plies 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.

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

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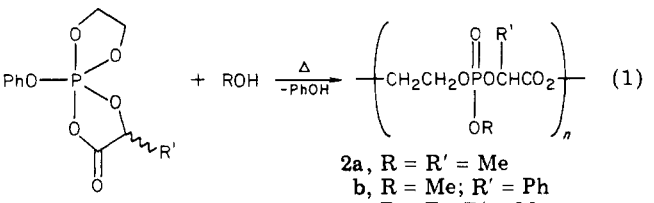
ABSTRACT: This paper describes the reaction of cyclic acyloxyphosphoranes **1** having a good leaving group, such as the phenoxyl group, with primary and secondary alcohols ("alcoholysis polymerization" of **1** or, alternatively, "polyphosphorylation of alcohol"). The reaction produces polyphosphate 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.

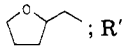
Synthetic polyphosphates have been attracting increasing attention from the standpoint of providing a simple model for polynucleotides and because of their potential utility as useful biopolymers, such as pharmacologically active ones. Various methods of preparing polyphosphates have been explored.[1-6] 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]

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



(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

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.

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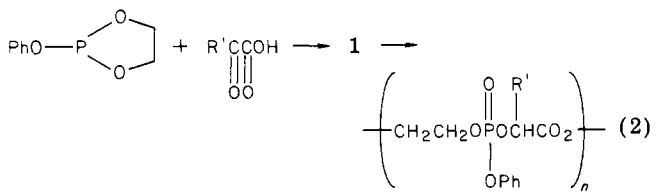
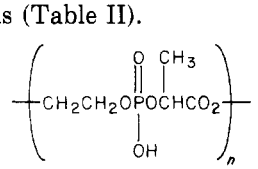


3

First, spiroacylpentaoxyphosphorane **1a** was prepared by the reaction of 2-phenoxy-1,3,2-dioxaphospholane with pyruvic acid (3.0 mmol of each) in 1.0 mL of benzonitrile.[10] It was confirmed that the reaction was completed at 0 °C overnight and yielded **1a** quantitatively. Then, 3.0 mmol of methanol was added to the system at room temperature. The reaction mixture was sealed under nitrogen, kept at the same temperature for 1 day, and heated at 120 °C for 48 h. The tube was opened and a usual workup gave a polymeric material in 35% yield.

The polymer was examined by ^{1}H NMR, ^{31}P NMR, and IR spectroscopy as well as by elemental analysis. The structure of polyphosphate triester **2a** (R = R′ = Me) was established on the basis of the following observations. The ^{1}H NMR spectrum of the polymer in $CDCl_3$ (Figure 1) shows broad signal A at δ 1.3–1.6 due to methyl protons (3 H), broad doublet B centered at δ 3.8 (J_{POCH} = 10 Hz) due to methoxy protons (3 H), broad signal C at δ 4.0–4.5 due to two methylene protons (4 H), and very broad signal D at δ 4.8–5.2 ascribed to methine proton (1 H). Besides these signals, small broad peak E was observed at δ 7.0–8.0, which is probably assignable to the hydroxy protons of the polymer end groups and of water included in the polymer due to its very hygroscopic nature. The ^{31}P NMR spectrum of the polymer shows only one signal, at δ −2.1,[15] assignable to the phosphate triester unit. Figure 2 shows the IR spectrum of the polymer. Three strong absorptions are observed: stretching bands A at 1750 cm^{-1} due to ester C=O, B at 1250 cm^{-1} due to P=O, and C at 1030 cm^{-1} ascribable to the P–O–alkyl group. Anal. Calcd for $(C_6H_{11}O_6P)_n$: C, 34.29; H, 5.28; P, 14.75. Found: C, 34.41; H, 5.13; P, 14.69. All of the above data strongly support the polymer structure of polyphosphate triester **2a**.

In a similar manner various alcohols reacted with **1** to produce polyphosphate triesters **2** having alcohol components (Table I). Polymer structures were determined by ^{1}H NMR, ^{31}P NMR, and IR spectroscopy (Table II) and by elemental analyses (Table III). Polymers **2a–g** are hygroscopic solid materials soluble in water and in polar organic solvents such as $CHCl_3$ and Me_2SO. Primary alcohols gave polyphosphate triesters whose structures are shown by **2a–f**. The secondary alcohol *i*-PrOH yielded a polymer consisting of two unit structures, polyphosphate triester **2g** and diester **2h**. The amount of diester unit **2h** in the polymer was determined as 30 molar percent from ^{1}H NMR analysis (Table II).



2h

Polymerization (eq 1) is induced by the nucleophilic attack of alcohol, which is accompanied by the nucleophilic displacement of the phenoxyl group by an alkoxyl group. Therefore we wish to term the reaction as *alcoholysis polymerization* of phosphorane **1**. Alternatively, in reaction 1 an alcohol is phosphorylated and incorporated into polymer **2**, and hence, the terminology *polyphosphorylation of alcohols* is proposed.

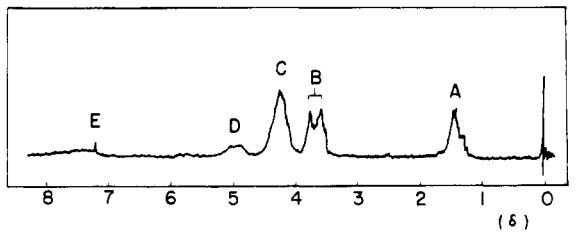


Figure 1. ^{1}H NMR spectrum of polymer **2a** in $CDCl_3$.

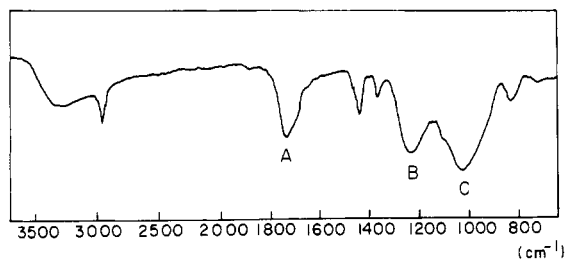
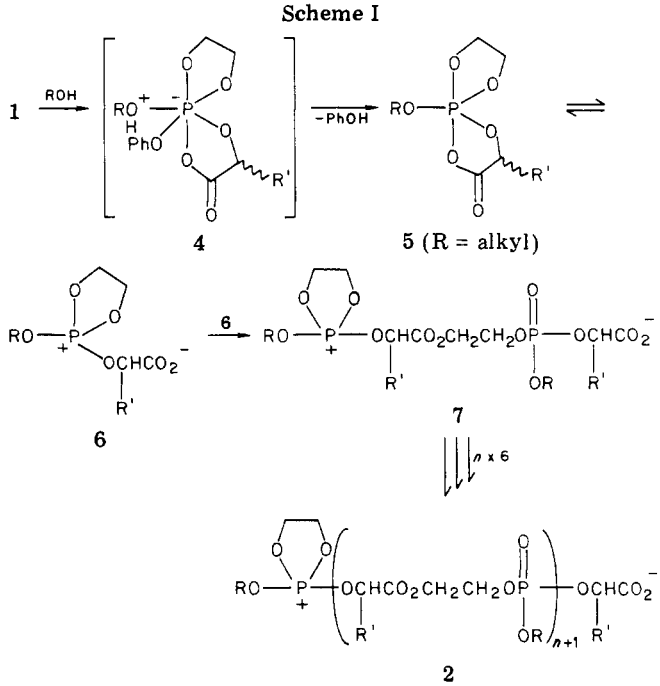


Figure 2. IR spectrum of polymer **2a** (neat).

Scheme I



The greatest advantage of alcoholysis polymerization is that one sort of spiroacylpentaoxyphosphorane possessing a good leaving group such as P–OPh in **1** can provide polyphosphate triesters **2** with various alcohol components by a single-step reaction.

A secondary alcohol (*i*-PrOH) does not give a polymer consisting exclusively of triester type **2g** and the polymer contained diester unit **2h** (~30%). This is probably due to the partial hydrolysis of the PO-*i*-Pr group of polymer **2g** during the work-up procedure of **2g** after the polymerization. The formation of gaseous products such as propylene was not detected during the reaction.

Reaction Mechanism. (Scheme I). The first step is probably a nucleophilic attack of alcohol onto the central phosphorus atom to form a hexacoordinated intermediate species **4**. A rapid proton scrambling takes place on oxygen atoms in **4** and phenol is liberated from **4** to give another spiroacylpentaoxyphosphorane **5**. The conversion of **1** to **5** is a new "transphosphoranylation" reaction[16] in which a phenoxyl group is replaced by an alkoxyl group because phenoxyl is a good leaving group. Under reaction conditions of higher temperature spirophosphorane **5** is in

Table I
Alcoholysis Polymerization of 1 under Various Reaction Conditions[a]

no.	ROH	R′ of 1	reaction			polymer		
			solvent	temp, °C	time,[b] h	% yield	structure	mol wt[c]
1	MeOH	Me	PhCN	120	48	35	**2a**	4180
2	MeOH	Me	MeCN	100	30	46	**2a**	1920
3	MeOH	Ph	MeCN	100	30	16	**2b**	1780
4	EtOH	Me	PhCN	120	48	32	**2c**	4150
5	EtOH	Me	PhCN	100	76	44	**2c**	2320
6	*n*-PrOH	Me	PhCN	100	240	49	**2d**	5060
7	*n*-PrOH	Me	MeCN	105	40	54	**2d**	1880
8	*n*-BuOH	Me	PhCN	105	100	73	**2e**	2690
9		Me	PhCN	100	200	80	**2f**	5660
10	*i*-PrOH	Me	$CHCl_3$	90	73	65	**2g**	

[a] 1 prepared in situ, 3.0 mmol of ROH in 1.0 mL of solvent under nitrogen. [b] Indicating the time after the reaction of 1 with alcohol at room temperature for 1 day. [c] Determined by vapor pressure osmometry in $CHCl_3$ at 35 °C.

Table II
Spectroscopic Data of Polyphosphate Triesters

polymer	^{1}H NMR ($CDCl_3$)[a] δ	^{31}P NMR[b]	IR (neat) ν, cm^{-1}
2a	1.3-1.6 (br m, CCH_3, 3 H)	−2.1	1750 (C=O)
	3.7-3.9 (br d, OCH_3, 3 H, J_{POCH} = 10 Hz)		1250 (P=O)
	4.0-4.5 (br m, OCH_2CH_2O, 4 H)		1030 (P—O—alkyl)
	4.8-5.2 (br m, CH, 1 H)		
2b	3.5-3.8 (br d, OCH_3, 3 H, J_{POCH} = 10 Hz)	−1.3	1740 (C=O)
	3.9-4.3 (br m, OCH_2CH_2O, 4 H)		1250 (P=O)
	5.6-6.0 (br m, CH, 1 H)		1050 (P—O—alkyl)
	7.1-7.6 (m, C_6H_5, 5 H)		
2c	1.1-1.6 (br m, CH_3, 6 H)	−2.0	1750 (C=O)
	3.8-4.5 (br m, OCH_2, 6 H)		1260 (P=O)
	4.6-5.1 (br m, CH, 1 H)		1050 (P—O—alkyl)
2d	0.85 (t, CH_3, 3 H, J = 8 Hz)	−2.8	1740 (C=O)
	1.4-1.7 (br m, CH_3, 3 H)		1250 (P=O)
	1.7-1.9 (br m, CCH_2C, 2 H) overlapping		1060 (P—O—alkyl)
	3.8-4.4 (br m, OCH_2, 6 H)		
	4.6-5.1 (br m, CH, 1 H)		
2e	0.8-1.0 (m, CH_3, 3 H)	−2.3	1750 (C=O)
	1.3-1.6 (br m, CH_3 + CCH_2CH_2C, 7 H)		1250 (P=O)
	3.7-4.4 (br m, OCH_2, 6 H)		1030 (P—O—alkyl)
	4.7-5.0 (br m, CH, 1 H)		
2f	1.4-1.7 (br m, CH_3, 3 H)	−2.3	1745 (C=O)
	1.7-2.1 (br m, CCH_2CH_2C, 4 H)		1260 (P=O)
	3.6-4.1 (br m, OCH_2 + OCH, 5 H) overlapping		1050 (P—O—alkyl)
	4.1-4.5 (br m, OCH_2CH_2O, 4 H)		
2g	1.1-1.4 (m, $C(CH_3)_2$, 4.2 H)	−3.5	1740 (C=O)
	1.4-1.7 (br d, CH_3, 3 H)		1250 (P=O)
	3.6-4.0 (br m, $CHMe_2$, 0.7 H)		1050 (P—O—alkyl)
	4.0-4.4 (br m, OCH_2CH_2O, 4 H)		
	4.4-5.1 (br m, CH, 1 H)		

[a] In every spectrum a very broad signal was observed in the δ 7.0-8.8 range. The signal intensity varied with all samples and was assigned to the OH protons of copolymer-terminal OH groups and of water remaining in the polymer sample due to incomplete drying. [b] Note 15.

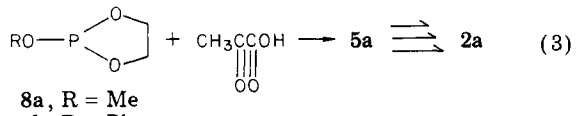
Table III
Elemental Analyses of Polyphosphates Triesters

polymer	formula	calcd			found		
		C	H	P	C	H	P
2a	$(C_6H_{11}O_6P)_n$	34.29	5.28	14.75	34.41	5.13	14.69
2b	$(C_{11}H_{13}O_6P)_n$			11.39			12.02
2c	$(C_7H_{13}O_6P)_n$	37.50	5.84	13.83	35.12	5.57	13.23
	$(C_7H_{13}O_6P{\cdot}H_2O)_n$	34.71	6.24	12.80			
2d	$(C_8H_{15}O_6P)_n$			13.01			12.89
2e	$(C_9H_{17}O_6P)_n$			12.29			13.05
2f	$(C_{10}H_{17}O_7P)_n$	42.86	6.12	11.06	39.43	5.92	11.31
	$(C_{10}H_{17}P{\cdot}H_2O)_n$	40.26	6.42	10.39			
2g	$(C_8H_{15}O_6P)_n$			13.01			12.70

equilibrium with its zwitterion form **6**. The intermediate **6** is a key species for both initiation and propagation of the polymerization. Two molecules of **6** yield dimeric zwitterion **7**. Successive attack of **6** on **7** leads to the macrozwitterion of polymer **2**. Phenol liberated during the reaction does not interfere with the polymerization.

In support of the above mechanism **5a** (R = R′ = Me) was prepared from 2-methoxy-1,3,2-dioxaphospholane (**8a**)

and pyruvic acid (eq 3). Then, heating of **5a** at 100 °C for 100 h gave polymer in 48% yield (MW = 4680), whose structure was confirmed as **2a** by ^{1}H NMR, ^{31}P NMR, and IR spectroscopy as well as by elemental analysis. Anal. Calcd for $(C_6H_{11}O_6P)_n$: P, 14.75. Found: P, 14.86. These results are taken to support the assumption that **5a** is actually involved in the methanolysis polymerization of **1a**.

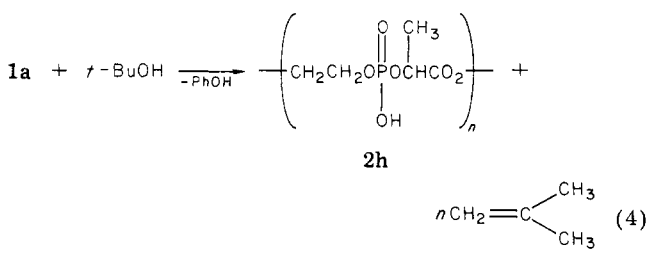


(3)

8a, R = Me
b, R = Ph

Significance as a Preparative Procedure. We emphasize again the advantage of using alcoholysis polymerization for preparing polyphosphate triesters having a variety of alkoxyl groups. Spiroacylpentaoxyphosphoranes **5** having a specific alkoxyl group may be prepared by the reactions of 2-alkoxy-1,3,2-dioxaphospholanes **8** with α-keto acids[10] and polymerization of **5** thus prepared would give polymer **5**. However, the preparation of **8** having an alkoxyl group requires two steps from phosphorus trichloride and the yield is generally low, while 2-phenoxy-1,3,2-dioxaphospholane (**8b**), a starting material for **1**, can readily be obtained by a one-step reaction in good yields (see Experimental Section).[17,18] In addition, the polyphosphate triesters **2** having specific alkoxyl groups can be prepared in a one-pot synthesis from 2-phenoxy-1,3,2-dioxaphospholane (**8b**); i.e., the isolation of spiroacylpentaoxyphosphorane **1** is not necessary, because the reaction of **8b** with an α-keto acid proceeds quantitatively and produces no byproduct. From the preparative viewpoint, therefore, alcoholysis polymerization of **1** is more convenient than the combination of two procedures, i.e., the preparation of **5** and its polymerization.

Polymerization with Tertiary Alcohol. The course of polymerization with a tertiary alcohol is a little different. The reaction of **1a** with *t*-BuOH proceeded very slowly, probably due to the steric hindrance of the *tert*-butyl group during formation of the hexacoordinated phosphorus intermediate **4**. The product was a polyphosphate consisting exclusively of diester unit **2h** with liberation of phenol as well as isobutylene. For example, an equimolar mixture of **1a** and *t*-BuOH in $CHCl_3$ at room temperature after 500 h gave **2h** in 64% yield (MW = 970 by vapor pressure osmometry) (eq 4). Evolution of isobutylene was confirmed by GC analysis. It is probable that isobutylene evolves when **4**, **6**, or the resulting triester polymer **2** (R = *t*-Bu) is produced. Elucidation of this point requires further studies.



2h

(4)

Biological Activity of Polymers. Polyphosphate is an interesting material as a simple model of polynucleotides. One possible application of the polymers obtained in the present study may be the preparation of pharmacologically active polymers or carrier polymers of pharmacological-active components. For such purposes a carrier polymer itself should be of very low toxicity.[19] Therefore, the acute toxicity of four polyphosphate triesters **2** was examined (Table IV). From these results polyphosphate triesters **2** are quite nontoxic and hence can be safely used as carrier polymers. There are many pharmacologically active alcohols which can be subjected to polyphosphorylation with **1**, leading to polyphosphate triesters having the pharmacologically active alcohol components as pendant groups in the polymer. This approach may allow the development of new polymer drugs.

Table IV
Acute Intraperitoneal Toxicity of Polyphosphate Triesters[a]

polymer	LD_{50}, mg/(kg mouse)
2c	>1000
2d	>1000
2f	~1000
3 (R' = Me)[b]	420

[a] Me_2SO solution of polymer sample was intraperitoneally injected in 20 mice (10 male and 10 female) with an amount of 5 mL of Me_2SO solution/(kg mouse). The LD_{50} values were obtained 14 days after injection. Dissection analyses of dead mice showed no abnormality. Me_2SO itself did not show toxicity with intraperitoneal injection at a dose rate of 10 mL/(kg mouse). [b] The polymer sample was prepared from **1a**.[7]

Experimental Section

Materials. Acetonitrile, benzonitrile, and chloroform solvents were purified as previously described.[9] Methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *tert*-butyl, and tetrahydrofurfuryl alcohols were commercial products and were dried over molecular sieves and distilled before use. 2-Phenoxy-1,3,2-dioxaphospholane (**8b**) was obtained by the reaction of triphenyl phosphite with ethylene glycol, according to a reported procedure;[17] bp 73–74 °C (0.2 mm) [lit. bp 70–76 °C (0.2 mm)]. 2-Methoxy-1,3,2-dioxaphospholane (**8a**) was prepared by the reaction of methanol with 2-chloro-1,3,2-dioxaphospholane which was obtained from phosphorus trichloride and ethylene glycol;[18] bp 59–61 °C (35 mm) [lit. bp 63–66 °C (40 mm)]. Pyruvic acid was a commercial reagent which was purified by distilling twice under nitrogen. Phenylglyoxylic acid was obtained by acid hydrolysis of benzoyl cyanide,[20] which was then purified by recrystallization from carbon tetrachloride; mp 65–67 °C (lit.[20] mp 64–66 °C). Spiroacylpentaoxyphosphoranes **1a**, **1b**, and **5a** were prepared by reactions of 2-phenoxy-1,3,2-dioxaphospholane–pyruvic acid, 2-phenoxy-1,3,2-dioxaphospholane–phenylglyoxylic acid, and 2-methoxy-1,3,2-dioxaphospholane–pyruvic acid, respectively, according to the procedures reported by us.[10]

Polymerization Procedure. A typical run was as follows. In a test tube a mixture of 2-phenoxy-1,3,2-dioxaphospholane (**8b**) and pyruvic acid was placed in 1.0 mL of benzonitrile under nitrogen. The tube was sealed with a glass stopper and kept at 0 °C overnight. The tube was opened and 3.0 mmol of methanol was added to the mixture at room temperature. Then the tube was sealed again, kept at the same temperature for 1 day, and heated at 120 °C for 48 h. A viscous reaction mixture resulted. The mixture was poured into a large amount (~50 mL) of diethyl ether to precipitate a polymeric material. It was separated and dried in vacuo to give 220 mg of a waxy polymer (35% yield). Results are shown in Table I.

The reaction of **1a** with *tert*-butyl alcohol at room temperature for 500 h gave polyphosphate diester **2h** in 64% yield. The structure of the polymer was determined as **2h** based on the following data: ^{1}H NMR (neat) δ 1.2–1.6 (br d, CH_3, 3 H), 3.5–4.4 (br m, OCH_2CH_2O, 4 H), 4.7–5.1 (br m, CH, 1 H), 7.8–8.2 (br s, OH); ^{31}P NMR (H_2O) δ −2.8;[15] IR (neat) 3400 (ν_{OH}), 1735 ($\nu_{C=O}$), 1210 ($\nu_{P=O}$), 980–1130 (ν_{POR}) cm^{-1}. The molecular weight was obtained as 980 by vapor pressure osmometry.

Measurements. The NMR spectra were recorded on a Hitachi R-20B NMR spectrometer (60 MHz for ^{1}H NMR and 24.3 MHz for ^{31}P NMR) at 35 °C. The IR measurements were carried out on a Hitachi grating IR spectrophotometer Model EPI-G3. The molecular weights of the polymers were measured by a vapor pressure osmometer (Hitachi Perkin-Elmer Model 115) in $CHCl_3$

at 35 °C for polyphosphate triesters **2a–g** and in DMF at 55 °C for polyphosphate diester **2h**.

Acute Toxicity Test. A polymer sample was dissolved in Me_2SO and the solution was intraperitoneally injected into 20 mice (10 male and 10 female). The injected amount of the solution was less than 5 mL/(kg mouse). The LD_{50} value was obtained from the number of surviving mice 14 days after the injection. The dead mice were subjected to dissection analysis and found that they suffered no symptom of anatomical abnormality. As a blank test Me_2SO itself was similarly examined; none of the mice died at a dose rate of 10 mL/(kg mouse) after 14 days.

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Optically Active Vinyl Polymers Containing Fluorescent Groups. 8. Synthesis and Properties of Copolymers of *N*-Vinylcarbazole and (–)-Menthyl Acrylate and (–)-Menthyl Methacrylate

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ABSTRACT: *N*-Vinylcarbazole was free radically copolymerized with (–)-menthyl acrylate and (–)-menthyl methacrylate in benzene at 55 °C to give optically active copolymers characterized by a marked induced optical rotation in the heteroaromatic co-units. Electronic absorption and emission properties, and the estimated reactivity ratios, are entirely consistent with quasi-random copolymerizations with, however, a tendency to alternation, especially for the *N*-vinylcarbazole unit. In contrast to the known behavior of copolymers of chiral monomers with other vinylaromatic monomers, the differential dichroic absorption exhibits a maximum value for copolymers containing approximately 40 mol % *N*-vinylcarbazole units. A similar maximum has been noted previously for copolymers of *N*-vinylcarbazole with (–)-menthyl vinyl ether and confirms the unique value of carbazole units as probes for asymmetric induction in polymer chains.

The investigation of chiroptical properties of stereoregular homopolymers[1-3] and copolymers[4-7] obtained from optically active α-olefins and vinylaromatic monomers led to the discovery of a very powerful tool in the assignment of a secondary structure for such polymers in solution. The scope and applicability of this type of characterization have been adequately reviewed.[8,9]

More recently we extended this method to copolymers of *N*-vinylcarbazole with optically active comonomers,[10,11] as well as to homopolymers of chiral carbazole-containing monomers,[12] with the aim of correlating primary and secondary structure with the complex spectroscopic properties of carbazole-containing macromolecules.[13,14]

At the same time a study of the practical potentiality of preparing macromolecules containing optically active heteroaromatic moieties starting from easily available chiral comonomers was undertaken. Preliminary results[10] obtained from copolymers of *N*-vinylcarbazole (**1**) with (–)-menthyl acrylate (**2**) and (–)-menthyl methacrylate (**3**) stimulated the synthesis of two series of copolymers using conventional free radically initiated polymerizations. A correlation between the physical–optical properties and structural characteristics related to chemical composition and distribution of monomeric units of the reported copolymers is presented.

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