

## Design of new polydiacetylenes as self assembling second order nonlinear optical polymers

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**ABSTRACT:** A series of diacetylenic monomers containing a polarizable aromatic substituent at one side and a flexible sidegroup with hydrogen bonding groups at the other side are reported. BPOD, 3-BPOD and NPOD are metallic red as polymerized and highly soluble in chloroform, phenol and trifluoroacetic acid. They undergo a dramatic color transition from red( $\lambda_{\max}$ ~510 nm) to purple( $\lambda_{\max}$ ~590 nm) upon the addition of a nonsolvent such as hexane. Films with excellent optical quality can be prepared by spin coating or casting the solutions of these polymers. These polydiacetylenes self assemble in an acentric stable polar organization without recourse to poling. Second harmonic signals are observed from the monomer crystals of these materials as well as the bulk polymers.

### Introduction

Linear and nonlinear optical (NLO) properties of materials are of importance for development of photonic and electronic technologies. Since the development of these technologies are critically dependent on the advances made in the NLO materials, considerable effort is currently invested in their investigation, including their molecular level design, synthesis, processing and fabrication into useful forms. The lower dielectric constant and easy processability of polymeric materials alone provide a number of major advantages over organic single crystals and inorganic NLO materials in electrooptic applications. In addition, since materials with desired optical and processing properties can be defined by tailoring at the molecular level, polymeric materials have attracted a great deal of attention over the last decade[1-4]. Further, improvements in the stability and processability of electroactive and optically nonlinear polymers have stimulated a renewed interest in the utilization of these fascinating materials as active electronic or optical elements in various thin film devices and sensors.

Polydiacetylenes (PDAs) are a class of conjugated polymers and have been investigated extensively as third order nonlinear optical materials due to their large third order susceptibilities( $\chi^{(3)}$ ~ $10^{-9}$ - $10^{-10}$  esu) [5] as well as ultrafast response times [6,7]. It has been suggested that PDAs with aromatic conjugating substituents directly attached to the main backbone will present new properties for these applications due to the following reasons. First, since the number of  $\pi$ -electrons per repeat unit increases through  $\pi$ -conjugation between the backbone and the side groups one expects the extent of electronic conjugation to increase[8-10]. Secondly there may be specific polarization dependent tensorial properties due to the orthogonal spatial arrangement of the conjugating backbone and the sidegroups. In fact,  $\chi^{(3)}$  of these PDAs are found to be almost one order of magnitude higher than those without such groups[11,12]. Conjugating side groups may modify backbone electronic properties in other unique ways [13,14].

Second order nonlinear optical (NLO) properties in bulk crystals or thin films of PDAs have not been extensively studied [15]. Given their centrosymmetric packing in these materials second order NLO properties are not expected due to symmetry considerations. However, electric field induced second harmonic generation(SHG) in PDA films [16] has been reported in which the symmetry is broken due to the external DC-field. Berkovic et al. [17] observed SHG in the monolayers of several diacetylenic monomers and polymers spread at the air-water interfaces in a Langmuir Blodgett(LB) trough. They believed that the SHG signals arise mainly from the side groups on the PDAs since the diacetylene core is centrosymmetric. Garito et al. [18] demonstrated electric-field-induced SHG from PDAs containing two different, highly asymmetric substituents (one is NLO active chromophore). They concluded that "the magnitude of the macroscopic NLO response in PDAs critically depend on the nature of the microscopic charge correlated  $\pi$ -electron states and also on the symmetry and the degree of the structural order".

Theoretical calculations have indicated donor-acceptor substituted PDAs to possess large second order nonlinearity and could potentially be among the best second order nonlinear optical materials [19]. PDAs, in fact, provide several advantages for second order nonlinear optical applications over other organic materials: (1) Since the polymer backbone is extensively conjugated, large optical nonlinearity is expected. (2) Noncentrosymmetrically aligned polymeric single crystals can be obtained without recourse to poling by careful choice of the monomer single crystals if they are packed in a noncentrosymmetric manner. (3) PDAs have good thermal and mechanical stability and can be obtained in various forms for device fabrication. For practical applications, it is ideal to obtain good optical quality films with preferred orientation as observed in poled polymeric systems. In a few cases when PDAs are soluble in common solvents isotropic or centrosymmetric films may be prepared by spin coating [20-22]. Spontaneous orientation of the polymer chains in the films which can be often seen in the spin coated films of polyimides [23,24] has not been observed in the films of PDAs. We may be able to break the centrosymmetric nature in PDAs by aligning the polymer chains by either chemical or physical means. Various techniques have been developed to induce orientation in the films. They include casting-stretching method of soluble PDAs [25], Langmuir-Blodgett method [26], and vacuum deposition-rubbing method [26]. These methods are known to produce homogeneous films and inplane backbone orientation.

In an earlier paper details of the synthesis and properties of some of these polymers in which a polarizable aromatic sidegroup is incorporated at one side to increase the hyperpolarizability of the system and a high entropy sidegroup is attached at the other side to promote the solubility of the polymers are presented [15]. In this paper in addition to reviewing the earlier results, we report a series of new soluble PDAs of the same class with further functionalization, elaborating on the already defined design principles. The side groups also allow intrachain hydrogen bonding capability crucial for the self assembly process. We also present a significant second harmonic generation from spin-cast bulk films of these new PDAs as well as from diacetylenic monomer crystals which are spontaneously obtained by self assembly of the molecules in the system without recourse to poling. We investigate the nature and mechanism of self assembly responsible for this second order NLO property in these new PDAs. The values we report here is surprisingly large considering that there is no traditional NLO active chromophore present in several PDAs and electric field induced poling was not carried out. We propose that acentric alignment necessary for the NLO properties observed here is mainly due to the combined effect of the asymmetry of the two side groups and the spontaneous alignment of the urethane moiety. This occurs in conjunction with the formation of intramolecular hydrogen bonds between the urethane side groups. The aromatic sidegroups in conjunction with the conjugated backbone segment form the asymmetric anharmonic electronic oscillator. The new PDAs reported here, the aromatic substituents have been further functionalized with an efficient electron acceptor. The ability to readily fabricate controlled organizations of optically active materials via molecular self-assembly processes is expected to open up completely new opportunities with regard to the thin film processing of these and related molecular optical materials.

## EXPERIMENTAL

Synthesis of the various diacetylene monomers has been reported elsewhere [28,29]. Polymerization in the solid-state of the monomers was carried out by  $^{60}\text{Co}$   $\gamma$ -ray irradiation with a dosage of 1 Mrad/hr. The unreacted monomer was extracted with hot methanol/ethanol. The percentage polymer conversion was calculated by comparing the weight of the polymer before and after the extraction.

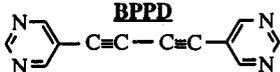
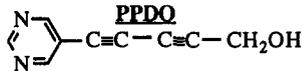
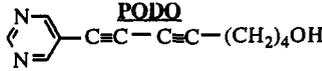
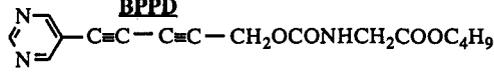
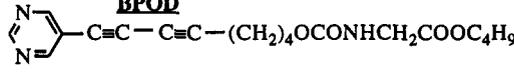
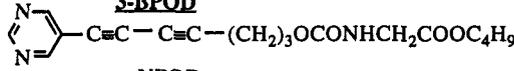
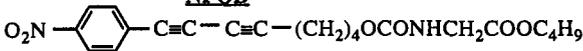
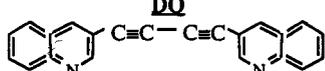
UV-visible spectra of the polymer solutions and the films were obtained on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer at different temperatures. FT-IR spectra of the polymer films were recorded at various temperature by using a Perkin-Elmer 1760X FT-IR. The film thickness was measured by using either an Ellipsometer or a Scanning Electron Microscope. Measurements of the dielectric properties of the films were performed with a Hewlett Packard model 4284A multifrequency LCR meter. The instrument was operated at 10 discrete frequencies ranging from 30 Hz to 1 MHz. Mercury confined within an O-ring was used as the top electrode. Measurements were carried out at different temperature on a computer controlled hot stage with a constant heating rate. SHG measurements were carried out according to the method reported earlier [30].

## RESULTS AND DISCUSSION

### (1) Solid-state polymerization

Table 1 shows the chemical structures and the reactivity to  $\gamma$ -radiation polymerization of the various diacetylenic monomers synthesized in this study. Among 7 diacetylenic monomers synthesized in this study only three monomer crystals were converted into polymer upon  $\gamma$ -radiation. They contain a longer alkyl spacer in the sidegroup compared to the other monomers. A higher degree of sidegroup flexibility from one sidegroup(R<sub>1</sub>) was required to satisfy the polymerizable monomer packing conditions when the other sidegroup(R<sub>2</sub>) is a bulky aromatic ring. The polymer crystals appeared metallic red. There was some spontaneous polymerization during the recrystallization and drying process of the monomer.

Table 1. Chemical structures and the polymer conversion of the various diacetylenes.

Monomers	Polymer conversion
 <p><b>BPPD</b></p>	NR
 <p><b>PPDO</b></p>	NR
 <p><b>PODO</b></p>	NR
 <p><b>BPPD</b></p>	NR
 <p><b>BPOD</b></p>	68%
 <p><b>3-BPOD</b></p>	46%
 <p><b>NPOD</b></p>	NA
<p><b>4-BCMU</b></p> $\text{H}_9\text{C}_4\text{OOCH}_2\text{CHNOCO}(\text{CH}_2)_4\text{-C}\equiv\text{C-C}\equiv\text{C}-(\text{CH}_2)_4\text{OCONHCH}_2\text{COOC}_4\text{H}_9$	~100% [31,32]
 <p><b>DO</b></p>	33% [33]

NR: not reactive NA: not available but experiment is currently underway.

Polymer conversion of BPOD, for example, reached up to 68% with 200 Mrads of dosage. GPC measurements of the 200 Mrads irradiated BPOD showed the number- and weight-average molecular weight of 32,000 g/M and 271,000 g/M respectively. Surprisingly the molecular weight of the 60 Mrads polymer was a little higher than that of the 200 Mrads, i. e.,  $M_n=42,000$  g/M and  $M_w=330,000$  g/M. It appears that the extended chains of the PDAs are partially scissioned into smaller fragments upon higher  $\gamma$ -irradiation. Similar observations were made for 3BPOD and NPOD.

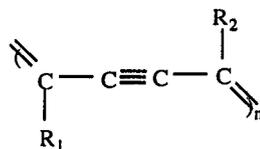
## (2) Solubility of the polymers

Table 2 shows the solubility of the various PDAs synthesized in this study. Absorption maxima of the polymers in thermodynamically good as well as poor solvents are also listed and compared with other known soluble PDAs. Dissolution of the polydiacetylenes is conjectured to arise from the conformational flexibility about the carbon-carbon single bonds in the polymer backbone. Further, the interaction between the side chains and the solvent molecules must be high enough to introduce such backbone carbon-carbon bond rotations. Poly(3-BPOD) has a significantly lower solubility in chloroform compared to poly(BPOD). It is quite surprising considering that the only structural difference in poly(3-BPOD) from that of poly(BPOD) is that the former has three methylene units attached next to backbone instead of four. It appears that higher flexibility from the methylene units as well as a polar functionality from the urethane moiety are required in the dissolution process of these rigid polymers. All the polymers show high solubility in phenol and trifluoroacetic acid. Efficient solvation of the side groups by the protic solvents by means of the hydrogen bonding between the side groups and solvents appears to be responsible for this high solubility.

## (3) Solvatochromism

Soluble PDAs in solution are known to undergo a dramatic chromic transition with changes in solvent system or temperature. Typically, red ( $\lambda_{\max} \sim 550\text{nm}$ ) or blue solid ( $\lambda_{\max} \sim 630\text{nm}$ ) furnish yellow solutions ( $\lambda_{\max} \sim 470\text{nm}$ ) in good solvents and turn red or blue upon the addition of nonsolvents or decreasing the temperature of the solution as in the case of the poly(n-BCMU) series of PDAs (31,32). Macroscopically, these transitions have been understood in terms of an order-disorder conformational change along the conjugated PDA backbone. At a microscopic level, the origin of the transitions is still a subject of debate.

Table 2. Solubility and absorption maxima of various polydiacetylenes.



Polymers	Solubility			Absorption maximum (nm)	
	Chloroform	Phenol	TFA	Good solvent	Poor solvent
Poly(4-BCMU) <sup>[31,32]</sup>	o	o	o	465	545
Poly(BPOD)	o	o	o	510	599
Poly(3-BPOD)	-	o	o	512	601
Poly(NPOD)	o	o	o	500	580
Poly(DQ) <sup>[33]</sup>	x	o	o	636	694, 730

\* TFA: trifluoroacetic acid. o: highly soluble -: moderately soluble x: not soluble.

Thermodynamically good solutions of poly(BPOD), poly(3-BPOD), and poly(NPOD) in which only one sidegroup is substituted with an aromatic moiety show the absorption maximum at 510, 512, and 500nm, respectively (Table 2). Absorption spectra of solutions of PDQ in which both sidegroups are aromatic quinolyl group showed longer wavelength absorption maxima in the range of 630-640nm depending on the solvent system. The absorption maxima of these solutions are significantly red shifted in contrast to those exhibited by the good solutions of all the other reported soluble PDAs. The good solutions of all the other reported soluble PDAs are yellow with the absorption maximum at about 470nm. They contain long, flexible sidegroups with certain numbers of methylene units directly attached to the backbone. Typically good solutions of poly(4-BCMU) in chloroform shows the  $\lambda_{\max}$  at 465nm. There is a gradual red-shift in the  $\lambda_{\max}$  in good solutions as we go from poly(4-BCMU) (no aromatic substituent present) to PDQ (both side groups are aromatic). Absorption maxima of the PDAs with one aromatic sidegroups lie in between the two. The only structural difference in these polymers from that of poly(4-BCMU) is that the former has at least one of the flexible urethane sidegroups replaced by a rigid aromatic group. The differences in the  $\lambda_{\max}$  in the good solutions of poly(4-BCMU) (yellow) and these polymers seem to arise from the presence of the  $\pi$ -conjugated aromatic sidegroups next to the backbone. Two possibilities exist to explain this behavior. (i) the electronic interactions ( $\pi$ -electron delocalization) between the backbone and the sidegroups can lead to an increase in the  $\lambda_{\max}$ . (ii) an increase in the effective delocalization length of the backbone due to the rigid sidegroups.

Upon the addition of a poor solvent such as hexane, toluene or acetonitrile to the solution of the PDAs in which only one sidegroup is substituted with an aromatic sidegroup, a dramatic spontaneous color transition from red to purple ( $\lambda_{\max}$ : ~580-600nm) takes place. Absorption spectra of PDQ in poor solutions show longer wavelength absorption maximum in the range of 690-730nm. For comparison, the  $\lambda_{\max}$  of poly(4-BCMU) in chloroform/hexane solution is 545nm. This further establishes that the aromatic sidegroups directly attached to the backbone can significantly modify the electronic properties of PDAs.

#### (4) Second order nonlinear optical (NLO) properties

Optical quality films of poly(BPOD), poly(3-BPOD) and poly(NPOD) were easily fabricated onto a glass substrate by casting or spin coating the polymer solutions. Transmission Electron Microscopy (TEM) and X-ray diffraction as well as Polarized Optical Microscopy studies indicate that the films of poly(BPOD) are amorphous and no crystallinity is present. However, a couple of small humps at low angles of X-ray diffraction pattern suggest the presence of certain degree of orientation in the film. Two broad rings from the diffraction pattern from TEM also support the results of the X-ray study. The angular and polarization dependence of second harmonic signals also confirm the inplane isotropy of the film as well as the existence of polar order with the symmetry axis perpendicular to the substrate. Similar characterization on poly(3-BPOD) and poly(NPOD) is underway and the results will be reported in the near future.

Second harmonic measurements from spin coated films of poly(BPOD) were performed both at 1.06  $\mu\text{m}$  and 1.54  $\mu\text{m}$  to estimate the effective magnitude of d-coefficient ( $d_{\text{eff}}$ ) [15]. The angular dependence of second harmonic signal observed from the polymer films imply a symmetry analogous to that of the poled polymer system [34]. The second harmonic due to 1.06  $\mu\text{m}$  is, of course, expected to be strongly resonantly enhanced. Only absorption corrections have been made for the second harmonic at 0.532  $\mu\text{m}$ . The measurements made at 1.54  $\mu\text{m}$  yield nonresonant values of  $d_{\text{eff}}$  which are an order of magnitude smaller than the values at 1.06  $\mu\text{m}$ . The large difference in the resonant and nonresonant values of  $d_{\text{eff}}$  is not surprising considering the strong absorption due to the polymer backbone. The results are summarized in Table 3. The error in the measurements due to thickness variations in the films and error in thickness measurements and refractive indices is estimated to be at most  $\pm 30\%$ . The observed second harmonic signals confirm that noncentrosymmetric arrangement spontaneously results, i.e., without poling, in spin coated or cast films. Similar observation was made from the spin cast films of poly(3-BPOD) and poly(NPOD). Significant SHG signals were also observed from the crystals of these asymmetrically substituted diacetylene monomers. The nonresonant values of second order susceptibility are comparable to those reported in ferroelectric liquid crystalline NLO polymers [35]. For comparison, monomer crystals as well as the spin coated films of 4-BCMU show no measurable signals under the same conditions.

Table 3.  $d_{\text{eff}}$  values obtained from spin coated films of poly(BPOD) at incident wavelength of 1.06  $\mu\text{m}$  and 1.54  $\mu\text{m}$ .

Film thickness ( $\mu\text{m}$ )	$d_{\text{eff}}$ (pm/V)		
	1.06 $\mu\text{m}$		1.54 $\mu\text{m}$
	w/o abs. correction	with correction	w/o abs. correction
0.31	0.74	5.57	0.50
0.25	0.78	4.43	0.38
0.19	0.88	3.32	0.29

\* Values from monomer crystals and spin cast films of poly(3-BPOD) and poly(NPOD) will be reported in a subsequent communication.

Figure 1 shows the changes in SH signal from the spin coated films of poly(BPOD) as a function of temperature. SH intensity starts to drop abruptly between 125-130°C and decreases only slightly below 130°C. However, on heating the film to temperatures well above 130°C the signal approaches nearly zero and becomes irreversible. Spin cast films of poly(3-BPOD) show similar behavior. Differential scanning calorimetry (DSC) studies of poly(BPOD) shows no endothermic transitions upon heating and degradation starts at around 231°C. Furthermore, no significant thermochromic behavior was observed [36,37]. This suggests that the changes observed in SH signals upon heating is not due to thermal transitions or segmental motion of the backbone. A relatively small blue shift and decrease in intensity in the absorption spectra was observed upon heating which also indicates that the PDA backbones are not significantly influenced by the thermal treatment.

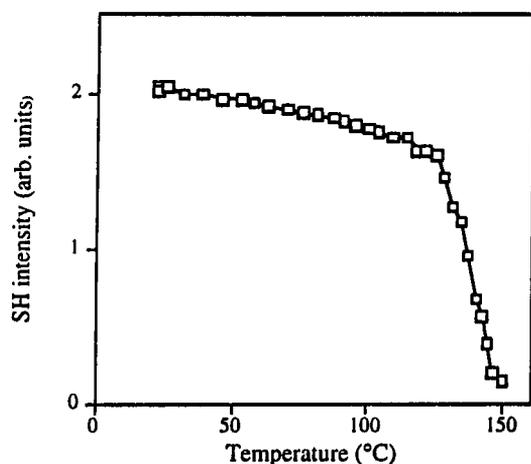


Figure 1. Second harmonic intensity from spin coated film of poly(BPOD) at various temperatures.

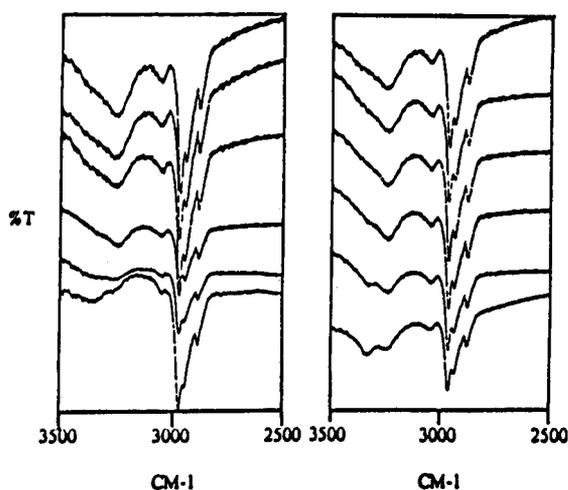


Figure 2. FT-IR spectra of spin cast films of poly(BPOD) in 2500-3500  $\text{cm}^{-1}$  region.

Left: recorded at 25, 50, 80, 110, 130, and 150°C.

Right: recorded after cooled to room temperature.

Figure 2 shows the FT-IR spectra of spin coated film of poly(BPOD) as a function of temperature. Since we believe the alignment of the urethane side groups by means of intramolecular hydrogen bond is largely responsible for acentric alignment necessary for the NLO properties, only two spectral regions of interests are discussed here. They are N-H stretching and carbonyl stretching in the urethanyl moiety. Extensively hydrogen bonded network of poly(BPOD) is shown in Figure 3. Figure 2 shows the spectral changes in the N-H stretching region upon heating (left) and subsequent cooling to room temperature (right). N-H stretching band in between 3100 and 3500  $\text{cm}^{-1}$  shows a relatively sharp peak centered at around 3257  $\text{cm}^{-1}$  with a small shoulder at higher wavenumber at room temperature. Consistent with other urethane substituted PDAs this clearly indicates the presence of hydrogen bonded N-H groups with a small fraction of non-hydrogen bonded N-H moiety. This peak broadens and intensity dramatically decreases at temperatures around 130 °C and a new band appears at higher wavenumber at higher temperature. The SH signal drops abruptly in the temperature region and can not be recovered upon cooling above this region. The spectral changes observed in this region suggest the breakage of the hydrogen bonds and development of free N-H groups which, in turn, results in a disruption of the acentric organization. Upon cooling to room temperature, this band returns to its original shape and intensity which indicates the reformation of the hydrogen bonds. On the other hand, the shoulder assigned as the free N-H band, becomes sharp and more intense as the sample is cooled from temperature above 130 °C. The hydrogen bonds are not recoverable when the sample is cooled from higher temperatures as a result of extensive randomization of the side groups. This prevents the necessary proximity of the adjacent urethane linkages to form hydrogen bonds. The changes in the urethane carbonyl peak confirm this observation. Similar observation was also made from the spin coated films of poly(3-BPOD).

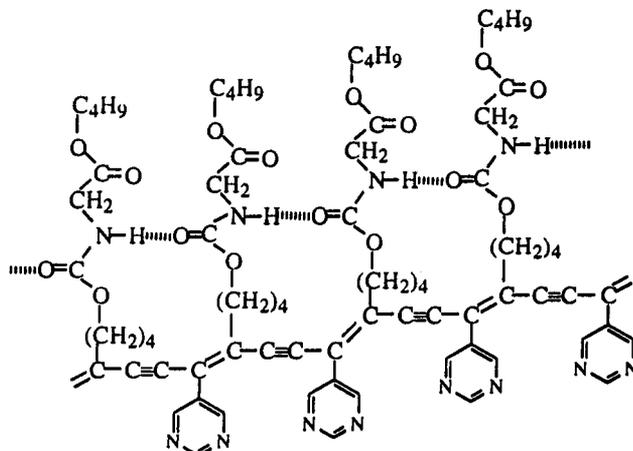


Figure 3. Proposed hydrogen bonded network of spin coated films of poly(BPOD).

Dynamic behavior of the molecular dipolar organization in the film at various temperatures is further investigated by dielectric spectroscopy. Figure 4 shows temperature dependence of the dielectric constant of the poly(BPOD) film at various frequencies. No significant segmental motion from the main chain is expected at moderately high temperatures due to the rigidity of the PDA backbone. The changes seen in the dielectric response at high temperatures is caused by the increase in the mobility of the dipolar units in the side groups. Dielectric constant starts to increase dramatically around 125-130 °C at 30Hz. Again, this is the temperature region at which SH signal drops abruptly and becomes irreversible above this temperature. This is a good indication that the restricted mobility of the side groups which was enforced by the hydrogen bonding now begins to relax and randomize at this temperature. It is in this temperature range the all trans conformation of the sidegroup methylene units begins to adopt other conformational possibilities [38].

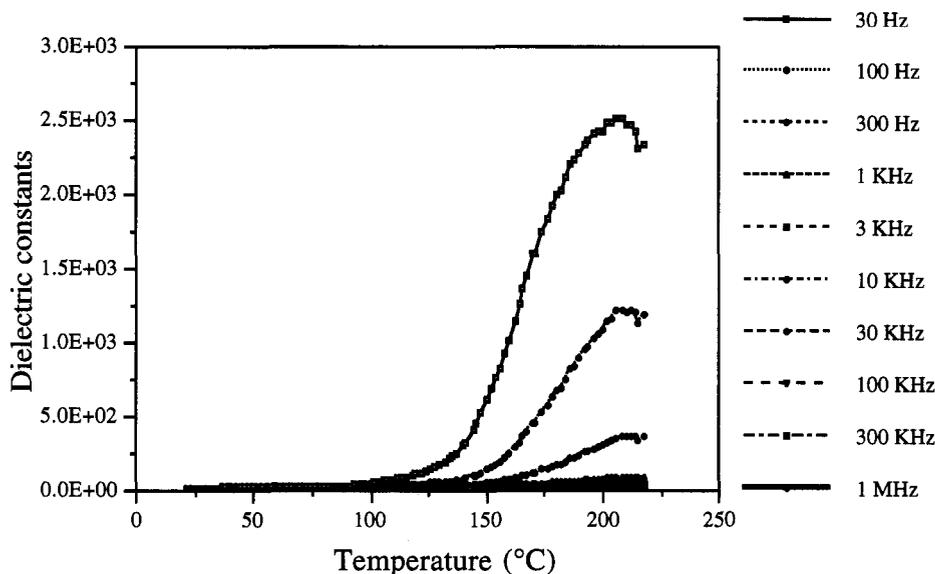


Figure 4. Temperature dependence of dielectric constants of spin coated films of poly(BPOD).

## Conclusions

A series of polydiacetylenes containing aromatic substituents directly attached to the main backbone has been reported. A dramatic color transition from red ( $\lambda_{\max} \sim 510$  nm) to purple ( $\lambda_{\max} \sim 590$  nm) upon the addition of a nonsolvent such as hexane is observed from the solutions of these new polymers. Significant second harmonic generation is observed from the monomer crystals of these materials as well as from the spin cast films of two of the polymers for which measurements have been made in the absence of nonlinear optically active chromophores and without recourse to poling. The polymer chains of these polydiacetylenes spontaneously assemble in an acentric stable polar organization upon spin casting. The principal design features have been to attach an electron withdrawing aromatic substituent to a conjugating polymer backbone. The second side group is designed to provide self assembling features in a defined spatial arrangement for the macromolecular system. While a polydiacetylene backbone has been selected for a number of well established reasons, including characteristic electronic and optical properties, we believe a variety of other conjugating backbones may be chosen.

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