Anionic Polymerization of 1-Vinylpyrene

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ABSTRACT: The anionic polymerization of 1-vinylpyrene occurs readily under a variety of reaction conditions. Carbanion and electron-transfer catalysts initiate polymerization in tetrahydrofuran and benzene over a wide temperature range. The vinylpyrene polymerization has all the characteristics of a "living" polymer system and copolymerization with monomers such as ethylene oxide, styrene, and isoprene resulted in AB and ABA type block copolymers. During the preparation of vinylpyrene–diene block copolymers, side reactions involving the growing polymeric diene anion and the pyrene ring can occur. These reactions cause premature termination of the polymerization process and introduce some uncertainty into defining the structure of the final product. Using conventional anionic polymerization initiators as models for the growing polymeric anions and pyrene as a model for the polyvinylpyrene segment in the block copolymer, it was shown that these side reactions involve both adduct formation and electron transfer. The effects of anion structure, solvent polarity, counterion, and temperature on the addition and electron-transfer reactions were investigated.

The anionic polymerization of vinyl monomers possessing aromatic rings larger than anthracene has only recently been reported in the literature. Monomers such as styrene,[1] the substituted styrenes,[2] vinylbiphenyl,[3] and vinylnaphthalene[4] undergo conventional anionic polymerization reactions. The monomer 9-vinylanthracene has also been investigated,[5] and its anionic polymerization exhibits several unusual features. It is not possible to obtain high molecular weight polymers and an abnormal propagation reaction and an electron-transfer reaction have been postulated.

The anionic polymerization of 1-vinylpyrene, the vinyl monomer with the largest aromatic ring yet studied, was recently reported by Tanikawa, *et al.*[6] These authors claimed that this polymerization is a typical "living" anionic system. We have investigated the anionic homopolymerization of 1-vinylpyrene, and our findings are in agreement with those of the Japanese workers. Since 1-vinylpyrene gives a living polymer, we have utilized conventional anionic techniques to synthesize a number of block copolymers, and we also report this work here.

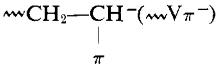
Experimental Section

1-vinylpyrene (1-Vπ) was synthesized from the pyrene-1-carboxaldehyde by the Wittig procedure, mp 89°, yield 85%.[6] The monomer was purified by column chromatography and recrystallization prior to each polymerization run. Pyrene (Princeton Organics, >99.99%) was used as received. Conventional anionic procedures[7] were used to dry, prepare, and manipulate reagents. Polymerization reactions were carried out in Pyrex units under high vacuum using break-seals to transfer reagents.

Optical spectra were recorded on a Cary 14 spectrophotometer and esr spectra on a Varian X-band spectrometer at 6-kHz modulation.

Results and Discussion

The anionic polymerization of 1-vinylpyrene could be initiated using both addition and electron-transfer initiators. The reaction was investigated in nonpolar solvents (benzene, cyclohexane) using *n*-butyllithium and in a polar medium (THF) using cumylpotassium, the α-methylstyrene tetramer dianion (αMeS_4^{2-}, $2K^+$), and the naphthalene anion radical. Solutions of the polymer anion


$$\sim\sim CH_2-\underset{\pi}{CH^-}(\sim\sim V\pi^-)$$

were stable overnight at ambient temperatures, and an optical spectrum of the polymer anion $\sim\sim V\pi^-$, K^+ in THF is shown in Figure 1. It is similar to that reported by Tanikawa,[6] the blue solution having absorption bands in the visible at 470 (ϵ 7500) and 620 nm (ϵ 9000) with shoulders around 590 and 660 nm. In benzene a similar spectrum is observed, except that the absorption maxima are shifted 30 nm to lower wavelengths. These solvent-dependent spectral shifts are consistent with the spectral studies of Hogen-Esch and Smid[8] on fluorenyl salts in various aprotic solvating media.

The effect of aromatic ring size on the absorption spectrum of living polymers derived from vinyl aromatic monomers can be seen in Table I. In general, as the ring size increases the longest wavelength absorption band undergoes a bathochromic shift and our assignment of 620 nm for the polyvinylpyrene anion appears reasonable. The apparently anomalous λ_{max} assignments reported for the poly(9-vinylanthracene) anion are probably the result of the complications that occur during the polymerization.[5]

It is also instructive to compare the polymer anion absorption maxima in Table I with those of the closely related arylmethide anions,[9] $ArCH_2^-, K^+$. The longest wavelength bands in this series are Ar = phenyl, 360 nm; Ar = 1-naphthyl, 560 nm, ϵ 0.7 × 10^4; Ar = 9-anthryl, 720 and 675 nm, ϵ 0.6 × 10^4; Ar = 1-pyrenyl, 630 and 600 nm, ϵ 0.8 × 10^4. The previously unreported 1-pyrenylmethide anion was prepared from 1,2-dipyrenylethane according to the published procedure.[9] The agreement between the two sets of spectra is good, and, in fact, the 1-pyrenylmethide anion matches the 1-vinylpyrene anion spectrum in Figure 1 after allowing for the slight bathochromic shift in the polymer anion. These results lend additional support to our spectral assignment for the poly(1-vinylpyrene) anion and cast further doubt on the

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[1] C. Geacintov, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **84**, 2508 (1962).

[2] M. Shima, D. N. Bhattacharyya, J. Smid, and M. Szwarc, *ibid.*, **85**, 1306 (1963).

[3] A. Rembaum, J. Moacanin, and R. Haack, *J. Macromol. Chem.*, **1**, 657 (1966).

[4] F. Bahsteter, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **85**, 3909 (1963).

[5] A. Rembaum and A. Eisenberg, *Macromol. Rev.*, **1**, 57 (1966).

[6] K. Tanikawa, H. Hirata, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jap.*, **42**, 2406 (1969).

[7] M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Wiley, New York, N. Y., 1968.

[8] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

[9] J. M. Pearson, D. J. Williams, and M. Levy, *ibid.*, **93**, 5478 (1971).

TABLE I
SPECTRA OF LIVING POLYMERS[a]

Living polymer from	λ_{max}, nm K+, THF, 25°	$\epsilon \times 10^4$
Styrene	342	1.2
Vinylbiphenyl	405	
1-Vinylnaphthalene	558	0.65
9-Vinylanthracene	397, 372	
1-Vinylpyrene	620	0.9

[a] See ref 7, p 172.

TABLE II
POLYMERIZATION OF 1-VINYLPYRENE[a]

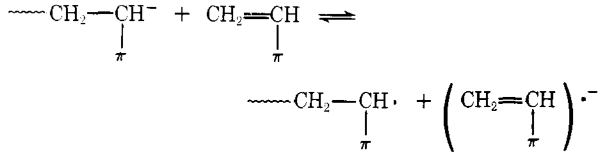
Initiator	[LE],[b] $M \times 10^4$	$\bar{M}_n \times 10^4$ Theor	Exptl	$[\eta]_{THF}{}^{25°}$	$\bar{M}_w/\bar{M}_n$
Cumylpotassium	11	2.7	3.0	0.09	1.14
	0.65	45.6	49.0	0.42	1.30
$(\alpha MeS)^{2-},2K^+$	16	3.6	3.8	0.10	1.17
	2.6	22.8	24.1	0.30	1.24

[a] Solvent, THF; temperature, −60°; $[M] = 1.3 \times 10^{-1}$ *M*. [b] [LE] = concentration of living ends; for cumyl potassium, $[I] = [LE]$ and for $(\alpha MeS)^{2-},2K^+$, $[I] = {}^1/_2[LE]$.

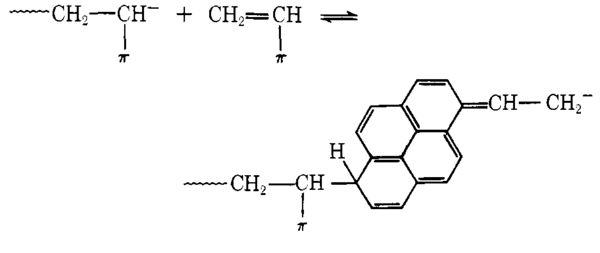
spectrum reported for the anion of 9-vinylanthracene. An absorption maximum for the poly(9-vinylanthracene) anion in the region of 700 nm would be more consistent with the present reasoning.

In the homopolymerization of 1-vinylpyrene, the relationship between molecular weight and initiator concentration appears to hold, *i.e.*, $\overline{DP} = [M]/[I]$ for the one-ended polymer and $\overline{DP} = [M]/{}^1/_2[I]$ for the two-ended polymer. Although it was not possible to accurately estimate the monomer purity, chromatographed and recrystallized samples gave high molecular weight polymers with molecular weight distributions approaching 1.1, as shown in Table II.

All the evidence from the homopolymerization studies indicates that 1-vinylpyrene gives a normal anionic living polymer. None of the complications encountered in the 9-vinylanthracene system was observed. Chain transfer to monomer (eq I) and formation of "dormant" polymer anions (eq II) do not occur in this polymerization system, although the electron affinity of pyrene is close to that of anthracene (ϵ_0 0.529 for pyrene, ϵ_0 0.642 for anthracene, measured in THF relative to biphenyl[10]).



$$\sim\!\sim CH_2-\underset{\pi}{CH^-} + CH_2{=}\underset{\pi}{CH} \rightleftharpoons \sim\!\sim CH_2-\underset{\pi}{CH\cdot} + \left(CH_2{=}\underset{\pi}{CH}\right)^{\cdot -} \quad (I)$$



(II)

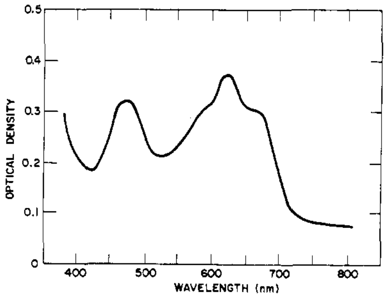
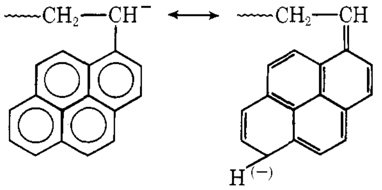


Figure 1. Absorption spectrum of living polyvinylpyrene in tetrahydrofuran at room temperature.

Since 1-vinylpyrene polymerizes anionically to give one- or two-ended living polymers, the synthesis of AB- and ABA-type block copolymers is feasible. Using conventional methods,[7] block copolymers of 1-vinylpyrene with ethylene oxide, styrene, and dienes have been synthesized. However, only the more unusual features of the block copolymer syntheses are discussed here.



Addition of ethylene oxide to a THF solution of $\sim\!\sim V\pi^-,K^+$ resulted in an immediate color change from blue to colorless, and the block nature of the product was confirmed by solubility and spectroscopic data. Addition of 1-vinylpyrene to a THF solution of living polystyrene ($\sim\!\sim S^-,K^+$) or a benzene solution of living polybutadiene ($\sim\!\sim B^-,Li^+$) resulted in the immediate formation of the blue color characteristic of $\sim\!\sim V\pi^-$. Molecular weight and copolymer composition control in these systems could be achieved using conventional techniques.[7] In the latter two polymerization reactions, the reverse monomer addition sequence, *i.e.*, addition of styrene or butadiene to $\sim\!\sim V\pi^-$, did not lead to the expected color changes. In both instances a deep red color developed. The visible spectrum of the $\sim\!\sim V\pi^-$-butadiene system is shown in Figure 2. The spectrum of the styrene system is very similar, but the intensities of the absorption bands are somewhat different. Both copolymerization reactions were characterized by low conversion of added monomer and isolation of very poorly defined copolymer products.

Arest-Yakubovich[11] and Szwarc[12] have shown that polymer carbanions can react with aromatic hydrocarbons by electron transfer and addition. It seems probable that the anomalous reactions observed in the block copolymer syntheses result from similar reactions involving the pyrene rings present in solution (monomer or polymer). In order to determine the nature of the reactions giving rise to the anomalous colored products, we studied spectroscopically the reactions of a series of polymer anions with pyrene (rather than 1-vinylpyrene, to avoid the complications of the polymerization process) as a model system.

Addition of an excess of pyrene to a THF solution of $\sim\!\sim S^-,K^+$ produces an immediate color change from orange to red, and the visible spectrum of the solution is shown in

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(10) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

(11) A. A. Arest-Yakubovich, *Vysokomol. Soedin.*, **6**, 290 (1965).

(12) S. N. Khanna, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 747 (1962).

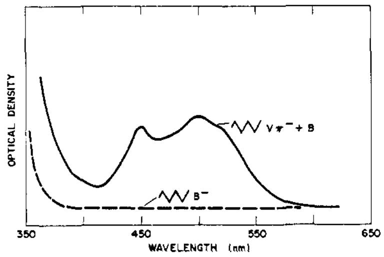


Figure 2. Absorption spectrum of the products resulting from the addition of butadiene monomer to a solution of living polyvinylpyrene anion. The absorption spectrum of living polybutadiene anion in the visible region is shown by the dashed curve.

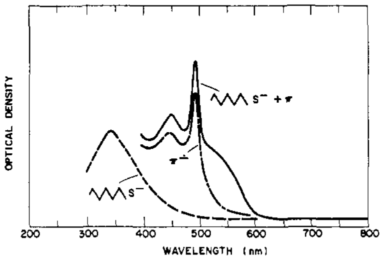
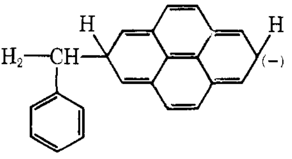


Figure 3. Absorption spectrum of the products resulting from the addition of pyrene to a solution of living polystyrene anion. Absorption spectra for the living polystyrene anion and the radical anion of pyrene are shown with the dashed curves.

TABLE III
REACTIONS BETWEEN A SERIES OF CARBANIONS AND PYRENE AT 20°

Anion	Counter-ion	Solvent	Addition	Electron transfer
∿S$^-$	K	THF	√	√
	Na	THF	√	√
	Na	Benzene		
	Li	THF	√	√
	Li	Benzene		
∿αMeS$^-$	Na	THF	√	√
	Na	Benzene		
∿D$^-$	Na	THF		
	Li	Benzene		
∿B$^-$	Li	Cyclohexane		
		Cyclohexane + THF	√	√
		Cyclohexane (40°)	√	√
∿I$^-$	Li	Cyclohexane		
∿Vπ^-	Na	THF		

Figure 3. Superimposed on this spectrum are the ∿S$^-$,K$^+$ and the pyrene anion-radical ($\pi\cdot^-$) spectra. The absorption peaks at 450 and 490 nm are due to the pyrene anion radical,[13] and the existence of the paramagnetic species was confirmed by esr spectroscopy. The esr spectrum was identical with that of an anion-radical solution prepared by reduction of pyrene over a potassium mirror and with that reported by Weissman, *et al.*[14] The broad absorption band beyond 500 nm in the spectrum in Figure 3 may be due to the presence of the addition product **1**. This assignment is supported by the spectra reported by Szwarc[15] for the adducts formed between the anion of α-methylstyrene and anthracene (450 nm) and benz[*e*]pyrene (620 nm).



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The results of the reactions between a series of polymer carbanions and pyrene are summarized in Table III. The adducts formed showed absorption maxima at ~500 (∿αMeS$^-$) and ~530 nm (∿B$^-$, ∿I$^-$). Using the absorption band at 490 nm of the pyrene anion radical, ϵ 49,000, we can estimate that in the styrene and α-methylstyrene systems approximately 10–15% of the "living ends" react by electron transfer, whereas in the diene systems approximately 5% of the anions react in this way.

Treatment of a THF solution of ∿Vπ^-,K$^+$ with excess pyrene did not produce any detectable spectral changes. It can be concluded, therefore, that electron transfer and addition between ∿Vπ^- and pyrene do not occur. This supports our earlier conclusion that the homopolymerization of 1-vinylpyrene is normal. The absence of any reaction between the anion of 1,1-diphenylethylene[16] and pyrene in THF is surprising. It is tempting to explain this in terms of a steric effect, but the data of Szwarc[15] on the dimeric dianion of 1,1-diphenylethylene ($^-$DD$^-$) invalidate this argument. The reaction between $^-$DD$^-$ and a series of aromatic hydrocarbons (Ar) was studied in detail by Szwarc, and the following mechanism was proposed.

$$^-\mathrm{DD}^- + \mathrm{Ar} \rightleftharpoons {}^-\mathrm{DD}\cdot + \mathrm{Ar}\cdot^- \qquad (1)$$

$$^-\mathrm{DD}\cdot \longrightarrow {}^-\mathrm{D}\cdot + \mathrm{D} \qquad (2)$$

$$^-\mathrm{D}\cdot + \mathrm{Ar} \longrightarrow \mathrm{D} + \mathrm{Ar}\cdot^- \qquad (3)$$

No adduct formation was detected, and the dissocation reaction (2) is the rate-determining step and drives the overall reaction forward. In the present investigation, eq 4, the situation is somewhat different.

$$\sim\!\!\sim\mathrm{SD}^- + \pi \rightleftharpoons \sim\!\!\sim\mathrm{SD}\cdot + \pi\cdot^- \qquad (4)$$

Reaction of ∿SD· may not provide a favorable route for shifting the equilibrium to the right, and electron transfer may occcur only to a very minor extent. Also, dissociation, eq 1, might be enhanced by the proximity of the two negatively charged end groups, the repulsive force favoring the reaction. This driving force is not available in eq 4, and hence the electron transfer is not favored. With the data presently available, further comments are not warranted.

The results in Table III show that polar solvents favor the electron-transfer and addition reactions, and this can be explained by solvation phenomena giving rise to more reactive carbanion species.[17]

The data for the ∿S$^-$ system also show that the counterion does not influence the reaction. In the diene systems at elevated temperatures, a slow reaction giving rise to colored products does occur. In an actual diene polymerization reaction, which is usually carried out at elevated temperatures in a nonpolar solvent for practical reasons, side reactions with a pyrene ring come into play.

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(13) D. Gill, J. Jagur-Grodzinski, and M. Szwarc, *Trans. Faraday Soc.*, **60**, 1424 (1964).

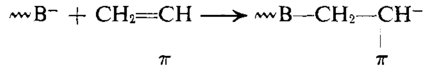
(14) G. J. Hoijtink, J. Townsend, and S. I. Weissman, *J. Chem. Phys.*, **34**, 507 (1961).

(15) J. Jagur-Grodzinski and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 7594 (1969).

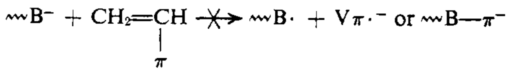
(16) Since the monomer, 1,1-diphenylethylene (D), does not homopolymerize, this anion was prepared by treatment of a solution of ∿S$^-$ with just enough D to convert ∿S$^-$ into ∿SD$^-$.

(17) D. N. Bhattachryya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

These model system studies with pyrene can be translated to the real polymerization systems and explain the anomalous results obtained in some of the block copolymer syntheses. Addition of 1-vinylpyrene monomer to a solution of living polybutadiene, $\sim B^-$, results in normal block copolymer formation. Apparently, the diene anion reacts more rapidly by addition to the vinyl function (eq 5) than with the pyrene nucleus (eq 6). Once all the diene anions have been converted to $BV\pi^-$, the polymerization of the 1-vinylpyrene segment proceeds in a normal manner.



$$\sim B^- + \underset{\pi}{CH_2{=}CH} \longrightarrow \sim B{-}CH_2{-}\underset{\pi}{CH^-} \qquad (5)$$



$$\sim B^- + \underset{\pi}{CH_2{=}CH} \not\longrightarrow \sim B\cdot + V\pi\cdot^- \text{ or } \sim B{-}\pi^- \qquad (6)$$

In the reverse addition sequence, *i.e.*, addition of butadiene monomer to $\sim V\pi^-$, it appears that the expected crossover reaction occurs and the polybutadiene anion is formed. However, this anion can either continue to polymerize any available butadiene monomer or react with the high local concentration of pyrene rings in the polyvinylpyrene segment of the copolymer. The reaction sequence is illustrated in eq 7–9, where $(\pi)_n$ refers to a pyrene ring on the PVπ segment of the copolymer chain.

$$\sim V\pi^- + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \sim V\pi{-}B^- \qquad (7)$$

$$\sim B^- + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \sim BB^- \qquad (8)$$

$$\sim B^- + (\pi)_n \longrightarrow \sim B\cdot + (\pi)_n\cdot^- \qquad (9a)$$

$$\text{or } \sim B(\pi)_n^- \qquad (9b)$$

Reactions 7 and 8 will result in block copolymers of well-defined structure and composition, whereas reactions 9a and 9b will yield ill-defined copolymer materials. The electron-transfer reaction products shown in reaction 9a lead to chain termination and chain coupling, whereas pseudotermination and branching occur as a result of the addition reaction shown in eq 9b. Our model studies with pyrene indicate, however, that block copolymer formation (eq 8) is the preferred reaction mode in nonpolar solvents at moderate or low temperatures.

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Synthesis of Block Polymers for Desalination Membranes. Preparation of Block Copolymers of 2-Vinylpyridine and Methacrylic Acid or Acrylic Acid

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ABSTRACT: Block copolymers containing cationic and anionic sequences were synthesized by the "living" anionic polymerization of 2-vinylpyridine and various methacrylate and acrylate esters, followed by the hydrolysis of the ester sequence to the free acid. These copolymers were soluble in either strongly acid or strongly basic aqueous media, but insoluble at neutral pH values, indicating that they were polyampholytes. The reduced specific viscosity of these polymers increased with dilution in protic solvents in a manner characteristic of a polyelectrolyte, but the viscosity in aprotic solvents was linearly related to the concentration. Salt rejection and flux rate of a dynamically formed membrane of the block polymers were found to be dependent on pH. Except for the region of 6.5–4.5, the isoelectric range of the block polymer, good salt rejection was observed; the flux rate was maximum near the isoelectric point.

A potentially important method for the desalination of water is membrane reverse osmosis. In studies of salt rejection, cation-exchange and anion-exchange membranes have been shown to have widely different, but sometimes complementary, selectivities for the rejection of different salts.[1–4] Thus a copolymer containing anionic and cationic blocks possibly could exhibit a more uniform rejection of all salts. In addition, the polymer compatibility present in a block copolymer could lead to the formation of a membrane carrying a random distribution of charged domains throughout the microstructure; however, a polymer containing this block structure of an acid sequence followed by a base sequence has not been reported. A copolymer having these uniform block lengths is reported.

Block copolymers of 2-vinylpyridine and various methacrylic acid esters or acrylic acid esters were synthesized by "living" anionic polymerization at low temperature (−78°). Base and acid hydrolysis of the ester sequences produced the block copolymers poly(2-vinylpyridine-*b*-methacrylic acid) and poly(2-vinylpyridine-*b*-acrylic acid). (In this paper, the -*b*- designation is used in reference to block copolymers exclusively.)

Results and Discussion

Preparation of Block Copolymers. For poly(2-vinylpyridine-*b*-methyl methacrylate) as well as poly(2-vinylpyridine-*b*-trimethylsilyl methacrylate), the block ratio con-

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(1) K. A. Kraus, H. O. Phillips, A. E. Marcinkowsky, J. S. Johnson, Jr., and A. J. Shor, *Desalination*, 1, 225 (1966).

(2) K. A. Kraus, A. J. Shor, and J. S. Johnson, Jr., *ibid.*, 2, 243 (1967).

(3) J. S. Johnson, Jr., K. A. Kraus, S. M. Fleming, H. D. Cochran, Jr., and J. J. Perona, *ibid.*, 5, 359 (1968).

(4) S. B. Sachs, W. H. Baldwin and J. S. Johnson, Jr., *ibid.*, 6, 215 (1969).