tional catalysis is unlikely, because if it takes place the plot should be parabolic, as shown in the following equation:

$$k_{\mathrm{cat}}/\alpha = k_1 + k_2\alpha[\mathrm{His}] + k_3\alpha^2[\mathrm{His}]^2$$

where [His] is the local concentration of histamine residues in PHis (which corresponds to the copolymer composition), k_1 is the rate constant for the catalysis by isolated imidazole functions, k_2 is the rate constant for bifunctional catalysis, and k_3 is the rate constant for terfunctional catalysis. The last term must be negligibly small in the reactions studied by us.

Very similar results were obtained for the solvolysis of 2,4-dinitrophenyl acetate catalyzed by PIm and PHis.[7]

Acknowledgment. The authors are indebted to Professor C. G. Overberger for his help in initiating this study and for many useful suggestions.

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Ratios of Weight and Number Average Molecular Weights to be Expected in Ionic Polymerization with Chain Termination but No Chain Transfer

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Received December 11, 1978

Recent work in Kennedy's Laboratory[1] indicated that in cationic polymerization carried out under conditions where chain transfer is absent, the ratio of the weight average and number average degree of polymerization, $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}}$, is substantially lower than 2, as would correspond to a most probable chain length distribution. This ratio was also found to decrease when the reaction was discontinued at low conversion. It is shown below that two factors are expected to lead to this result: (1) $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}} < 2$ if the polymerization is discontinued at a time when part of the chains are still actively growing. (2) $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}} < 2$, even if the polymerization process is allowed to run its course, since the relative probability of chain termination and chain propagation as the monomer concentration is gradually reduced.

In the following we make the following assumptions: (a) The propagation of all chains is initiated simultaneously. (b) The Poisson distribution of the lengths of chains which were still actively growing at the time at which the polymerization was discontinued can be approximated by a single degree of polymerization P.

Table I

$\epsilon P_{\max}$	$\exp(-\epsilon P_{\max})$	$\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}}$
0.1	0.905	1.033
0.2	0.819	1.067
0.5	0.606	1.165
1.0	0.368	1.322
1.5	0.223	1.465
2.0	0.135	1.589
2.5	0.082	1.692
3.0	0.050	1.774

For polymerizations in which the ratio of the termination and propagation rate is independent of the length of the chain, the distribution function of the number of chains with a degree of polymerization P is given by[2]

$$N(P) = \epsilon \exp(-\epsilon P) \tag{1}$$

where ϵ is the fractional probability that the chain will terminate rather than add a monomer unit. In our case $\epsilon = k_{\mathrm{t}}/k_{\mathrm{p}}M$ and we shall first assume that ϵ can be treated as constant, i.e., that the change in monomer concentration, M, can be neglected. If the growing chains have attained a degree of polymerization $P_{\max}$ at the time the reaction was discontinued, the fraction of "living" chains was $\exp(-\epsilon P_{\max})$. The number and weight average degrees of polymerization will then be

$$\bar{P}_{\mathrm{n}} = \frac{\int_0^{P_{\max}} P\epsilon \exp(-\epsilon P)\,\mathrm{d}P + P_{\max}\exp(-\epsilon P_{\max})}{\int_0^{P_{\max}} \epsilon \exp(-\epsilon P)\,\mathrm{d}P + \exp(-\epsilon P_{\max})} = \frac{1}{\epsilon}[1 - \exp(-\epsilon P_{\max})] \tag{2}$$

$$\bar{P}_{\mathrm{w}} = \frac{\int_0^{P_{\max}} P^2\epsilon \exp(-\epsilon P)\,\mathrm{d}P + (P_{\max})^2\exp(-\epsilon P_{\max})}{\int_0^{P_{\max}} P\epsilon \exp(-\epsilon P)\,\mathrm{d}P + (P_{\max})\exp(-\epsilon P_{\max})} = \frac{2[1 - (1 + P_{\max})\exp(-\epsilon P_{\max})]}{\epsilon[1 - \exp(-\epsilon P_{\max})]} \tag{3}$$

$$\frac{\bar{P}_{\mathrm{w}}}{\bar{P}_{\mathrm{n}}} = \frac{2[1 - (1 + \epsilon P_{\max})\exp(-\epsilon P_{\max})]}{[1 - \exp(-\epsilon P_{\max})]^2} \tag{4}$$

Note that $(\bar{P}_{\mathrm{n}})_\infty$, the number average molecular weight as $P_{\max} \rightarrow \infty$, i.e., when the polymerization is allowed to run its course, is equal to $1/\epsilon$, so that $\epsilon P_{\max}$ may be obtained from

$$\epsilon P_{\max} = \ln \{(\bar{P}_{\mathrm{n}})_\infty/[(\bar{P}_{\mathrm{n}})_\infty \bar{P}_{\mathrm{n}}]\} \tag{5}$$

Also, since $P_{\max} = k_{\mathrm{p}}(M)t$ (as long as (M) may be treated as constant), we have $\epsilon P_{\max} = k_{\mathrm{t}}t$ where t is the polymerization time.

Table I shows how the fraction of living chains and $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}}$ depend on $\epsilon P_{\max}$.

It may be seen that even if only a rather small fraction of the chains is still growing at the time the polymerization is discontinued, the $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}}$ ratio falls substantially under the value of 2, corresponding to the most probable chain length distribution.

The variation in the monomer concentration during the polymerization can be taken into account in the following way: If the concentrations of actively growing chains and of the monomer were C_0 and M_0, respectively, at $t = 0$, then they will be at any time t

$$C = C_0 \exp(-k_{\mathrm{t}}t) \tag{6}$$

$$M = M_0 \exp\left[-\int k_{\mathrm{p}}C_0 \exp(-k_{\mathrm{t}}t)\,\mathrm{d}t\right] \tag{7}$$

It is convenient to introduce the dimensionless parameters $X = k_{\mathrm{p}}C_0/k_{\mathrm{t}}$, $\tau = k_{\mathrm{t}}t$, so that

$$M = M_0 \exp\left[-\int_0^\tau X \exp(-\tau')\,\mathrm{d}\tau'\right] = M_0 \exp[-X(1 - e^{-\tau})] = M_0 f(\tau) \tag{8}$$

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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., $\tau \to \infty$. 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 $\bar{P}_w/\bar{P}_n \to 2$ as $X \to 0$, while $\bar{P}_w/\bar{P}_n \to 1$ as $X \to \infty$. 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.

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

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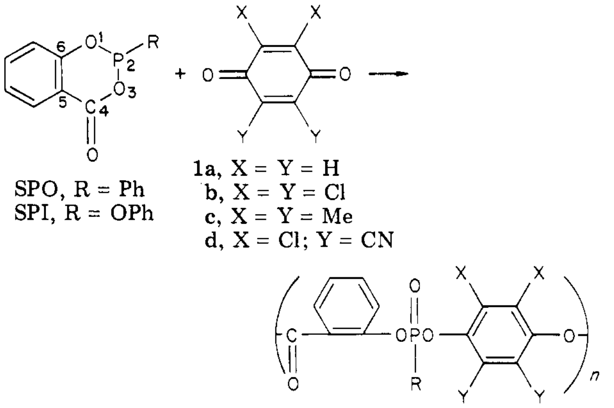
Received October 10, 1978

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

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