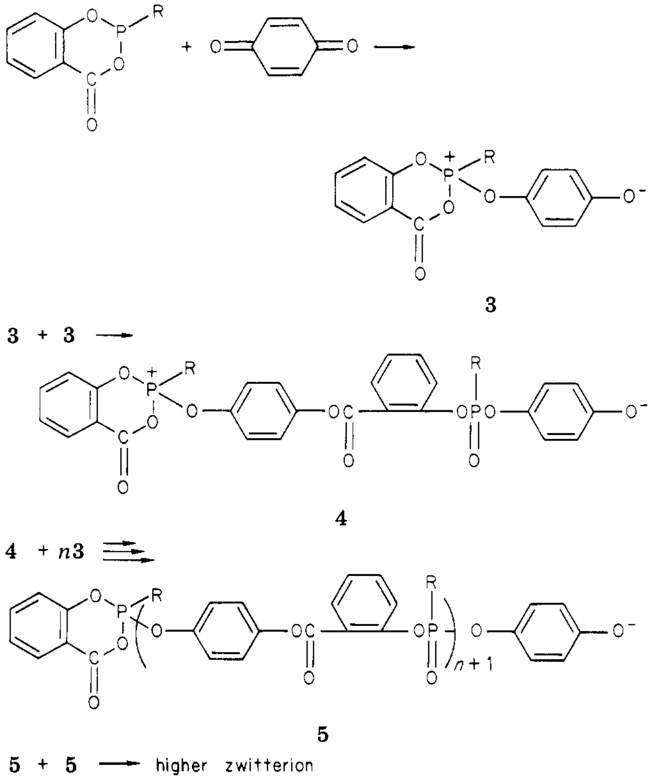


SPI

1a

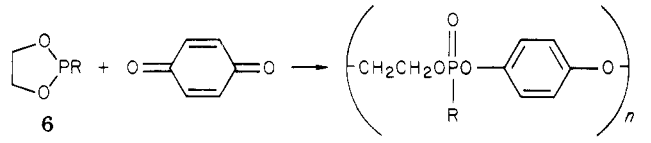
2e

Scheme of Copolymerization. On the basis of the general pattern of the spontaneous alternating copolymerization, as well as the reactivity characters of respective monomers, the following scheme is assumed to explain the present alternating copolymerization.



The first step is the reaction of SPO or SPI with p-benzoquinone to give a genetic zwitterion 3 of the phosphonium and phenoxide groups, which is an important key intermediate in both the initiation and propagation. Then, the reaction between two molecules of 3 occurs, in which the phosphonium ring of the one molecule is opened by nucleophilic attack of the phenoxide group of the other molecule, and the propagating species 4 is formed. 4 grows to 5 by the successive reaction with 3 to give the 1:1 alternating copolymer 2. The reaction between two propagating zwitterions 5 is also possible, which increases sharply the molecular weight.

In relation to the copolymerizations of the present study, a Japanese patent[6] is to be mentioned, which describes the alternating copolymerizations of cyclic phosphorus compound 6 with p-benzoquinones at higher temperatures (e.g., 100 °C). The systems of SPO in the present study



7

could give the alternating copolymers at room temperature. From these results SPO has increased reactivities with the combination of p-benzoquinones.

References and Notes

(1) Spontaneous alternating copolymerization has been reviewed in the following papers: (a) T. Saegusa, *CHEMTECH*, **5**, 295 (1975); (b) T. Saegusa, S. Kobayashi, Y. Kimura, and H. Ikeda, *J. Macromol. Sci., Chem.*, **9**, 641 (1975); (c) T. Saegusa, S. Kobayashi, and Y. Kimura, *Pure Appl. Chem.*, **48**, 307 (1976); (d) T. Saegusa, *Angew. Chem., Int. Ed. Engl.* **16**, 826 (1977); (e) T. Saegusa and S. Kobayashi, *Pure Appl. Chem.* **50**, 281 (1978).

(2) (a) T. Saegusa, T. Yokoyama, Y. Kimura, and S. Kobayashi, *Macromolecules*, **10**, 791 (1977); (b) T. Saegusa, Y. Kimura, N. Ishikawa, and S. Kobayashi, *ibid.*, **9**, 724 (1976); (c) T. Saegusa, S. Kobayashi, and J. Furukawa, *ibid.*, **10**, 73 (1977).

(3) (a) T. Saegusa, S. Kobayashi, and Y. Kimura, *J. Chem. Soc., Chem. Commun.*, 443 (1976); (b) T. Saegusa, S. Kobayashi, Y. Kimura, and T. Yokoyama, *J. Am. Chem. Soc.*, **98**, 7843 (1976).

(4) T. Mukaiyama, T. Fujisawa, Y. Tamura, and Y. Yokota, *J. Org. Chem.*, **29**, 2572 (1964).

(5) L. V. Nesterov and R. A. Sabirova, *Zh. Obshch. Khim.*, **35**, 2006 (1965); *Chem. Abstr.*, **64**, 8073 (1966).

(6) H. Kobayashi, H. Ohama, and Y. Kodaira, *Japanese Patent* 71-02352; *Chem. Abstr.*, **74**, 14269 (1971).

Fluorescence of Model Compounds with Two Groups Forming Intramolecular Excimers[1]

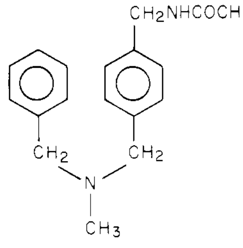
T.-P. LIAO, Y. OKAMOTO, and H. MORAWETZ*

Polymer Research Institute, Polytechnic Institute of New York, Brooklyn, New York 11201.

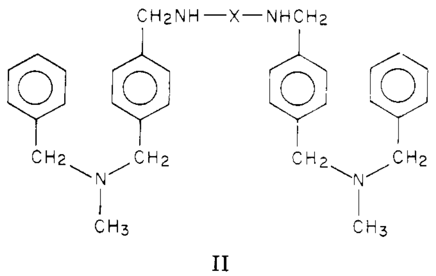
Received January 25, 1979

A number of investigators have found that intramolecular excimers can form in copolymers of monomers such as styrene, vinylnaphthalene, or N-vinylcarbazole only from nearest neighbor monomer residues carrying the aromatic chromophore.[2-5] On the other hand, it is well established that the excimer yield is increased by energy migration from the primary site of energy absorption to a site at which the conformation is particularly favorable for excimer formation.[2,6,7] This is the reason why the ratio of the fluorescence intensities at the excimer and the "monomer" band, I_D/I_M, is higher in polystyrene than in 2,4-diphenylpentane, the analogue containing only two chromophore groups.[8,9]

Recently, Reid and Soutar[10] have suggested that I_D/I_M in copolymers of monomers such as styrene or vinylnaphthalene should be proportional to $f_{aa}\bar{l}_a$, where f_{aa} is the fraction of linkages between the aromatic monomer residues and $\bar{l}_a$ is the mean sequence length of aromatic monomer residues. At nearly the same time, a study was published from Monnerie's laboratory[11] in which I_D/I_M was determined for the meso and the racemic 2,4-diphenylpentanes as well as for the isotactic and the syndiotactic 2,4,6-triphenylheptanes and 2,4,6,8-tetraphenylnonanes. Results of this study show that (1) the syndiotactic oligomers are characterized by much lower I_D/I_M ratios than the isotactic species and (2) that I_D/I_M increases sharply



I



II

a, X = $-C(=O)-$
b, X = $-C(=O)(CH_2)_2C(=O)-$
c, X = $-C(=O)(CH_2)_3C(=O)-$
d, X = $-C(=O)(CH_2)_4C(=O)-$

0024-9297/79/2212-0535$01.00/0