

## Topochemical Diacetylene Polymerization in Layered Metal Phosphate Salts

GUANG CAO AND THOMAS E. MALLOUK\*

*Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712*

Received February 27, 1991

UV- and X-ray induced polymerization of diacetylene groups in layered salts of 3,5-octadiyne bisphosphate (ODBP) with di- and trivalent metals (Zn, Mg, Mn, Ca, Cd, La, Y, and Sm) was studied. Diffuse reflectance UV-visible spectra were used to monitor the course of the polymerization reactions. From these spectra, it was found that the highest degree of polymerization was obtained with the Zn, Mg, and Mn salts; short-chain oligomers were formed with La, Y, and Sm, while the Ca and Cd salts had the lowest reactivity. These trends can be rationalized in terms of structural models for the juxtaposition of diacetylene groups in the monomeric salts and on the basis of the similarity of the spacing of phosphate coordination sites in the basal plane (4.8 Å for Zn, Mg, and Mn, and 5.6 Å for La, Y, and Sm) and the polydiacetylene repeat distance (4.93 Å). The nucleation and growth of the polymeric phase within these layered solids followed inverse exponential kinetics and could be fitted to the Avrami equation (M. Avrami, *J. Chem. Phys.* 7, 1103 (1939)). © 1991 Academic Press, Inc.

### Introduction

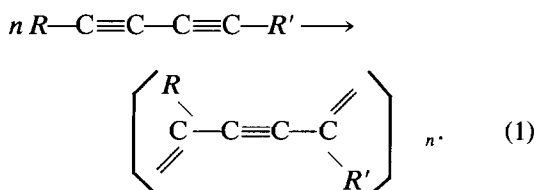
Metal-organic solids with alternating inorganic and organic layers are interesting materials because they have flexible yet stable structures. Well-studied examples of these include the phosphonate and phosphate salts of di-, tri-, and tetravalent metals, which comprise alternating layers of approximately planar metal-oxygen-phosphorus nets and organic groups (1). The ionically bonded metal-oxygen network adopts, for a given metal ion, the same structure for a wide range of organic groups and therefore directs the packing of these groups in a predictable manner. For example, mixed phosphate/phosphonate compounds in which bulky organic groups pillar the layers have been prepared (2). These salts con-

tain void spaces of tunable size and shape, and show interesting molecular recognition properties when intercalated or ion-exchanged with guest species (3). A second, less widely exploited property of layered metal-organic compounds is the availability of different structure types which may be synthesized with a given organic group by using different metal ions and/or reaction conditions. This property gives one the opportunity to control the polymerization of an organic monomer by systematically altering its juxtaposition with other monomers within the layered metal phosphate or phosphonate host structure. In this paper we report polymerization reactions of diacetylenes incorporated into layered metal phosphate salts. The diacetylene polymerization reaction was chosen for this study for two reasons: first, we wish to explore the possibility of synthesizing metal diacety-

\* To whom correspondence should be addressed.

lenic phosphonate films, which can be prepared by sequential absorption procedures developed in our laboratory (4). In principle, this approach could yield new ultrathin negative resists for deep-UV, X-ray, or electron beam microlithography, of which there have been a limited number of attempts (5) using diacetylene-containing Langmuir-Blodgett films. Studies of bulk phases, compared with films of molecular dimensions, are obviously much easier to carry out and can provide information necessary for assessing such possibilities. Second, from the solid state chemistry point of view, diacetylene polymerization itself is interesting because it represents a unique class of solid state reactions whose reactivity has been shown to be governed by the so-called topochemical principle (6). The resulting polydiacetylenes have shown significant potential for use in ultrafast signal processing because of their unusual nonlinear optical properties (7). The incorporation of a diacetylene functionality into inorganic matrices, besides being a challenge itself (since only one successful case has been reported (8)) may offer an opportunity to create lattices of aligned monomers to which the principle of topochemical reactivity may apply.

The mechanism of the solid state polymerization of diacetylenes has been well studied and is rationalized (6*b*, *d*) to proceed as a radical stepwise 1,4 addition to the conjugated triple bonds according to Eq. (1):



This reaction gives rise to polymers with a fully conjugated backbone (which is responsible for the large value of the nonresonant third-order nonlinear optical susceptibility,  $\chi^{(3)}$ ) (7). The polymerization can be brought about by UV irradiation, by annealing at

elevated temperature, or under the action of high-energy radiation.

It has been shown quantitatively (9) that as the polymerization undergoes a stepwise 1,4 addition and the length of conjugation increases, the electronic spectra display absorptions of intermediates at increasing wavelengths which can be accurately predicted based on theoretical modeling of the intermediate species. In the solid state, environmental factors can impose compressive or tensile strains on the polymer backbone which may cause shifts in the absorption edge. It should also be noted that in the solid state, electronic transitions will be broadened by crystal dispersion, and furthermore they may be offset by "solvent interactions" with polarizable side groups. The magnitude of these effects can be on the order of 15% of the transition energy (10), and therefore it is not possible to determine polymer chain length from solid state electronic spectra alone. Within a homologous series of compounds, however, it is valid to use the correlation between oligomer chain length and electronic absorption onset (9) to compare relative polymer chain lengths. This relationship was therefore used in this study to correlate the approximate degree of polymerization of layered salts of 3,5-octadiyne bisphosphate with the structures of its precursor monomeric salts.

The arrangement of diacetylene rods in a crystal lattice determines the reactivity for polymerization. A set of rules collectively called "the topochemical principle" has been derived based on crystallographic evidence (11, 6*d*). As depicted in Fig. 1, topochemical polymerization occurs only when (a) the difference in the translational period of the monomer  $d_1$  and the polymer  $d_2$  approaches zero (in reactive diacetylenes,  $d_1$  is in the range of 4.7 to 5.2 Å, and  $d_2$  is almost invariably around 4.93 Å); (b)  $s_1$  is smaller than 4.0 Å, with a lower limit of 3.4 Å, which represents the van der Waals contact distance of the two rods; (c) the

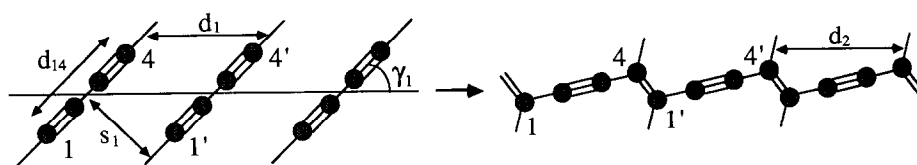


FIG. 1. Illustration of the topochemical principle for diacetylene polymerization. See text for explanation of symbols.

angle between the diacetylene rod and the translational vector,  $\gamma_1$ , is close to  $45^\circ$  ( $d_1$ ,  $s_1$ , and  $\gamma_1$  are related by  $s_1 = d_1 \sin \gamma_1$ ). All three geometrical requirements of diacetylene crystal packing must be met in order to secure a close contact between the C4 atom of one diacetylene rod and the C1' atom of the neighboring rod, in the reactive monomer. This contact distance is given by  $(d_1^2 + d_{14}^2 - 2d_1d_{14} \cos \gamma_1)^{1/2}$ , where  $d_{14}$  is the distance between the C4 and C1 atoms within a diacetylene rod.

There has to date been only one report of diacetylene incorporation into a layered inorganic matrix which leads to the topochemical formation of high molecular weight polymers: the photopolymerization of aminodiacetylene cations,  $RNH_3^+$ , in layer perovskite halide salts ( $RNH_3$ )<sub>2</sub>CdCl<sub>4</sub> (8). In ( $RNH_3$ )<sub>2</sub>M<sup>II</sup>X<sub>4</sub> and ( $H_3NR'$ )<sub>2</sub>M<sup>II</sup>X<sub>4</sub> ( $M = Cr, Mn, Fe, Cu, Cd; X = Cl, Br$ ) the metal and halide ions form infinite layers of corner-sharing octahedra separated by the organic cations, which are hydrogen bonded to the axial halide ions (12). This weak, non-direction-specific hydrogen bonding appears to be a crucial element in the design of polymerizable diacetylene salts, since it allows the diacetylene rods to come into close contact with one another and therefore leads to highly efficient solid state polymerization.

## Experimental

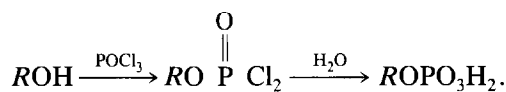
### Materials and Methods

Chemicals and experimental methods used to prepare and characterize the com-

pounds discussed in this paper were the same as those previously described (1j-l), except that UV-visible diffuse reflectance spectra were obtained with a Varian DMS 300 spectrophotometer equipped with a diffuse reflectance attachment, and the spectra were recorded against a BaSO<sub>4</sub> reference.

### Compound Synthesis

*Synthesis of sodium monobasic 3,5-octadiyne bisphosphate, NaH<sub>3</sub>(O<sub>3</sub>POCH<sub>2</sub>CH<sub>2</sub>C<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>OPO<sub>3</sub>) [NaH<sub>3</sub>(ODBP)].* Because the high temperature (150°C) required in the preparation of phosphonic acids via the Michaelis-Arbuzov reaction can cause acetylene or diacetylene compounds to polymerize or decompose, monoesters of phosphate ROPO<sub>3</sub>H<sub>2</sub> (structurally similar to phosphonic acids RPO<sub>3</sub>H<sub>2</sub>) were prepared, under milder conditions, according to the following scheme:



Synthesis of 3,5-octadiyn-1,8-diol was done by the Glaser coupling reaction (13) of 3-butyne-1-ol. To a mixture of 22 g freshly prepared CuCl (0.22 mole), 36 g of NH<sub>4</sub>Cl (0.67 mole), 15 ml concentrated aqueous ammonium hydroxide solution, and 200 ml H<sub>2</sub>O was added 12.5 (0.178 mole) of 3-butyne-1-ol (Aldrich). At room temperature, O<sub>2</sub> was passed through the mixture while it was stirred. A slightly positive pressure (5 Torr) of O<sub>2</sub> was maintained. As the reaction proceeded, the mixture became warm due to the heat released by the reaction. Twenty-

four hours later the uptake of  $O_2$  had ceased and the color of the mixture had changed from the initial yellow to blue-green. After the mixture was neutralized with HCl, it was extracted with ether in a continuous extractor for 5 hr. Evaporation of ether and removal of the unreacted 3-butyn-1-ol afforded the diol as a crystalline solid. The extraction was done with protection from light since the product is light sensitive, turning red gradually in the light. The product weighed 9.4 g. (75% yield).

The 1,3-octadiyn-1,8-diol (9.4 g, 0.068 mole) prepared in the previous step was dissolved in 20 ml dry ether and added dropwise with stirring to 52 of  $POCl_3$  (0.34 mole) which had been cooled below  $5^\circ C$  with ice. (This addition and the following procedures were done with protection from light.) Following the addition, the solution was allowed to warm to room temperature and stirring was continued for 30 min. Removal of ether and excess  $POCl_3$  *in vacuo* at room temperature was followed by slow and careful addition of 10 ml water, while the remaining liquid was cooled in ice water. (From this point on, protection from light was not crucial.) To the resulting brownish aqueous solution was added 100 ml acetonitrile, and the white sodium salt of ODBP was precipitated from the solution by slow addition of 10 M NaOH solution until the pH reached 1.0. The solid was washed with acetonitrile and dried *in vacuo*. Elemental analyses (Calcd.: C, 30.02; H, 3.46. Found: C, 29.91; H, 3.51.) and titration with NaOH in aqueous solution (two inflection points at pH 3.9 and 9.7, corresponding to a one-third equivalent and an additional two-thirds equivalent base added, respectively) were in agreement with the composition  $NaH_3(O_3POCH_2CH_2C_4CH_2CH_2OPO_3)$ . The salt isolated weighed 15.6g, and the yield was thus 72%. A  $^1H$  NMR spectrum of  $NaH_3(ODBP)$  in  $D_2O$  with 1,4-dioxane as an internal reference showed a triplet of 2H at 2.63 ppm ( $\delta$ ) and a quartet of 2H at 3.98 ppm

(the quartet rather than a triplet splitting pattern is due to the  $^{31}P$  atom of the phosphate group).  $NaH_3(ODBP)$  was slightly light sensitive, turning red over weeks. However, in solution at 0.08 M concentration it was stable for months without noticeable change.

*Synthesis of ODBP salts of di- and trivalent metals.* Since good crystallinity is desired with these materials, and yet it cannot be achieved through the usual Ostwald ripening process at elevated temperatures (*I*) because polymerization of diacetylene units in the amorphous state may take place, a simple yet effective method was devised. A clear 0.04 M solution of a salt of the appropriate di- or trivalent metal ion (Zn, Mn, Mg, Ca, or Y, La, Sm) and an equivalent amount of  $NaH_3(ODBP)$  were combined in a 100-ml beaker, which was then placed inside a 250-ml beaker containing 20 ml of 5 M aqueous ammonia solution. (In case a precipitate formed upon mixing solutions of the metal salt and phosphate, HCl was added to dissolve the precipitate.) The larger beaker was then tightly covered with parafilm and the clear solution was stirred magnetically. Precipitation occurred over various lengths of time as the volatile ammonia diffused into the inner solution, gradually increasing its pH. The compounds prepared by this method had not only far better crystallinity than those prepared with slow addition of NaOH solution, they also had constant composition, in contrast to those with poor crystallinity. The precipitates were filtered and washed in the dark, then dried in an aluminum desiccator over  $P_2O_5$ .

#### *UV and X-Ray Induced Polymerization of ODBP Salts*

*UV induced polymerization.* Powders of ODBP salts were spread onto a 1- × 2-in. quartz slide and fixed with tape. Samples were then irradiated with IR-filtered UV-visible light from a 100-W xenon arc lamp for various lengths of time, during which the

color of the samples changed from white to yellow, orange, or red. The color changes were monitored quantitatively with diffuse reflectance spectroscopy.

*X-ray induced polymerization.* Powders of ODBP salts were placed in a cavity sample holder and were pressed flat. With a Philips X-ray diffractometer at a fixed  $2\theta$  angle of  $45^\circ$  the sample was irradiated with  $\text{CuK}\alpha$  radiation for various lengths of time. Diffuse reflectance spectra were taken by first carefully covering the sample with a quartz slide without disrupting the surface (X rays do not penetrate deeply into the sample) and then pressing the quartz slide of the sample against the measuring window.

## Results and Discussion

### *Structural Studies of ODBP Salts of Di- and Trivalent Metals*

Our premise that diacetylenic bis-phosphate  $\text{H}_2\text{O}_3\text{POROPO}_3\text{H}_2$ , being structurally similar to alkyl bis-phosphonic acid  $\text{H}_2\text{O}_3\text{PRPO}_3\text{H}_2$ , may form phosphates of di- or trivalent metal ions, adopting structures corresponding to those of metal phosphonates, must at least not encounter any contradicting evidence. Elemental analysis and TGA results (Table I) revealed that ODBP salts had the compositions of  $M^{\text{II}}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  ( $M = \text{Zn, Mg, Mn, Ca, Cd}$ ) and  $M^{\text{III}}\text{H}(\text{ODBP}) \cdot 0.5\text{H}_2\text{O}$  ( $M = \text{Y, La, Sm}$ ). These formulations are parallel with those of the simple phosphonates,  $M^{\text{II}}(\text{O}_3\text{PR}) \cdot \text{H}_2\text{O}$  and  $M^{\text{III}}\text{H}(\text{O}_3\text{PR})_2$ , except for the additional 0.5 mole of water in the trivalent metal salts. The water molecules are most likely to be intercalative, not involved in coordination to metal ions, because they are easily lost when the compounds are heated just over  $80^\circ\text{C}$ . By comparison,  $M^{\text{II}}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  ( $M = \text{Mg, Mn, Ca, Cd}$ ) salts lose water above  $150^\circ\text{C}$ . Infrared spectra show that these water molecules are involved in extensive hydrogen bonding, as manifested by the broad and

strong absorption centered at  $3450\text{ cm}^{-1}$ . Therefore, their location in the crystalline solids must be near the phosphate group of ODBP, and they are hydrogen bonded to the oxygen atom linking P and C atoms.

Although the crystallinity of these compounds was greatly improved with the ammonia diffusion method, their XRD powder patterns were generally not good enough for unambiguous indexing. Figure 2 compares a set of typical XRD patterns for the lanthanum salt of ODBP precipitated by slow addition of NaOH to the precursor solution and by the ammonia diffusion method. Changes in the powder pattern induced by UV polymerization of this compound (Fig. 2c) are slight. The layered structure of these compounds was evident from the prominent progression of diffraction maxima (typically 2–4 well-resolved reflections) corresponding to layer spacings. Table II lists the layer spacings of these ODBP salts.

Although the above findings are not in contradiction with the premise mentioned earlier, ultimate proof of the premise may be difficult. However, estimations can be made for the structural arrangement of diacetylene units in  $M^{\text{II}}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  based on the above layer spacings of ODBP salts, the molecular dimensions of ODBP, and the premise of structural similarity to the analogous metal alkylbisphosphonate salts. Figure 3 shows one possible structural arrangement of ODBP molecules in  $M^{\text{II}}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  ( $M = \text{Mg, Mn, Zn}$ ) with typical bond lengths indicated (14). The translational period of  $4.8\text{ \AA}$  is the  $c$  axis of an orthorhombic  $M^{\text{II}}(\text{O}_3\text{PR}) \cdot \text{H}_2\text{O}$  structure in which alkyl groups lie in the mirror plane. The angle  $\gamma_1$  is estimated to be  $40 \pm 10^\circ$ , which is within the range to be reactive.

Similar estimations for ODPB salts of Ca and Cd are difficult to make, because in the  $\text{Ca}(\text{O}_3\text{PCH}_3) \cdot \text{H}_2\text{O}$  structure (with which  $\text{Cd}(\text{O}_3\text{PCH}_3) \cdot \text{H}_2\text{O}$  is isostructural) there is a lack of alignment among the alkyl groups. They are disposed "staggered" to one an-

TABLE I  
ANALYTICAL DATA FOR ODBP SALTS

Compound	Elemental analysis				Thermogravimetric analysis		
	Calculated (%)		Found (%)		Weight loss (%)		Temperature range
	C	H	C	H	Calculated	Found	°C
Zn(ODBP) <sub>1/2</sub> · H <sub>2</sub> O	20.85	2.62	21.02	2.64	7.82	7.75	70–100
Cd(ODBP) <sub>1/2</sub> · H <sub>2</sub> O	17.81	2.18	17.85	2.22	6.49	6.60 <sup>a</sup>	150–270
Ca(ODBP) <sub>1/2</sub> · H <sub>2</sub> O	23.42	2.95	22.30	3.36	8.78	8.80	170–240
Mg(ODBP) <sub>1/2</sub> · H <sub>2</sub> O	25.37	3.19			9.51	9.38	160–200
Mn(ODBP) <sub>1/2</sub> · H <sub>2</sub> O	21.84	2.75			8.19	8.13	155–210
LaH(ODBP) · 0.5H <sub>2</sub> O	21.69	2.28	21.63	2.30	2.03		
SmH(ODBP) · 0.5H <sub>2</sub> O	21.14	2.21	20.42	2.13	1.98	1.90	64–80
YH(ODBP) · 0.5H <sub>2</sub> O	24.45	2.56	24.28	2.61	2.29	2.27	50–82

<sup>a</sup> Estimated, since the ODBP moiety begins to decompose at 270°C.

other with irregular distances between them along the *a*-axis (11). But this structural information leads one to predict less tendency for ODBP salts of calcium and cadmium to polymerize than those of the other divalent

metals. As for the ODBP salts of trivalent metals, a recent single crystal X-ray structure of LaH(O<sub>3</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> by Wang *et al.* (1*n*) shows that the phosphonate groups are aligned along the *c*-axis direction. In this

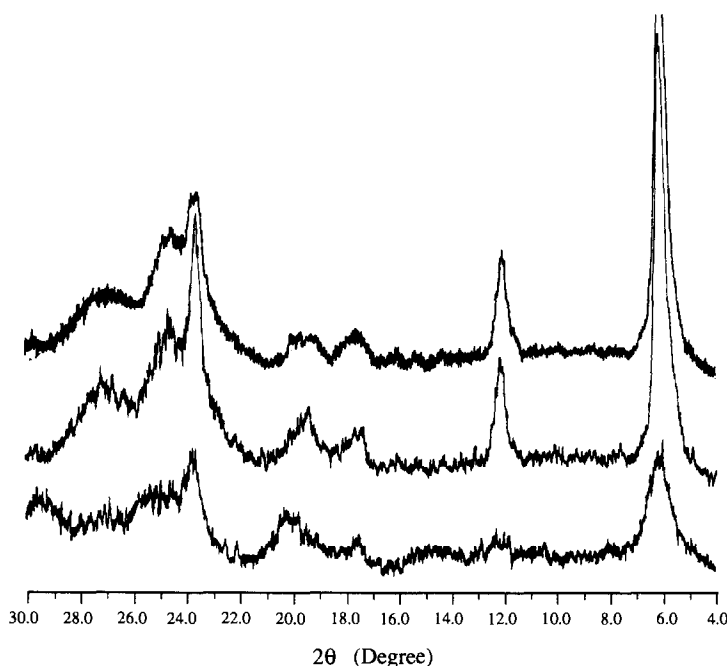


FIG. 2. Powder XRD patterns for LaH(ODBP) · 0.5H<sub>2</sub>O prepared by slow addition of NaOH to the precursor solution (lower) and by the ammonia diffusion method (middle). The top trace was taken after UV polymerization of the compound prepared by the ammonia diffusion method.

TABLE II  
LAYER SPACINGS OF ODBP SALTS

$M^{II}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$	$d_{\text{layer}} (\text{\AA})$	$M^{III}\text{H}(\text{ODBP}) \cdot 0.5\text{H}_2\text{O}$	$d_{\text{layer}} (\text{\AA})$
Mg	13.6(1)	Y	14.3(1)
Mn	13.7(1)	La	14.5(1)
Zn	13.6(1)	Sm	14.7(1)
Ca	13.8(1)		
Cd	13.6(1)		

structure the P-C bond makes an angle of about  $77^\circ$  to the  $c$ -axis and is approximately perpendicular to the  $a$ -axis; the  $b$ -axis is the stacking axis. We can therefore infer that in the  $\text{LnH}(\text{ODBP}) \cdot 0.5\text{H}_2\text{O}$  salts, the diacetylene groups are juxtaposed along the  $c$ -axis direction with a spacing of approximately 5.6  $\text{\AA}$ , as in  $\text{LaH}(\text{O}_3\text{PC}_6\text{H}_5)_2$  (I*n*) and  $\text{LnH}(\text{O}_3\text{PC}_n\text{H}_{2n+1})_2$  (I*l*). If the angle between the P-O bond and the layer plane in  $\text{LnH}(\text{ODBP}) \cdot 0.5\text{H}_2\text{O}$  is the same as the P-C angle (ca.  $77^\circ$ ) in  $\text{LaH}(\text{O}_3\text{PC}_6\text{H}_5)_2$ , then the angle  $\gamma_1$  (see Fig. 1) is estimated to be  $35^\circ$ , and the  $s_1$  value (calculated as  $s_1 = d_1 \sin \gamma_1$ ) is about 3.2  $\text{\AA}$ , close to the ideal 3.4- $\text{\AA}$  value for topochemical reactivity. Therefore, we expect the diacetylene rods to adopt a reactive arrangement in  $\text{LnH}(\text{ODBP}) \cdot 0.5\text{H}_2\text{O}$ . However, because the  $c$ -axis spacing is significantly larger than the ideal 4.93- $\text{\AA}$  repeat distance in polydia-

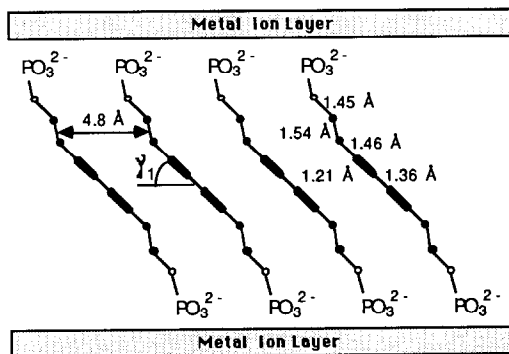


FIG. 3. Possible structural arrangement of ODBP molecules in  $M^{II}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  ( $M = \text{Mg}, \text{Mn}, \text{and Zn}$ ).

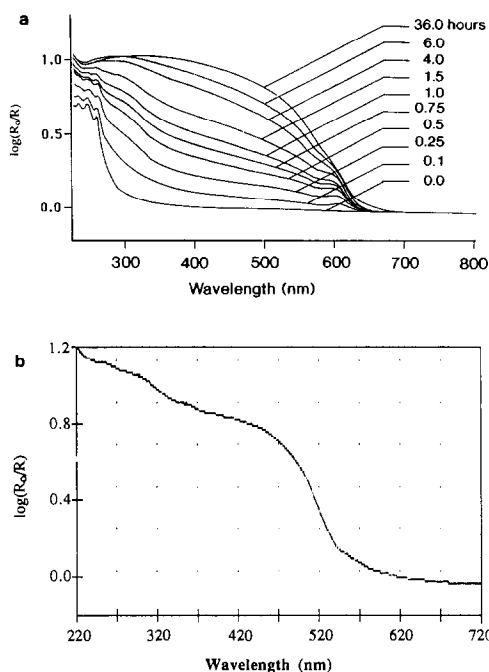


FIG. 4. Diffuse reflectance spectra of (a)  $\text{Zn}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  irradiated with a Xe lamp for the indicated length of time and (b)  $\text{Mg}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  irradiated for 18 hr.

cetylenes, we do not expect long chains to grow within this structure.

#### UV- and X-Ray Polymerization of ODBP Salts of Di- and Trivalent Metals

$M^{II}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  ( $M = \text{Mg}, \text{Mn}, \text{Zn}$ ). Compounds in this group are reactive upon UV irradiation, as manifested by their color change from white to orange or red. These changes are recorded in diffuse reflectance spectra (Fig. 4) which show that with increasing time of irradiation the absorption peaks of monomeric diacetylene (15) in the UV region (228, 240, 254 nm) disappear while a broad, featureless absorption extending to the visible region grows. The extension of this absorption threshold is the longest for  $\text{Zn}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$ , to about 640 nm, giving the sample its red color, and to only 540 nm for both manganese and magne-

sium ODBP salts. As mentioned in the Introduction, the conjugation length of a polydiacetylene is correlated to its electronic absorption features (9). By comparing the observed spectroscopic behavior of ODBP salts to the calculated absorption positions of a polymerizing diacetylene system, the following conclusions may be drawn: (a) since the diffuse reflectance spectra are featureless, the polydiacetylene obtained must be less than well ordered, may have a distribution of chain lengths, and has possibly some irregular cross-linking; (b) among the Mg, Mn, and Zn salts,  $\text{Zn}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  appears to have the highest degree of polymerization, since its absorption threshold is at the longest wavelength by ca. 100 nm. For  $\text{Zn}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$ , however, because its featureless spectrum has its absorption threshold beyond the theoretical limits for the absorption peak position of polydiacetylene with an infinite chain length (590 nm), the conjugation length can be estimated only to be longer than 9 or 10 diacetylene units. In well-studied high molecular weight polydiacetylenes it is common to see the maximum absorption wavelength exceed 590 nm, and this has been attributed to excitonic absorption and side-group "solvent effects" (10).

X rays noticeably cause polymerization reactions to occur in ODBP salts of zinc, magnesium, and the three trivalent metals. The resulting polymers have very similar diffuse reflectance spectra. It was observed that with X-ray irradiation, the layer spacings of these compounds change very slightly. For  $\text{Zn}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$ , for example, the layer spacing changes from 13.55 to 13.71 Å.

$M^{\text{II}}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  ( $M = \text{Ca}, \text{Cd}$ ). These two compounds change very slightly with UV irradiation. After prolonged exposure (3 days) to UV light, they show only a slight yellow coloration. Their diffuse reflectance spectra (Fig. 5) show that the absorptions caused by UV irradiation extend only to 540 nm, and the shape of the absorption curve

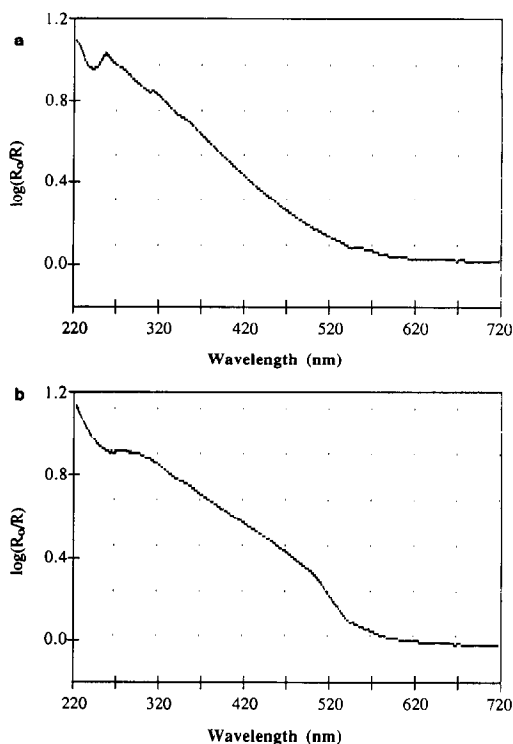


Fig. 5. Diffuse reflectance spectra of  $M(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$  after 3 days of exposure to UV light. (a)  $M = \text{Ca}$ ; (b)  $M = \text{Cd}$ .

(high absorption in the short wavelength region) suggests that a large fraction of the absorption is most likely caused by dimeric, trimeric, and cross-linked diacetylenes.

$M^{\text{III}}\text{H}(\text{ODBP}) \cdot 0.5\text{H}_2\text{O}$  ( $M = \text{Y}, \text{La}, \text{Sm}$ ). Like their divalent counterparts, these compounds polymerize when irradiated with either UV light or X rays, affording oligomeric products. Shown in Fig. 6 are the diffuse reflectance spectra of  $\text{SmH}(\text{ODBP}) \cdot 0.5\text{H}_2\text{O}$  irradiated with UV and X rays for the indicated lengths of time. As predicted from the structure of  $\text{LaH}(\text{O}_3\text{PC}_6\text{H}_5)_2$  ((1n), the diacetylene groups are reactive, but apparently only oligomers can be formed topologically with compounds in this series.

It was noted that the yttrium compound converts to its products when irradiated with UV light or X rays more slowly than



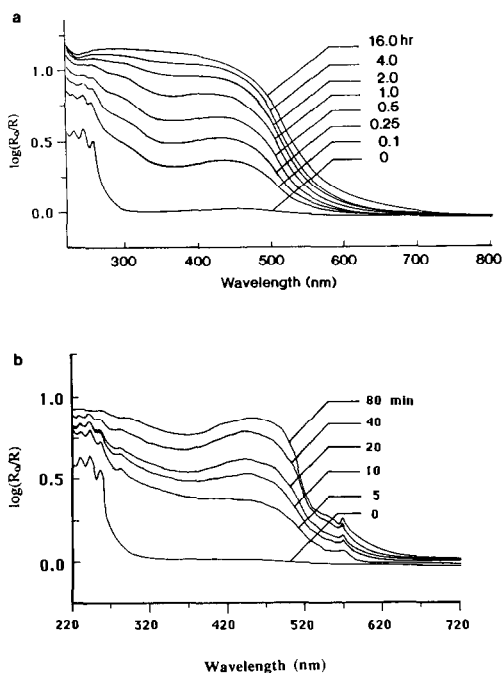


FIG. 6. Diffuse reflectance spectra of SmH(ODBP) · 0.5H<sub>2</sub>O irradiated with (a) UV and (b) X rays for the indicated length of time.

the samarium and lanthanum compounds. A study of time-dependent conversion was carried out. As shown in Fig. 7, the conversion from monomer to polymer is qualitatively represented by  $\log(R_0/R)$ , i.e., the logarithm of the reciprocal of reflectivity. The  $\log(R_0/R)$  values are taken at an arbitrarily chosen wavelength, 420 nm (the following arguments do not change if a different wavelength is chosen within the absorption range). The time-conversion plot reveals that while the samarium compound polymerizes faster than the yttrium compound by a ratio of 3 to 2 when irradiated with UV light, the ratio is about 3 to 1 when irradiation is with X rays. Hence, it may be argued that while the difference in the conversion rate with UV irradiation between samarium and yttrium compounds can be accounted for by a slight difference in the arrangement of diacetylene moieties in the crystal lattice (since Y has a smaller

ionic radius than Sm and therefore shorter site-to-site distances within the supposed planar metal–oxygen–phosphorus 2D network), the extra difference in the conversion rate (ca. 2:1) with X-ray irradiation may be attributable to the difference in the X-ray cross section between Sm and Y. The total cross sections per atom for Sm and Y with  $\text{CuK}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation are  $1.13 \times 10^{-19} \text{ cm}^2$  and  $1.44 \times 10^{-20} \text{ cm}^2$ , respectively (16). Therefore the X-ray induced polymerization processes most likely involve excitation (energy or electron) transfer from the heavy metal to the diacetylene, which activates the latter for polymerization. This conclusion is also supported by the fact that metal-free H<sub>4</sub>(ODBP) polymerizes extremely slowly, relative to its Sm and Y salts, when exposed to X rays. This method of sensitization by atoms with high

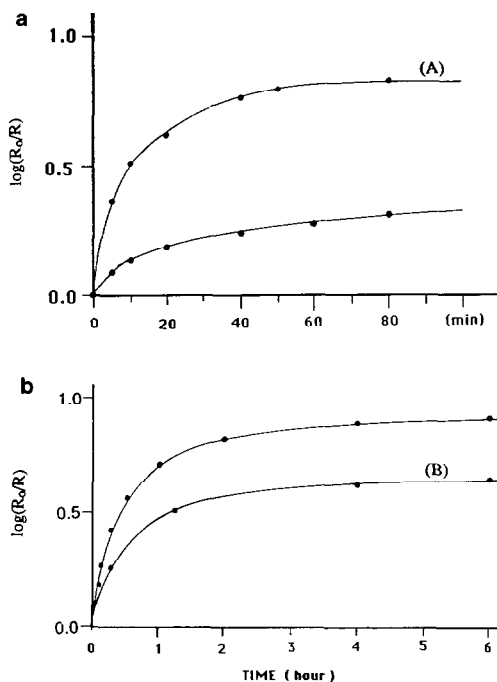


FIG. 7. Plot of  $\log(R_0/R)$  at 420 nm vs irradiation time with (a) X rays and (b) UV, showing the large difference in conversion rate between (A) SmH(ODBP) · 0.5H<sub>2</sub>O and (B) YH(ODBP) · 0.5H<sub>2</sub>O.

X-ray cross sections has previously been explored for applications in X-ray micro-lithography (17).

### *Structural Control of Polymerization Reactivity in ODBP Salts*

While the fact that ODBP salts of di- and trivalent metals (except Ca and Cd) polymerize when irradiated suggests that the diacetylene units within the crystal lattice of these compounds prior to polymerization are in the required reactive arrangement according to the topochemical principle, our failure to obtain polydiacetylenes with high conjugation length (or high molecular weight) may be attributed to the covalent bonding of diacetylene units to the inorganic matrices. Because of this covalent fixation of diacetylene rods, as the polydiacetylene chain propagates once polymerization is initiated, strain imposed on the propagating chain by the inorganic matrices will inevitably develop. Such strain may be brought about from two structural changes accompanying polymerization: (1) the reorientation of the terminal C–C single bond ( $C_4$ – $C_5$ ) of the diacetylene rod (see Fig. 1); and (2) the change of translational period to about 4.93 Å in the polydiacetylene, no matter what the initial value in the monomeric state may be (the translational period in monomeric  $Zn(ODBP)_{1/2} \cdot H_2O$  is believed to be about the same as the *c* axis spacing of  $Zn(O_3PR) \cdot H_2O$ , 4.8 Å). Eventually such strains will present an energy barrier too high for the propagating polydiacetylene chains to overcome, leading to chain termination.

The reactivity of ODBP salts of divalent metals can be understood with the premise that these salts adopt the *M*–*O*–*P* network of the corresponding metal phosphonates as discussed above. The ODBP salts of Zn, Mg, and Mn show relatively high reactivity because the diacetylene units in these compounds are likely to be aligned and arranged in the reactive fashion according to the topo-

chemical principle, as depicted in Fig. 3. On the other hand the low reactivity of the calcium and cadmium ODBP salts correlates well with the lack of alignment of organic groups in the corresponding phosphonate structures. The lanthanum, samarium, and yttrium salts are predicted to be reactive, but to give predominantly short chain length oligomers because of the poor match between the *c*-axis dimension (ca. 5.6 Å) and the polydiacetylene repeat distance (4.93 Å).

The longer polymer chain length achieved by polymerizing  $Zn(ODBP)_{1/2} \cdot H_2O$ , compared with the presumably isostructural ODBP salts of magnesium and manganese, is perhaps due to the fact that the zinc ion, being almost certainly octahedrally coordinated in its monomeric ODBP salt, has a far greater tendency to be 4- or 5-coordinated than the other two metal ions, whose coordination number is almost exclusively 6 under usual circumstances. This coordination flexibility of the zinc ion can, in principle, render greater tolerance for distortions caused by the strains developed during the propagation process of diacetylene polymerization, thereby delaying termination of a polydiacetylene chain.

### *Polymerization Kinetics*

It has been found that the polymerization of molecular crystals of diacetylenes exhibit either inverse exponential or sigmoidal kinetic curves (18). A model of polymerization kinetics controlled by lattice strain (19) has been successful in accounting for the polymerization kinetics of some well-studied diacetylene systems and the observed kinetic behavior of diacetylenes in general. However, this model involves parameters related to the distal separations of diacetylene units before and after polymerization, the elastic moduli of monomers and polymers in the polymerization direction, and the dependency of activation energies in the initiation and propagation steps on the poly-

mer fraction. Considering the complexity of the model and the poorly defined polymerization systems of the ODBP salts, it is obviously inappropriate to apply this model to the present system.

However, the Avrami equation (20), which was introduced to describe reactions

$$\alpha = V_n/V = 1 - \exp(-kt^n) \quad (2)$$

in which the solid state transformation occurs by nucleation and growth of regions of a new phase, as pointed out by Bloor(21), is capable of describing the observed kinetics of diacetylene polymerization in general, although it suffers from difficulties in microscopic interpretations. The following is an attempt to describe the polymerization kinetics observed in ODBP salts with the Avrami equation.

In Eq. (2),  $V_n$  is the volume of a new phase in the solid state transformation,  $\alpha$  is the volume fraction of the new phase, and  $n$  is a parameter which depends on the anisotropy of the solid. For the constant nucleation rate of the new phase,  $n$  is defined by

$$n = d + 1, \quad (3)$$

where  $d$  is the dimensionality. Noninteger values of  $n$ , which may be smaller or larger than the value given by (3), occur when the nucleation rate is not constant. When  $n = 1$ , the Avrami equation becomes a simple first-order kinetic equation, and the corresponding time-conversion curve is of inverse exponential shape.

Semiquantitative time-dependent conversion curves of the ODBP compounds (semiquantitative because the natural logarithm of the ratio of reflectivity in the diffuse reflectance spectra at time  $t_1$ , when the polymerization reaction has reached maximum conversion, and at time  $t_2$ , when the polymerization reaction is still noticeably in progress, was taken as the polymer volume fraction in this kinetic analysis) all display inverse-exponential-like shapes similar to the curves shown in Fig. 7. If it is assumed

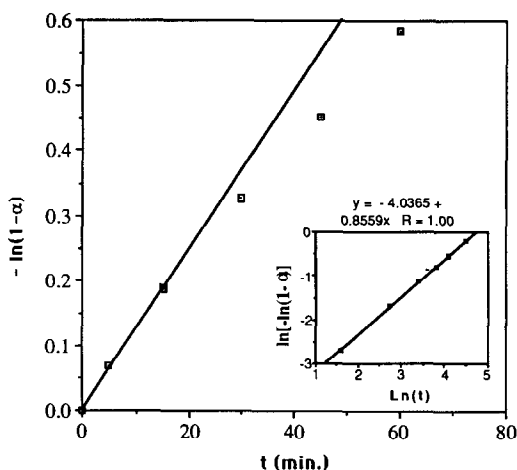


FIG. 8. Plot of  $-\ln(1-\alpha)$  vs time for UV induced polymerization of  $\text{Zn(ODBP)}_{1/2} \cdot \text{H}_2\text{O}$ . The slope of the linear curve in the inset is 0.856, the  $n$  value, and the intercept at  $\ln(t) = 0$  gives  $\ln(k) = -4.037$ ; therefore, the rate constant  $k = 0.0176/\text{min}$ . See text.

that the initiation step of the reaction is nucleation of a new polydiacetylene phase, which occurs at a constant rate, the observed kinetic curves should be fitted with the  $n = 1$  case of the Avrami equation. The plot of  $[-\ln(1-\alpha)]$  vs  $t$  should be a straight line. Figure 8 is a plot of  $[-\ln(1-\alpha)]$  vs time ( $t$ ) for the polymerization of  $\text{Zn(ODBP)}_{1/2} \cdot \text{H}_2\text{O}$  irradiated with UV light. The  $\alpha$  values are taken from the ratio of the  $\log(R_0/R)$  value in the diffuse reflectance spectra (Fig. 4a) at time ( $t$ ) to the  $\log(R_0/R)$  value at  $t = 36$  hr.

As can be seen from the plot, at low conversions (ca. 25% conversion, first 20 min) the experimental points fall on a straight line, indicating that the proposed kinetics may be followed; at higher conversions, the experimental points deviate from the straight line, showing signs of initiation rate dependence on polymer fraction. One possible cause for such dependence is that at higher conversion, a substantial amount of polymeric (or oligomeric) diacetylene has been produced, which acts as a quencher

for the excited monomeric diacetylenes, thereby lowering the efficiency of reaction initiation. This effect has been observed in UV-induced polymerization of molecular crystals of some diacetylenes (22).

The negative deviation from first-order kinetics in Fig. 8 suggests an  $n$  value smaller than 1 in the Avrami equation. The  $n$  value can be obtained simply by plotting  $\ln[-\ln(1-\alpha)]$  vs  $\ln(t)$ , and the resulting linear curve has a slope equal to  $n$  and an intercept at  $\ln(t) = 0$  equal to  $\ln(k)$ . The inset in Fig. 8 is such a plot for the UV polymerization of  $\text{Zn}(\text{ODBP})_{1/2} \cdot \text{H}_2\text{O}$ . Data for the polymerization of  $\text{SmH}(\text{ODBP}) \cdot 0.5\text{H}_2\text{O}$  irradiated with UV light and X rays were similarly treated, and the corresponding plots are shown in Fig. 9. The rate constants and  $n$  values obtained from the plots are given in the figure captions.

## Conclusions

Topochemical polymerization of several layered metal salts of ODBP can be induced by UV or X-ray irradiation. The degree of polymerization is dependent on the arrangement of diacetylene units within the monomeric solid and is highest in the case of the salts of divalent Mg, Mn, and Zn. Even in these favorable cases, however, we have not obtained polydiacetylenes with a high degree of polymerization and attribute this to covalent fixation of the diacetylene groups to the inorganic host lattice. A more flexible linkage between the diacetylene-bearing molecule and the inorganic host, which still juxtaposes the former in a polymerizable arrangement, should lead to higher degrees of polymerization. The synthesis of related solids with this property is currently in progress.

## Acknowledgments

This work was supported by grants from the National Science Foundation (PYI Award CHE-8657729) and by the Robert A. Welch Foundation. TEM also thanks the

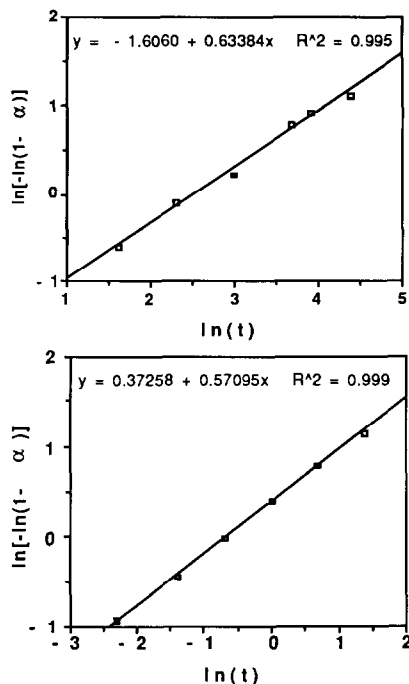


FIG. 9. Plots of  $\ln[-\ln(1-\alpha)]$  vs  $\ln(t)$  for polymerization of  $\text{SmH}(\text{ODBP}) \cdot 0.5\text{H}_2\text{O}$ . The rate constants are  $0.201 \text{ min}^{-1}$  and  $1.45 \text{ min}^{-1}$  and the  $n$  values are 0.634 and 0.571 for polymerizations induced by X rays and UV, respectively.

Camille and Henry Dreyfus Foundation for support in the form of a Teacher-Scholar Award.

## References

- (a) A. CLEARFIELD, in "Design of New Materials" (A. Clearfield and D. A. Cocke, Eds.), p. 121, Plenum, New York (1986); (b) G. ALBERTI, U. COSTANTINO, S. ALLULI, AND J. TOMASSINI, *J. Inorg. Nucl. Chem.* **40**, 1113 (1978); (c) G. ALBERTI, U. COSTANTINO, AND M. L. L. GIOVAGNOTTI, *J. Chromatogr.* **45**, 180 (1979); (d) M. B. DINES AND P. DIGIACOMO, *Inorg. Chem.* **92**, 20 (1981); (e) M. B. DINES AND P. C. GRIFFITH, *Inorg. Chem.* **22**, 567 (1983); (f) M. B. DINES, R. E. COOKSEY, AND P. C. GRIFFITH, *Inorg. Chem.* **22**, 1003 (1983); (g) M. B. DINES AND P. C. GRIFFITH, *Polyhedron* **2**, 607 (1983); (h) J. W. JOHNSON, A. J. JACOBSON, J. F. BRODY, AND J. T. LEWANDOWSKI, *Inorg. Chem.* **23**, 3844 (1984); (i) D. CUNNINGHAM, P. J. D. HENNELLY, AND T. DEENEY, *Inorg. Chim. Acta* **37**, 95 (1979); (j) G. CAO, H. LEE, V. M.

- LYNCH, AND T. E. MALLOUK, *Inorg. Chem.* **27**, 2781 (1988); (k) G. CAO, H. LEE, V. M. LYNCH, AND T. E. MALLOUK, *Solid State Ionics* **26**, 63 (1988); (l) G. CAO, V. M. LYNCH, J. S. SWINNEA, AND T. E. MALLOUK, *Inorg. Chem.*, in press; (m) P. PALVADEAU, M. QUEIGNEC, J. B. VENIEN B. BUJOLI, AND J. VILLIERAS, *Mater. Res. Bull.* **23**, 1561 (1988); (n) R.-C. WANG, Y. P. ZHANG, P. J. SQUATTRITO, R. R. FRAUSTO, AND A. CLEARFIELD, *Chem. Mater.*, in press.
2. (a) M. B. DINES, K. P. CALLAHAN, P. C. GRIFFITH, AND R. E. COOKSEY, in "Chemically Modified Surfaces in Catalysis and Electrocatalysis" (J. Miller, Ed.) ACS Symp. Ser. Vol. 192, p. 223, American Chemical Society, Washington, DC (1982); (b) S. CIEMG, G. Z. PENG, AND A. CLEARFIELD, *Ind. Eng. Chem. Prod. Res. Dev.* **23**, 219 (1984); (c) G. ALBERTI, U. COSTANTINO, J. KORNYEI, AND M. L. LUCIANI, *React. Polym.* **4**, 1 (1985); (d) C.-Y. YANG AND A. CLEARFIELD, *A. React. Polym.* **5**, 13 (1987).
3. (a) J. W. JOHNSON, A. J. JACOBSON, W. M. BUTLER, S. E. ROSENTHAL, J. F. BRODY, AND J. T. LEWANDOWSKI, *J. Am. Chem. Soc.* **111**, 381 (1989); (b) J. W. JOHNSON, J. F. BRODY, AND R. M. ALEXANDER, *Chem. Mater.*, in press; (c) J. L. COLON, C.-Y. YANG, A. CLEARFIELD, AND C. R. MARTIN, *J. Phys. Chem.* **92**, 5777 (1988).
4. (a) H. LEE, L. J. KEPLEY, H.-G. HONG, AND T. E. MALLOUK, *J. Am. Chem. Soc.* **110**, 618 (1988); (b) H. LEE, J.-G. HONG, S. AKHTER, AND T. E. MALLOUK, *J. Phys. Chem.* **92**, 2597 (1988); (c) S. AKHTER, H. LEE, H.-G. HONG, T. E. MALLOUK, AND J. M. WHITE, *J. Vac. Sci. Technol. A* **7**, 1608 (1989).
5. J. B. LANDO, in "Polydiacetylenes" (D. BLOOR AND R. CHANCE, Eds.), p. 363, Nijhoff, Dordrecht, The Netherlands (1985).
6. (a) M. D. COHEN AND M. J. SCHMIDT, *J. Chem. Soc.*, 1996 (1964); (b) G. WEGNER, *Z. Naturforsch. B* **24**, 824 (1969); (c) G. WEGNER, in "Molecular Metals", (W. E. Hatfield, Ed.), p. 225, Plenum, New York (1979); G. WEGNER, *Pure Appl. Chem.* **49**, 443 (1977).
7. (a) G. M. CARTER, Y. J. CHEN, M. F. RUBNER, D. J. SANDMAN, M. K. THAKUR, AND S. K. TRIPATHY, in "Nonlinear Optical Properties of Organic Molecules and Crystals" (D. S. Chemla and J. Zyss, eds.), Vol. 2, p. 85, Academic Press, Orlando, FL (1987); (b) G. M. CARTER, M. K. THAKUR, J. V. HRYNIEWICZ, Y. J. CHEN, AND S. E. MEYER, in "Crystallographically Ordered Polymers" (D. J. Sandman, Ed.), ACS Symp. Ser. Vol. 337, p. 168, American Chemical Society, Washington, DC (1987).
8. (a) R. C. LEDSHAM AND P. DAY, *J. Chem. Soc., Chem. Commun.*, 921 (1981); (b) P. DAY AND R. C. LEDSHAM *Mol. Cryst. Liq. Cryst.* **86**, 163 (1982).
9. (a) H. SIXL, in "Polydiacetylenes" (D. Bloor and R. Chance, Eds.), p. 41, Nijhoff, Dordrecht, The Netherlands (1985); (b) R. J. LEYRER AND G. WEGNER, *Ber. Bunsenges. Phys. Chem.* **83**, 470 (1979).
10. M. SCHOTT AND G. WEGNER, in "Nonlinear Optical Properties of Organic Molecules and Crystals" (D. S. Chemla and J. Zyss, Eds.), Vol. 2, p. 3, Academic Press, Orlando, FL (1987).
11. (a) R. J. BAUGHMAN, *J. Polym. Sci. Polym. Phys. Ed.* **11**, 603 (1973); (b) V. ENKELMANN, *Adv. Polym. Sci.* **63**, 91 (1984).
12. (a) K. KNORR, I. R. JAHN, AND G. HEGER, *Solid State Commun.* **15**, 231 (1974); (b) V. W. DEPMEIER, *Acta Crystallogr., Sect. B* **32**, 303 (1976); (c) C. BELLITINO AND P. DAY, *J. Chem. Soc., Dalton Trans.*, 1207 (1978).
13. L. BRANDSMA, "Preparative Acetylenic Chemistry," 2nd ed., p. 219, Elsevier, New York (1988).
14. A. KARPFFEN, in "Polydiacetylenes" (D. Bloor and R. Chance, Eds.), p. 115, Nijhoff, Dordrecht, The Netherlands (1985).
15. J. B. ARMITAGE AND M. C. WHITING, *J. Chem. Soc.*, 2005 (1952).
16. "International Tables for X-Ray Crystallography," Vol. IV, pp. 55-60, Kynoch Press, Birmingham, England (1974).
17. N. TAYLOR, *Solid State Technol.*, 73 (May 1980).
18. (a) K. C. YEE, *J. Org. Chem.* **44**, 2571 (1979); (b) D. BLOOR, D. J. ANDO, C. L. HUBBLE, AND R. L. WILLIAMS, *J. Polym. Sci., Polym. Phys. Ed.* **18**, 779 (1980); (c) G. N. PATEL, *Macromolecules* **14**, 1170 (1981).
19. (a) R. H. BAUGHMAN, *J. Chem. Phys.* **68**, 3110 (1978); (b) R. H. BAUGHMAN AND R. R. CHANCE, *J. Chem. Phys.* **73**, 4113 (1980).
20. (a) M. AVRAMI, *J. Chem. Phys.* **7**, 1103 (1939); (b) M. AVRAMI, *J. Chem. Phys.* **8**, 212 (1940); (c) M. AVRAMI, *J. Chem. Phys.* **9**, 177 (1941); (d) F. C. TOMPKINS, in "Treatise on Solid State Chemistry," Vol. 4, "Reactivity of Solids" (N. B. Hannay, Ed.), p. 193, Plenum Press, New York (1976).
21. D. BLOOR, in "Polydiacetylenes" (D. Bloor and R. Chance, Eds.), p. 1, Nijhoff, Dordrecht, The Netherlands (1985).
22. (a) H. ECKHARDT, T. PRUSIK, AND R. R. CHANCE, in "Polydiacetylenes" (D. Bloor and R. Chance, Eds.), p. 25, Nijhoff, Dordrecht, The Netherlands (1985); (b) H. MATSUDA, H. NAKANISHI, T. HOSOMI, AND M. KATO, *Macromolecules* **21**, 1238 (1988).