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SOLID STATE POLYMERIZATION OF DIACETYLENES WITH π-CONJUGATING SUBSTITUENTS FOR THIRD-ORDER NONLINEAR OPTICAL PROPERTIES

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SOLID STATE POLYMERIZATION OF DIACETYLENES WITH π-CONJUGATING SUBSTITUENTS FOR THIRD-ORDER NONLINEAR OPTICAL PROPERTIES

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Key Words: Solid State Polymerization, Photochemical Polymerization, Diacetylenes, Polydiacetylenes, Nonlinear Optical Property

ABSTRACT

Topochemical reactivity of some conjugated diacetylenes with π-conjugating substituents upon exposure to γ-radiation, UV-visible radiation and upon thermal annealing is described. Few of the diacetylenes undergo solid state polymerization to provide corresponding polydiacetylenes. The reflectance spectra of the resultant polydiacetylenes showed significant backbone-side-group electron coupling. The third-order nonlinear susceptibility of two of the polydiacetylenes obtained were evaluated using Maker's fringe technique. The third-order nonlinear susceptibility, $\chi^{(3)}$ value obtained for the two samples were in the order of 10^{-11} esu for the fully polymerized polydiacetylene films. These values are comparable to the values reported previously for PDAs with aromatic sidegroups.

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INTRODUCTION

Disubstituted conjugated diacetylenes (R-C≡C-C≡C-R’, DAs) undergo topochemical 1,4-addition polymerization reaction upon thermal annealing, exposure to UV-visible radiation or γ-rays, to give polydiacetylenes (PDAs) with an ordered and extensively conjugated backbone with alternating double and triple bonds (Figure 1) [1]. The reaction can be induced by X-rays or also by high pressure. The resultant polymers are highly colored and show novel electronic and optical properties because of their unsaturated backbone. Most of these polymers are red, blue or green in color and some polymers are either brown or black. Red polymers absorb in the region of 550 nm, whereas blue and green polymers show maximum wavelength absorption in the region of 630-680 nm. Some PDA solids show thermochromic changes.

After Wegner [2] elucidated the reaction process, many diacetylenic monomers with various sidegroups were synthesized with the objective of obtaining polymer single crystals with novel properties. Numerous DA monomers were prepared, but not all DAs have been found to be solid state active. As the reaction is lattice controlled, it was reasoned that the molecular packing in the crystal lattices of only reactive diacetylenes is conducive to solid state reactions. It was proposed that the distance between the reacting carbons should be less than 4 Å. Only the sidegroups influence the molecular packing and, in the process, dictate the reactivity of the monomer and to some extent, the properties

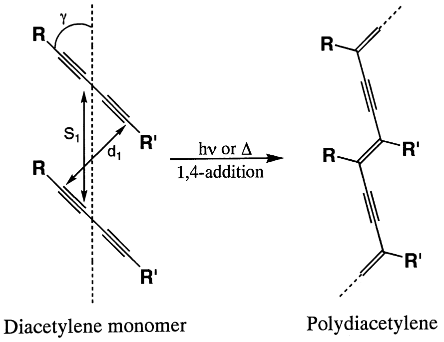


Figure 1. Topochemical polymerization of diacetylenes. Monomer packing requirements for the solid state polymerization 4.8Å < d_1 < 5.6Å, 3.4Å < S_1 < 4.0Å, $\gamma = 45°$.

of polymer [3]. In view of this, structure-reactivity-property relationship has become a study of both fundamental and practical importance for molecular modeling and designing of monomers and polymers with desired properties.

Polydiacetylenes have found many interesting and novel applications. They are being used as time-temperature indicators, in dosimetry, photocross-linking and semiconducting devices [4, 5]. The high and fast third-order nonlinear optical response ($\chi^{(3)}$) is one of the most important properties exhibited by polydiacetylenes [6]. As a result, PDAs are considered to be candidate materials for futuristic applications in optical telecommunications, image reconstruction, integrated optics, optical signal switching and processing, data storage, optical memory and logic technologies [7]. As a consequence, a search for PDA crystals with larger $\chi^{(3)}$ response is a desirable objective. The $\chi^{(3)}$ response of any material depends on the extent of π-electron delocalization along the backbone of its constituent molecules [8]. Increasing the number of π-electrons per repeat unit could be one approach to obtain PDAs with higher $\chi^{(3)}$. PDAs with π-conjugated sidegroups can be expected to show larger and faster $\chi^{(3)}$ due to electronic coupling between such sidegroups and backbone.

Relatively few PDAs with substituents in formal π-conjugation with backbone have been reported, and this has partly been due to a lack of solid state reactivity in many precursor diacetylenes [9]. Recently, there has been considerable interest with some success in synthesis of such PDAs and study of their properties [10-12]. We have been working on synthesis of diacetylene monomers with π-conjugating sidegroups and in this paper, we report our results on the kinetics of polymerization, electronic spectral properties and nonlinear optical properties of some such polymers.

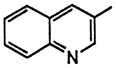
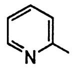
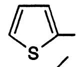
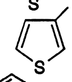
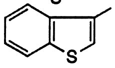
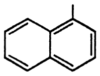
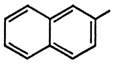
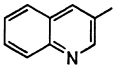
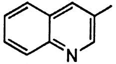
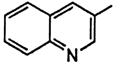
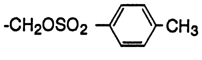
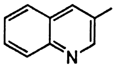
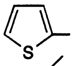
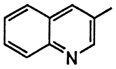
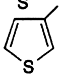
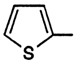
EXPERIMENTAL

Synthesis of the monomers was carried out following different schemes and the details will appear elsewhere [13]. The monomers **1** to **13** used for this study are listed in Table 1.

Solid State Polymerization

All the monomers were freshly recrystallized from an appropriate solvent before polymerization. The purity of the DAs were checked by HPLC and found to me above 98.5%. Thermal polymerization was carried out by heating the samples in sealed glass tubes in a constant temperature oil bath at appropriate

TABLE 1. Reactivity of Diacetylenes (R-C≡C-C≡C-R') Towards Solid State Polymerization

Compd. No.	R	R'	Solid state reactivity γ	UV	heat
1		R	O	O	O
2		R	O	O	O
3		R	X	X	X
4		R	X	X	X
5		R	X	X	X
6		R	X	X	X
7		R	X	X	X
8		$-CH_2OH$	O	O	O
9		 $-CH_2OCONH$	O	O	O
10		 $-CH_2OSO_2$ $-CH_3$	O	O	O
11			X	X	X
12			X	X	X
13		$-CH_2OH$	X	X	X

O : reactive; X : unreactive

temperatures. A ^{60}Co gamma source was used for polymerization by γ -radiation. Samples were taken in evacuated and sealed glass tubes for γ-irradiation. A dose rate of 0.1 Mrad/h was used for all the experiments. Photopolymerization was carried out by exposing suspension of finely powdered samples in water to UV radiation of required wavelength. Monomer free samples were prepared by extracting the partially polymerized samples with suitable solvents. The polymers were characterized by CP/MAS ^{13}C NMR as well as by powder X-ray diffraction studies.

Preparation of Polycrystalline Thin Films

The thin films of the monomers **1** and **9** were prepared by spin-coating. Typically, the monomer (20 mg) was dissolved in chloroform (10 ml). A quartz glass slide (3 x 1 cm) was placed on the spin coating apparatus platform. It was heated to 40˚C, and then the monomer solution (200 ml) was pipetted out on the quartz plate. After 10 seconds, the plate was spun at a speed of 1000 rpm for 30 seconds. A uniform polycrystalline thin film was obtained after few attempts. The spin coated monomers were polymerized by γ-irradiation for third harmonic generation (THG) measurement.

THG Measurement

Third-harmonic generation (THG) measurement for two of the polymers were carried out by means of the Maker fringe method [14]. The fundamental beam used was 1.8-2.16 mm pulsed (ca. 5 ns of pulse width) laser light. The power of laser light used was about 2 mj/pulse. A fused quartz plate, whose $\chi^{(3)}$ is 1.0 x 10^{-14}esu, was used as a reference sample [15]. The polymer from **1** and **9** in form of thin film on quartz plates were used for THG measurements.

RESULTS AND DISCUSSION

Structure and Reactivity

All the monomers were tested for reactivity by all the three modes of polymerization, and their reactivities are given in Table 1. Most of them were found to be either unreactive or showed low levels of polymerization. The distance of approx. 4 Å between reacting carbons is a necessary criterion for a successful topochemical 1,4-addition polymerization reaction in conjugated diacetylenes [16]. Single crystal X-ray structure determination was carried out on seven diacetylenes [13]. Table 2 shows the lattice parameters of these DA monomers, whereas Table 3 summarizes the distances and angles in the crystals relevant for 1,4-addition polymerization for these DAs. Among these, only **1** satisfies all the packing parameters in the crystal lattice. In spite of favorable packing parameters, **1** undergoes conversion into crystalline blue polymer only up to 22%. **2** undergoes 85% conversion into amorphous blackish brown polymer. The possibility of a non-topochemical solid state reaction can explain the high polymer conversion as the lattice parameters are not within the prescribed limits [17]. From the crystal structure of **3**, it was found that the diacetylene molecules are nonplanar rendering the system disordered [18]. This probably contributes to the non-reactivity of **3**. Among the unsymmetrical diacetylenes, **11** and **12** are

TABLE 2. Lattice Parameters of Diacetylene Monomers

diacetylene	space group	a	b (in Å)	c	α	β (in degrees)	γ
1	$P2_1/n$ monoclinic	4.81	13.69	11.91	90	95.34	90
2	$P2_1/n$ monoclinic	6.24	3.98	21.47	90	92.77	90
3	$P2_1/n$ monoclinic	5.89	13.98	13.15	90	102.59	90
5	$P2_1/n$ monoclinic	13.28	3.96	14.12	90	92.11	90
6	$P2_1/n$ monoclinic	7.53	6.01	17.97	90	101.10	90
11	$P2_1/n$ orthorhombic	6.98	28.76	12.49	90	90	90
13	$P2_1/n$ orthorhombic	22.66	7.48	9.38	90	90	90

unreactive whereas, **8** and **10** are fairly reactive and gave brownish black polymers. Monomer **9** is also reactive and provides a bluish green polymer. The low reactivity of most of the monomers underlines the difficulty of preparing PDAs with π-conjugated substituents.

TABLE 3. Distance d_1 and Angle γ of Diacetylenes

diacetylene	d_1 (in Å)	γ (in degrees)
1	4.807	47.5
2	3.973	66.2
3	5.887	40.5
5	3.958	62.3
6	6.012	21.8
11	6.980	64.0
13	7.482	70.0

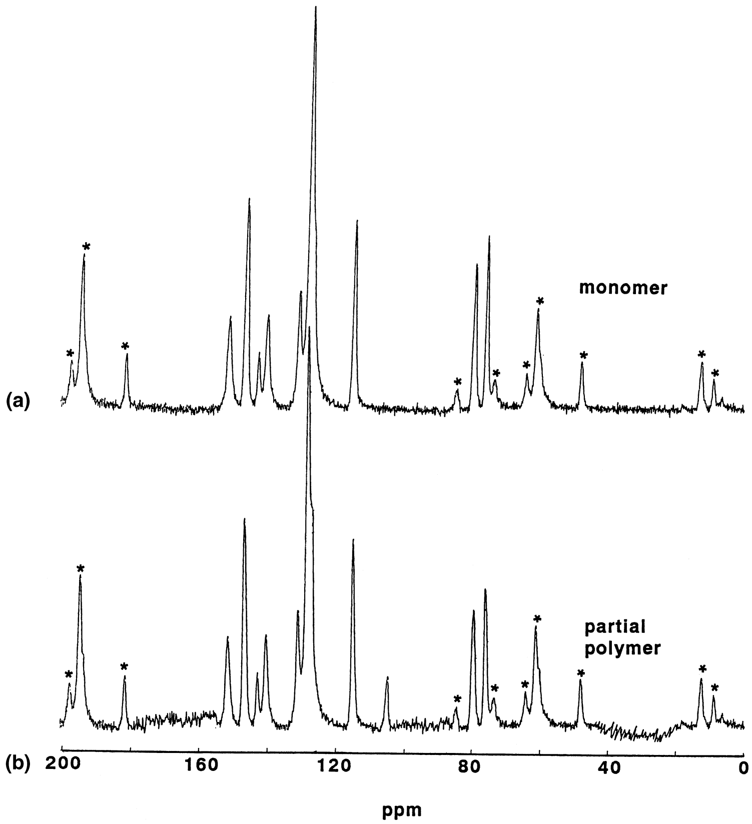


Figure 2. ^{13}C CP/MAS spectrum of **1**. (a) monomer, (b) partial polymer. Peaks with asterisk are for the spinning side bands.

In order to confirm the structure of the polymer, the solid state CP/MAS ^{13}C NMR were recorded for the monomers **1** and **9** and also for their partial polymers. Figure 2 shows the CP/MAS spectra of **1** and its partial polymer. It can be observed that the peaks for acetylenic carbons of the monomer appear at 76 and 79 ppm. Upon polymerization, a new peak at 105 ppm appears which corresponds to the acetylenic carbon of the polymeric backbone. In the spectra of the partial polymer, this peak can be seen whereas the peaks for monomeric acetylenic carbons are of reduced intensity. Another new peak for the alkene carbon of the polydiacetylene backbone should appear at around 120 to 130 ppm. However, due to the quinolyl carbon peaks present at that region, this particular peak is camouflaged. Similar results were observed for the monomer **9** and its polymer. These results confirm beyond doubt that the polymerization of **1** and **9** produced PDA via 1,4-addition reaction.

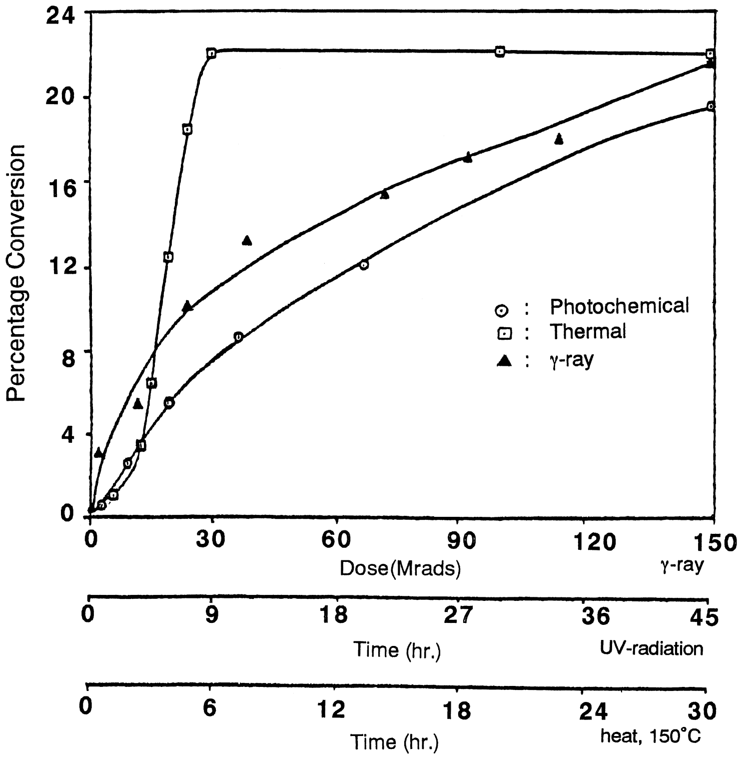


Figure 3. Plots of polymer conversion curves for **1**.

Kinetics of Polymerization

The polymer conversion curves for **1** in all three modes of irradiation are shown in Figure 3. Kinetic curve for thermal polymerization showed an autocatalytic behavior after an initial induction period. Photo and γ-ray polymerization of **1** did not show such autocatalytic behavior. Similar observations, which are not unusual, were made in the literature for other diacetylines also [19]. The polymer conversion of **1** did not exceed 20-25% in any mode of polymerization. The reaction being topochemical, the low conversion of **1** could be explained in terms of growing mismatch between monomer and the propagating polymer lattices as the reaction proceeds. As a result of this, a high degree of strain is induced in the parent lattice which prevents the polymerization from proceeding further. The bulky nature of the quinolyl sidegroups and also the absence of any mechanical tuners, like aliphatic sidechains, contribute to the growing mismatch. The powder XRD scan for **1** and its polymer was recorded to investigate the cause for low polymer conversion. Figure 4 shows the powder

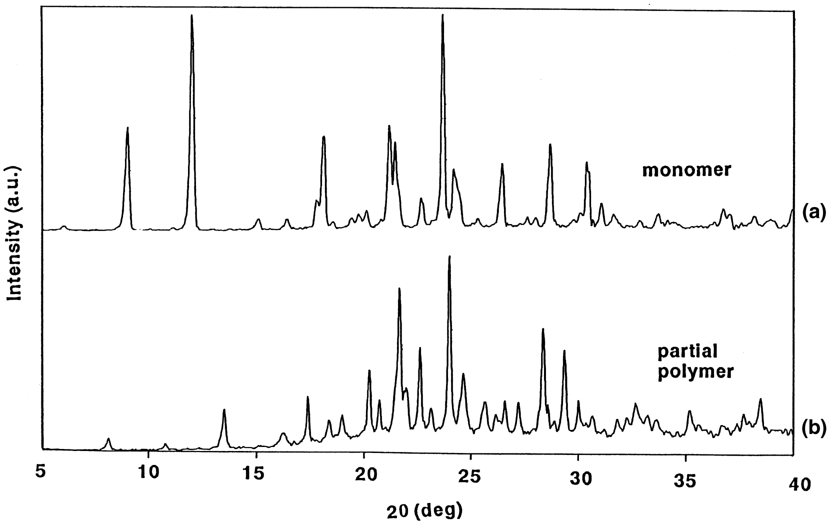


Figure 4. Powder XRD of **1.** (a) monomer, (b) partial polymer.

XRD spectra of **1** and that of its partial polymer. It can be seen that the polymer has new peaks which are different from the monomer's peaks. This suggests that the lattice geometry of the polymer is different from that of the monomer which resulted in lattice mismatch. As a consequence, the polymerization stops after partial conversion. Monomers **8**, **9**, and **10** are reactive upon γ-ray irradiation and photochemical irradiation. Figure 5 shows polymer conversion curves for monomers **8**, **9** and **10** for γ-irradiation. The maximum percentage conversion for these three monomers are 65, 80 and 75% respectively. In these cases, the curves are similar to that for quinoline and thiophene containing diacetylenes reported earlier [19]. Other diacetylenes were found unresponsive to either γ-rays, UV-radiation or annealing.

Reflectance Spectral Properties

The reflectance spectra of partially polymerized samples of **1**, **8**, and **9** are shown in Figure 6. The polymer from **2** also shows a featureless reflectance curve similar to that for poly**8** spanning over the entire visible region. This is in contrast to the absorption/reflectance spectra shown by different polydiacetylenes reported in the literature which show well defined sharp peaks in the red (~550 nm) or blue (~630-650 nm) regions, accompanied by fine structure. However, partial polymers of **1** and **9** showed unusually long wavelength transitions at 756 nm and 730 nm, respectively.

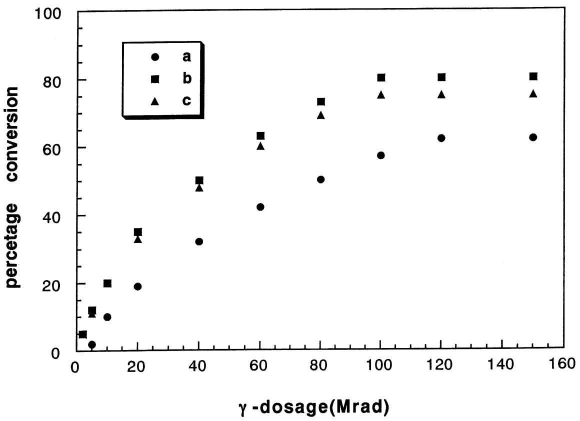


Figure 5. Plots of polymer conversion curves vs. γ-dosages. (a) **8**, (b) **9** and (c) **10**.

Monomer-free polymers were obtained by soxhlet extraction using methanol solvent. The reflectance maxima of monomer free polymers from **1** and **9** are shown in Table 4. In spite of the blue shift in the reflectance spectral peaks of these two polymers upon extraction, which is due to disorder introduced into the backbone structure by extraction process, these values still represent the longest wavelength transitions of all reported polydiacetylenes. The other reported PDAs which exhibit maximum wavelength absorption are polyCPDO (R = N-carbazolyl, R' = -CH_2OH) and polyDCH (R=R'= -CH_2-N-carbazolyl). PolyDCH, in which the sidegroups are not in π-conjugation with the backbone shows maximum wavelength absorption at 656 nm whereas, polyCPDO with the sidegroups π-conjugated to backbone exhibited its λ_{max} at 675 nm [21, 22]. A red shift of about 10 nm in the long wavelength absorption maximum of polyCPDO and polyDCH was attributed to the π-conjugation between the backbone and the sidegroups. However, other factors such as enhanced polarizability and strain in the crystal have been offered as alternative explanation for this small shift [23].

The long wavelength absorption maximum observed for poly**1** is due to the π-conjugative interaction between the backbone and the rigid and planar quinolyl sidegroups. This interaction, in turn, causes extension of backbone conjugation supported by interchain π-cloud interactions. In poly**9**, the longest absorption λ_{max} is shorter than that of poly**1** because of the reduced conjugation between the sidegroups and the backbone as one of the rigid quinolyl groups is replaced by a flexible methylenylphenyl urethane group. The reduced conjugative interaction could lead to reduced interchain interactions. Enhanced polarizability of the

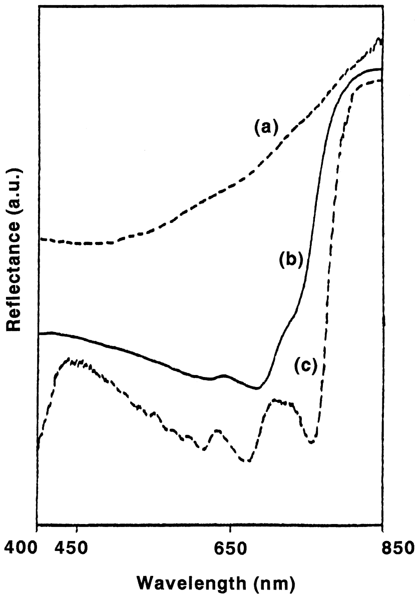


Figure 6. Reflectance spectra of partial polymers from (a) **8**, (b) **9** and (c) **1**.

system due to electron rich sidegroups cannot alone explain such a large red shift in the λ_{max} of poly**1** and poly**9** and we feel that a change of such magnitude must have a significant contribution from the electronic coupling of the backbone and sidegroups.

PolyCPDO retains its long wavelength absorption maximum at 675 nm even after extraction because of quantitative conversion of monomer into polymer. The long λ_{max} of poly**1** and poly**9** blue shifted to 730 nm and 675 nm respectively upon extraction due to low polymer conversion. The removal of the unreacted monomer leads to a disordered crystal lattice and this leads to a blue shift in the λ_{max}. At present, our goal is to obtain PDA crystals having both quantitative conversion like polyCPDO and long wavelength absorption as that of poly**1** and poly**9**. With the help of molecular and crystal engineering, we hope to develop such materials with certain modifications in poly**1** and poly**9** type of systems, as these materials are expected to have numerous potential applications in photonics.

Nonlinear Optical Susceptibility

Table 5 shows the $\chi^{(3)}$ values for the polydiacetylene thin films from **1** and **9**. For PDA from **1**, the $\chi^{(3)}$ value at 2.16 μm is 2.2 x 10^{-12} esu which is higher

TABLE 4. Reflectance/Absorbence Maxima of PDAs

diacetylene	partial polymer (nm)	monomer-free polymer (nm)	absorption edge (nm)
1	756, 670, 613	730	830
9	730, 680	675	830
PolyCPDO	—	675	800
PolyDCH	—	656	

by one order of magnitude than the $\chi^{(3)}$ of quartz. Further, it was found from the powder XRD analysis, that the polymer crystals are deposited on the quartz plate at random, i.e. there is no regularity in the overall direction of the polymer backbone on the quartz plate. In view of this, the $\chi^{(3)}$ value of a single crystal of polymer from **1**, in the direction of the main chain should be 5 times the experiment value, [24] which turns out to be about 1.1 x 10^{-11} esu for a fully polymerized single crystal. At the pumping wavelength 2.01 μm, the $\chi^{(3)}$ value of the polymer is highest, apparently due to the maximum resonance effect.

Likewise, fully polymerized PDA thin film of **9** exhibits $\chi^{(3)}$ value of 2.0 x 10^{-12} esu at 2.10 μm. Considering the random orientation of the crystallites of the thin film, the value for $\chi^{(3)}$ of 1.0 x 10^{-11} esu along the main chain direction is obtained.

PDA crystals, powders, thin films and solutions have been studied with reference to third-order nonlinear optical susceptibility ($\chi^{(3)}$) properties. The

TABLE 5. $\chi^{(3)}$ Values of PDA Thin Film from **1** and **9**

Wavelength (μm)	$\chi^{(3)}$ (x 10^{-12} esu) **1**	**9**
1.83	1.9	1.7
2.01	2.7	2.3
2.10	2.3	2.0
2.16	2.2	1.5

coefficient of $\chi^{(3)}$ response of PDAs has been found to be of the order of 10^{-10} esu and the response time is in the picosecond range. Nakanishi *et al*. reported the $\chi^{(3)}$ response of PDAs with p-conjugated aromatic sidegroups. $\chi^{(3)}$ response was found to be an order of magnitude higher that that of PDAs without such conjugation [25]. In the case of present polymers, the maximum $\chi^{(3)}$ value is in the order of 10^{-10} esu which is comparable to the reported values.

CONCLUSION

In conclusion, we have reported polymerization behavior and reflectance spectra of some diacetylenes with π-conjugated aromatic substitutents. Many of them are either unreactive or show low reactivity. Crystal structure of some of these DAs indicate their unfavorable molecular packing for successful solid state 1,4-addition polymerization. poly**1** and poly**9** show long wavelength absorption maxima, corresponding to some of the lowest energy electronic transition reported for PDA. Qualitative conversion of the monomer into polymer could help in retaining the structural order without compromising on the long wave-length absorption maxima.

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