The relaxation times T_{1xz}^{REV} and $T_{1\rho}$ of the crystalline fraction in the temperature region around 20 °C are governed by the same motional process. However, the dominant interaction for these relaxation times is the dipolar interaction. Again, for this relaxation mechanism we have the two correlation times $\tau_1 = 1/D$ and $\tau_2 = 1/4D$. Since the main contribution to the fluctuating dipolar interaction comes from the two ^{19}F nuclei within a CF_2 group whose internuclear vector is nearly perpendicular to the axis of rotation, it is τ_2 that dominates T_{1xz}^{REV} and $T_{1\rho}$. In other words, T_{1xz}^{REV} reaches a minimum when $\tau_2 = 0.6 \times 3.6\ \mu s$,[13] which corresponds to $D = 18$ kHz. Extrapolation of the data plotted in Figure 9 predicts that this would occur at 35 °C. Similarly, the $T_{1\rho}$ minimum is expected, where $2\omega_1\tau_2 = 1$ or $D = {}^1/_2\omega_1$. For a spin-lock field of 60 kHz this would be at 37 °C, where the diffusion rate is 30 kHz.

References and Notes

(1) Wilson, C. W.; Pake, G. E. *J. Chem. Phys.* **1957**, *27*, 115.
(2) Slichter, W. P. *J. Polym. Sci.* **1957**, *24*, 173.
(3) Hyndman, D.; Origlio, G. F. *J. Appl. Phys.* **1960**, *31*, 1849.
(4) McCall, D. W.; Douglass, D. C.; Falcone, D. R. *J. Phys. Chem.* **1967**, *71*, 998.
(5) McBrierty, V. J.; McCall, D. W.; Douglass, D. C.; Falcone, D. R. *Macromolecules* **1971**, *4*, 584.
(6) Ellett, D.; Haeberlen, U.; Waugh, J. S. *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 71.
(7) Garroway, A. N.; Stalker, D. C.; Mansfield, P. *Polymer* **1975**, *16*, 171.
(8) Mehring, M.; Griffin, R. G.; Waugh, J. S. *J. Chem. Phys.* **1971**, *55*, 746. (a) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1975**, *8*, 291. (b) *Ibid.* **1977**, *10*, 384.
(9) English, A. D.; Vega, A. J. *Macromolecules* **1979**, *12*, 353.
(10) Pembleton, R. G.; Wilson, R. C.; Gerstein, B. C. *J. Chem. Phys.* **1977**, *66*, 5133.
(11) Binsch, G. *J. Am. Chem. Soc.* **1969**, *91*, 1304.
(12) (a) Mehring, M. *NMR. 1976* **1976**, *11*. (b) Haeberlen, U. *Adv. Magn. Reson., Suppl. 1* **1976**.
(13) Vega, A. J.; Vaughan, R. W. *J. Chem. Phys.* **1978**, *68*, 1958.
(14) English, A. D.; Garza, O. T. *Macromolecules* **1979**, *12*, 351.
(15) Rhim, W.-K.; Elleman, D. D.; Vaughan, R. W. *J. Chem. Phys.* **1973**, *59*, 3740.
(16) Rhim, W.-K.; Elleman, D. D.; Schreiber, L. B.; Vaughan, R. W. *J. Chem. Phys.* **1974**, *60*, 4595.
(17) Eby, R. K.; Sinnott, K. M. *J. Appl. Phys.* **1961**, *32*, 1765.
(18) Sperati, C. A.; Starkweather, H. W. *Fortschr. Hochpolym. Forsch.* **1961**, *2*, 465.
(19) Ryland, A. L. *J. Chem. Educ.* **1958**, *35*, 80.
(20) McBrierty, V. J. *Polymer* **1974**, *15*, 503.
(21) Vega, A. J.; English, A. D. *J. Magn. Reson.* **1980**, *37*, 107.
(22) McCrum, N. G.; Read, B. E.; Williams, G. "Anelastic and Dielectric Effects in Polymeric Solids"; Wiley: New York, 1967. Also see ref 4.
(23) Starkweather, H. W., unpublished review.
(24) Bunn, C. W.; Howells, E. R. *Nature (London)* **1954**, *174*, 549.
(25) Spin-lattice relaxation times were measured and semiquantitatively agree with those reported in ref 4. There is no indication that the α relaxation is detectable with T_1 measurements.
(26) Diehl, P.; Khetrapol, C. L. *NMR. 1969* **1969**, *1*.
(27) Petersen, N. O.; Chan, S. I. *Biochemistry* **1977**, *16*, 2657.
(28) Bocian, D. F.; Chan, S. I. *Annu. Rev. Phys. Chem.* **1978**, *29*, 307.
(29) Bates, T. W.; Stockmayer, W. H. *Macromolecules* **1968**, *1*, 12, 17.
(30) Brown, R. G. *J. Chem. Phys.* **1964**, *40*, 2900.
(31) Martin, G. M.; Eby, R. K. *J. Res. Natl. Bur. Stand., Sect. A* **1968**, *72A*, 467.
(32) Clark, E. S. *J. Macromol. Sci.—Phys.* **1967**, *B1* (4), 795.
(33) Rabolt, J. F.; Piermarini, G.; Block, S. *J. Chem. Phys.* **1978**, *69*, 2872.
(34) (a) Rabolt, J. F.; Fanconi, B. *Polymer* **1977**, *18*, 1258. (b) Reneker, D. H.; Fanconi, B. *J. Appl. Phys.* **1975**, *46*, 4144.
(35) Reneker, D. H.; Fanconi, B. M.; Mazur, J. *J. Appl. Phys.* **1977**, *48*, 4032.
(36) Clark, E. S.; Muus, L. T. International Union of Crystallography, 6th International Congress, Rome, 1963; A-96. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1964**, *5*, 17.
(37) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(38) Hentshel, D.; Sillescu, H.; Spiess, H. W. *Makromol. Chem.* **1979**, *180*, 241.
(39) McBrierty, V. J.; McCall, D. W.; Douglass, D. C.; Falcone, D. R. *J. Chem. Phys.* **1970**, *52*, 512.
(40) Spiess, H. W. *NMR. 1978* **1978**, *15*.
(41) Baram, A.; Luz, Z.; Alexander, S. *J. Chem. Phys.* **1976**, *64*, 4321.
(42) Reference 12a, p 39.
(43) Campbell, R. F.; Meirovitch, E.; Freed, J. H. *J. Phys. Chem.* **1979**, *83*, 525.
(44) Freed, J. H.; Bruno, G. V.; Polnaszek, C. F. *J. Phys. Chem.* **1971**, *75*, 3385.
(45) Vega, A. J.; Fiat, D. *J. Magn. Reson.* **1974**, *13*, 260.

Time-Resolved Fluorescence Emission Spectroscopy of Poly(phenylacetylene)

J. R. MacCallum,[1a] **C. E. Hoyle,**[1b] **and J. E. Guillet***

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.

Received April 16, 1979

ABSTRACT: The fluorescence characteristics of a sample of poly(phenylacetylene) are reported for solutions in fluid and solid matrices. It is proposed that two emitting states are responsible for the fluorescence, and variation with solvent depends more on the polarizability of the solvent than on its physical state.

The photophysical behavior of polyenes has been the subject of much discussion, and anomalies still exist between theoretical predictions and experimental observations.[2-6] Recently, evidence has been presented illustrating corresponding trends among polymeric materials incorporating polyene structures.[7-11] Some of the unusual spectroscopic properties of polyenes can be rationalized by postulating the existence of two excited singlet states, one with B_u symmetry and the other with A_g symmetry. Transitions from the $^1A_g{}^0$ ground state are allowed to the $^1B_u{}^*$ state, but dipole forbidden to the $^1A_g{}^*$ state. These two excited states are separated by a small energy gap which varies with solvent polarizability.[6]

There is a notable distinction between the characteristics of polymeric systems which incorporate polyenes and those of small molecules, in that the polymeric chromophores apparently exhibit emission from two states.[10,11] For example, it has been shown that the fluorescence emission spectrum of a styrene/phenylacetylene copolymer comprises two bands, one centered at 420 nm and the other at 490 nm.[11] The higher energy component has a shorter lifetime than that at lower energy. Two possible mecha-

0024-9297/80/2213-1647$01.00/0

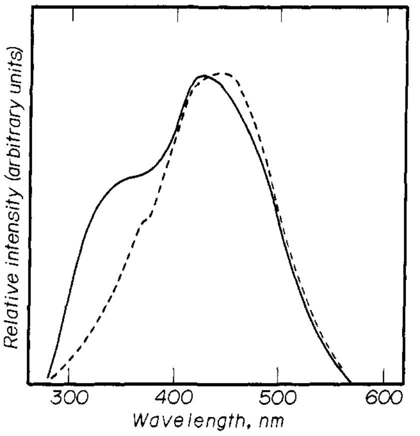


Figure 1. Steady-state emission spectra of poly(phenylacetylene) deposited as a thin film on a quartz plate, obtained by front-face viewing. Excitation wavelength: (—) 290 nm; (- - -) 300 nm.

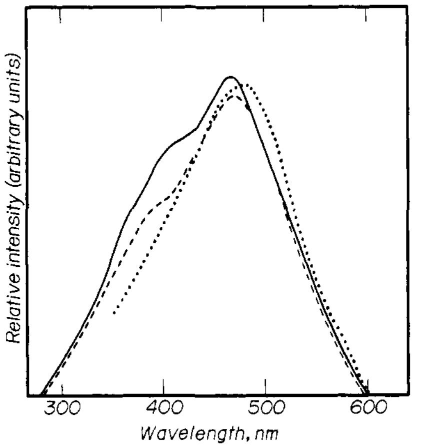


Figure 2. Steady-state emission spectra of poly(phenylacetylene) suspended in polystyrene film (0.1 wt %). Excitation wavelength: (—) 280 nm; (- - -) 320 nm; (···) 350 nm.

nisms have been proposed to account for this behavior: (1) extension of excited-chromophore sequence length by backbone rotation during the lifetime of the excited species, or (2) direct electronic energy transfer from the shorter to the longer polyenes which make up the polymeric sample. The former mechanism may well predominate in fluid solution, the latter being more important in fixed environments such as polymer films.

In this paper, investigation of the fluorescence of polymeric polyenes has been extended to a homopolymer of phenylacetylene in which the polyene sequence lengths are longer than those of the copolymer examined in earlier work.

Experimental Section

The techniques used have already been described.[11] The phenylacetylene homopolymer (PA) was synthesized by polymerizing the purified, degassed monomer in a sealed tube at 150 °C, using di-*tert*-butyl peroxide as initiator. The monomer was taken to about 15% conversion and the resultant polymer purified by multiple reprecipitation. The number-average molecular weight as measured by GPC was 6.2×10^3, with a broad distribution. All spectroscopic observations were made at 25 ± 2 °C.

Results

Steady-state fluorescence spectra of the PA polymer (PPA) are given in Figures 1–3. The comparative spectra with poly(styrene-*co*-phenylacetylene) (SPA)[11] show that the general shape of the fluorescence of the homopolymer is very similar to that of the copolymer. The excitation spectra shown in Figure 4 indicate at least two emitting states are responsible for the emission spectrum of the polymer.

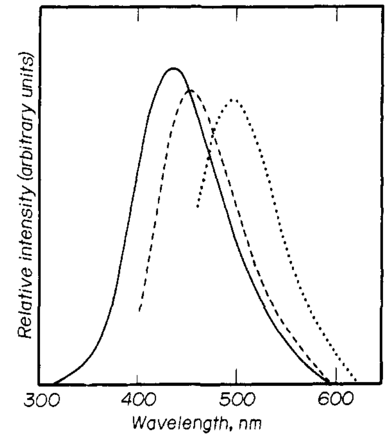


Figure 3. Steady-state emission spectra of poly(phenylacetylene) in degassed CH_2Cl_2 solution (1.7×10^{-3} M in repeat unit). Excitation wavelengths: (—) 300 nm; (- - -) 390 nm; (···) 460 nm.

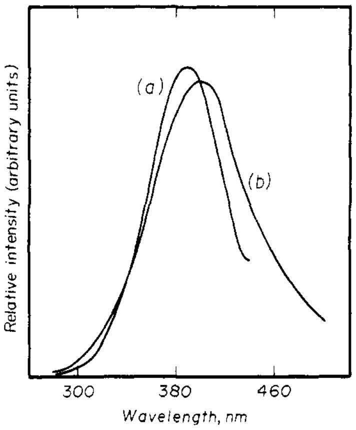


Figure 4. Steady-state excitation spectra of poly(phenylacetylene) suspended in polystyrene film (0.1 wt %). Emission wavelength: (a) 460 nm; (b) 530 nm.

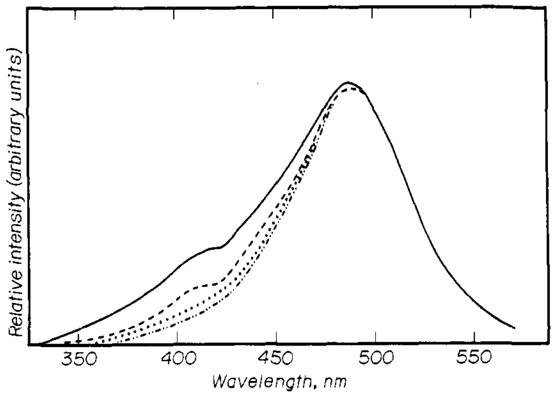


Figure 5. Time-resolved fluorescence spectra of poly(phenylacetylene) dissolved in polystyrene film. Excitation wavelength, 313 nm. The lower and upper limits for the time-resolved spectra are given as the interval from the lamp maximum: (—) lower, 0, upper, 1.6 ns; (- - -) lower, 1.8, upper, 4.4 ns; (···) lower, 4.6, upper, 10.4 ns; (··-) lower, 10.8, upper, 24.8 ns.

Time-resolved spectra (TRS) of PA dissolved in polystyrene film are shown in Figure 5. At short times (<5 ns) there appear to be two emission bands, the shorter-lived emission with a maximum around 420 nm and the other with the maximum at approximately 490 nm. In methylene chloride solution the TRS show emission almost exclusively from the short-wavelength (high energy) state

Table I
Lifetimes of Phenyl-Substituted Polymeric Polyenes[a]

polymeric polyene	τ_1, ns	τ_2, ns	conditions
poly(phenylacetylene)	1.8	5.5	methylene chloride solution, degassed
poly(phenylacetylene)	2.1	5.5	polystyrene film
poly(styrene-*co*-phenylacetylene)	1.8	5.5	methylene chloride solution, degassed
poly(styrene-*co*-phenylacetylene)	2.3	5.5	polystyrene film
poly[(*p*-methoxyphenyl)acetylene]	1.5	5.5	acetonitrile solution

[a] For the samples so far investigated, the emission can be described as the sum of two exponentials.

Table II
Polarization of Poly(phenylacetylene)

	λ_{ex}	λ_{em}	P
polystyrene film	320	420	0.25
	320	500	0.09
	420	500	0.22
methylene chloride solution	320	400	0.05
	320	500	0.03
	430	500	0.07

(Figure 6). It is important to note that the solutions were degassed, whereas the films were measured in air. Decay curves for the emission in polystyrene films were nonexponential for filters with cutoffs at 410 and 440 nm and essentially exponential for filters with cutoffs at 520 and 590 nm. The data for the nonexponential decays fitted almost perfectly to a rate law corresponding to a sum of two exponential decays. The lifetimes of the two states were determined from the decay curve and the results, along with data for similar polymeric polyenes are shown in Table I.

Steady-state polarization of PPA in polystyrene films, and in solution, was measured at different excitation and emission wavelengths. The results are given in Table II.

Discussion

The average sequence length of conjugated double bonds in this polymer is much greater than for the copolymer used in previous work,[11] and yet the emission characteristics are very similar. The fluorescence appears to be made up of contributions from two states, one with a lifetime of 2 ns and maximum emission at 420 nm, the other with a lifetime of 5 ns and maximum at 490 nm. The relative contribution of the two depends on the solvent. In fluid solutions, the higher energy state is predominant whereas in solid polymer films either of PA itself or of PA in polystyrene, the lower energy level is the major emitting species. This observation may be complicated by the fact that oxygen was present in the films (concentration ca. 10^{-3} M)—if the emission at 420 nm were preferentially quenched by O_2, then the apparent differences might be reconciled. However, it is most unlikely that this extent of preferential quenching could occur, particularly as the 420-nm emission has a shorter lifetime, which, within experimental error, is the same in the two solutions (see Table I). Furthermore, oxygen has little effect on states with lifetimes <10 ns.

The polarization measurements can also be interpreted in terms of two principal emitting states. The polarization data obtained in films (P_0) should correspond to P_0 values as defined by the Perrin equation[12] but are somewhat lower than the value of 0.45 determined by Moore and Song[13] for diphenyloctatetraene. Determination of P_0 for a given state requires measurement of emission from that state alone, and TRS indicate that the only conditions in which this requirement is fulfilled are the longer wavelength excitation and emission measurements. Substituting the P_0 values with those for polarization obtained in solution (P) and the measured lifetime (τ) in the Perrin equation results in a value of 8 ns for the depolarizing relaxation process in solution. Since the excited chromophore is part of the macromolecular backbone, this process is probably that of molecular tumbling. Furthermore, the smaller polarization measured by excitation at 320 nm and emission at 500 nm suggests that some electronic energy transfer takes place from the higher to the lower energy state.

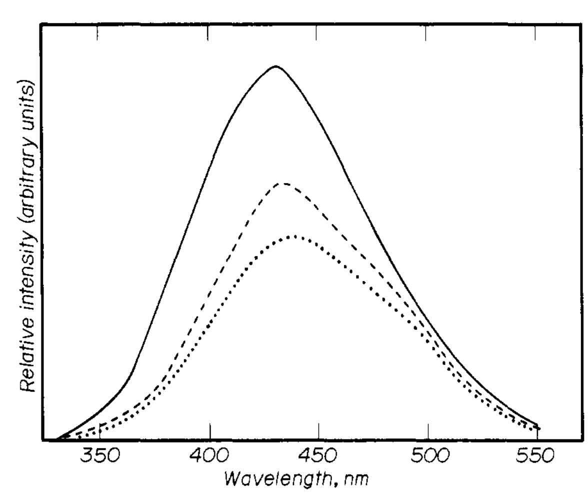


Figure 6. Time-resolved fluorescence spectra of poly(phenylacetylene) dissolved in degassed CH_2Cl_2 (1.7×10^{-3} M in repeat unit). Excitation wavelength, 313 nm. The lower and upper limits for the time-resolved spectra are given as the interval from the lamp maximum: (—) lower, 0, upper, 0.23 ns; (---) lower, 0.46, upper, 6.4 ns; (···) lower, 6.6, upper, 18.4 ns.

Conclusion

The fluorescence emission from PPA appears to result from the sum of contributions from two excited states. Its characteristics may depend upon the mobility of the chromophores, which is affected by both conformational restraints in the chain itself and the physical state of the polymer (i.e., solid or solution). For example, an excited polymeric polyene (SPA) dissolved in solid glassy polystyrene contained a higher proportion of the lower energy emitting state than when methylene chloride was the solvent. In a previous paper[11] it was tentatively suggested that chain extension, favored by a good solvent, was the governing factor in determining the contribution of the two excited states. From data published in a number of papers reporting investigations on different polymeric polyenes it can be concluded that the preferred solvent for the lower energy state is polystyrene > poly(methyl methacrylate) > methylene chloride > acetonitrile. One explanation of these results is that this sequence reflects the solvent/polymer compatibility.

Another possibility exists. In a recent paper, Andrews and Hudson[6] derived a relationship which predicts quantitatively the effect of solvent on the absorption/emission spectra of polyenes. The basis for the derivation is a model in which two singlet levels lie close together and the lower energy one is the emitting state. The difference in energy between the two states is governed by the polarizability of the solvent. It may be that the bulk of the photophysical properties of polymeric polyenes can be rationalized by a modification of the Andrews–Hudson model. In a previous paper it was proposed that the theory of convergence applies to polymeric polyenes resulting in a limit to the polychromatic range of the macromolecular chromophores. This conclusion is borne out by the very small difference in fluorescence behavior between the homopolymer and the copolymer, although there is a marked difference in the length of polyene sequences. Thus the two excited singlet levels, corresponding to $^1B_u{}^*$ and $^1A_g{}^*$ in small-molecule polyenes, will also converge to limiting energy levels. For the phenyl-substituted polyenes used in this work the two levels correspond to the emission at 420 and 490 nm. It is possible, therefore, that in these phenyl-substituted polyenes light is absorbed into, and emitted from, two states whose relative contribution is governed by the polarizability (α) of the solvent. High values of α favor absorption and emission from the lower energy state. Values of α for the solvents used for polymeric polyenes are 0.34 for polystyrene, 0.29 for poly(methyl methacrylate), 0.26 for methylene dichloride, 0.21 for and acetonitrile. The difference in the convergent energy levels is approximately 3400 cm^{-1}, a value which is within the range reported for small-molecule polyenes.[14] Further confirmation of this proposal must await additional experiments now under way in the laboratories.

Acknowledgment. Financial support for this research by the National Research Council of Canada is gratefully acknowledged by the authors.

References and Notes

(1) (a) Department of Chemistry, The University, St. Andrews, Scotland. (b) Armstrong Cork Co., Lancaster, PA 17603.
(2) Hudson, B.; Kohler, B. E. *Annu. Rev. Phys. Chem.* **1974,** *25,* 437.
(3) Birks, J. B.; Birch, D. J. S. *Chem. Phys. Lett.* **1975,** *31,* 608.
(4) Hug, G.; Becker, R. S. *J. Chem. Phys.* **1976,** *65,* 55.
(5) Gavin, R. M.; McVey, J. K.; Rice, S. A.; Weisman, C. *J. Chem. Phys.* **1978,** *68,* 522.
(6) Andrews, J. R.; Hudson, B. S. *J. Chem. Phys.* **1978,** *68,* 4857.
(7) Davydov, B. E.; Karpacheva, G. P.; Samedova, T. G.; Yandarova, M. M. *Eur. Polym. J.* **1971,** *7,* 1569.
(8) North, A. M.; Ross, D. A.; Treadaway, M. F. *Eur. Polym. J.* **1974,** *10,* 441.
(9) North, A. M.; Ross, D. A. *J. Polym. Sci., Polym. Symp.* **1976,** *No. 55,* 259.
(10) Guillet, J. E.; Nemzek, T. L.; North, A. M.; Ross, D. A. *J. Chem. Res.* (*S*) **1977,** 49.
(11) Guillet, J. E.; Hoyle, C. E.; MacCallum, J. R. *Chem. Phys. Lett.* **1978,** *54,* 337.
(12) Perrin, F. *Ann. Phys.* (*Paris*) **1929,** *12,* 169.
(13) Moore, T. A.; Song, P.-S. *Chem. Phys. Lett.* **1973,** *19,* 128.
(14) Andrews, J. R.; Hudson, B. S. *Chem. Phys. Lett.* **1978,** *57,* 600.

Alcoholysis Polymerization of Cyclic Acyloxyphosphorane to Polyphosphate Triesters: Polyphosphorylation of Alcohol

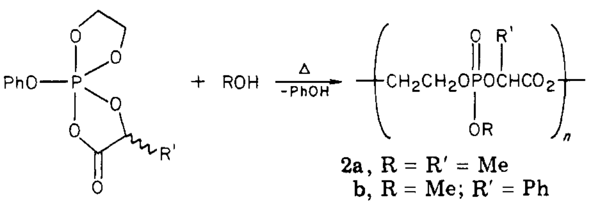
Shiro Kobayashi, Takatsugu Hashimoto, and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan 606.

Received May 1, 1980

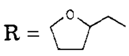
ABSTRACT: This paper describes the reaction of cyclic acyloxyphosphoranes **1** having a good leaving group, such as the phenoxyl group, with primary and secondary alcohols ("alcoholysis polymerization" of **1** or, alternatively, "polyphosphorylation of alcohol"). The reaction produces polyphosphate triesters **2a–g** which have various incorporated alcohol components. Polymer **2g**, derived from isopropyl alcohol, was found to contain diester-type unit **2h** due to the partial hydrolysis of **2g** during the work-up procedure. The tertiary alcohol *tert*-butyl alcohol yielded diester-type polymer **2h** with the evolution of isobutylene. A mechanism is proposed in which the replacement of the phenoxyl group with an alkoxyl group and subsequent polymerization via zwitterion intermediates are involved. Acute toxicity tests of four polyphosphate triesters showed that they are quite nontoxic, and, therefore, the possibility of utilizing them for carriers of pharmacologically active components in polymeric drugs is suggested.

Synthetic polyphosphates have been attracting increasing attention from the standpoint of providing a simple model for polynucleotides and because of their potential utility as useful biopolymers, such as pharmacologically active ones. Various methods of preparing polyphosphates have been explored.[1–6] Very recently we disclosed new methods for preparing polyphosphates,[7] polyphosphonates,[8] and polyphosphinates[9] by "thermally induced ionic polymerizations" of cyclic acyloxyphosphoranes.[10–12] In the course of the studies on the reactions of cyclic acyloxyphosphoranes we have found that they are reactive amphiphiles; i.e., they react with both nucleophiles and electrophiles.[13] The present paper reports the reaction of cyclic acylpentaoxyphosphoranes **1** having a phenoxyl group with primary and secondary *alcohols as nucleophiles* to give polyphosphate triesters **2** containing incorporated components (eq 1). Phenol was liberated during the reaction.[14]



(1)

1a, R′ = Me
b, R′ = Ph

2a, R = R′ = Me
b, R = Me; R′ = Ph
c, R = Et; R′ = Me
d, R = *n*-Pr; R′ = Me
e, R = *n*-Bu; R′ = Me
f, R =  ; R′ = Me
g, R = *i*-Pr; R′ = Me

In our previous studies **1** was obtained from 2-phenoxy-1,3,2-dioxaphospholane and α-keto acids,[10] and its polymerization afforded polyphosphate **3**[7] (eq 2). The reaction (eq 1) in the present paper provides a new single-step process for preparing polyphosphate triesters **2** having various alcohol components as pendant groups in the polymer.

Results and Discussion

Alcoholysis Polymerization of Spiroacylpentaoxyphosphorane with Primary and Secondary Alcohols.

0024-9297/80/2213-1650$01.00/0