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Exploratory Syntheses of Polymers Possessing Electrically Conducting, Liquid Crystalline, Piezoelectric, and Nonlinear Optical Activity

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EXPLORATORY SYNTHESSES OF POLYMERS POSSESSING ELECTRICALLY CONDUCTING, LIQUID CRYSTALLINE, PIEZOELECTRIC, AND NONLINEAR OPTICAL ACTIVITY*

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ABSTRACT

Studies of the synthesis of organic polymers potentially possessing electrically conductive, piezoelectric, and nonlinear optical properties are described. The electrically conducting polymer studies center on polyaromatic quinondiimines, analogs of the known conducting polymer polyaniline. Various polycondensation polymers based on anthraquinone and on heterocyclic quinones were examined. Multiazoarylene polymers were also synthesized by oxidative coupling of aromatic diamines. Their films were found to be *n*-dopable but were not very conductive. Polyesters and polyformals containing multiazoarylene units also were not highly conductive. Liquid crystal properties were observed for multiazobisphenol sebacate polyesters. Toward piezoactive polymers, a polyvinylidene fluoride macromonomer was synthesized via telomerization of vinylidene fluoride with methanol. Films of poly(bicyclobutane-1-carbonitrile) were found to show piezoactivity. 2-Ethyl-2-butylmalonimide was synthesized and subjected to ring-opening polymerization with the aim of synthesizing novel piezoactive β -pleated sheet polymalonimides. As to NLO polymers, AB polyesters

containing highly polar quinodimethanes as the active group were synthesized. However, they were soluble only in highly polar solvents that were not very suitable for spin-casting films. Accordingly, AB polyesters were synthesized from *p*-hydroxy- α -cyanocinnamate monomers. These polyesters were soluble in appropriate spin-casting solvents and displayed enhanced NLO activity over the parent monomers.

GENERAL INTRODUCTION

Modern high-technology industries require increasingly sophisticated materials. Such materials are required to show novel electronic and optical properties. These requirements are superimposed on the traditional requirements of good mechanical properties. These dual requirements offer a stimulating challenge to the synthetic organic polymer chemist. Often the best outcome will be a trade-off between the demands of functional performance and processability.

The improved functional performance of the polymers over small molecules often depends on an extended, more or less rigid chain. This makes the polymer less tractable through increasing crystallinity, higher glass transition temperature, and decreasing solubility. However, the same factor may lead to liquid crystal behavior, which restores processability. The interplay of these factors can be seen in the work described.

ELECTRICALLY CONDUCTING POLYMERS [1]

Aromatic Polyquinonimines

Introduction

The need for specialty polymers with electrical properties has led to extensive research in this field. It is well known that electronic mobility in polymers is greatly enhanced along a planar polymer molecule with conjugated bonds. The conductivity may be in the range of 10^{-5} to 10^{-9} S/cm. When such a solid is doped, it becomes metallike in conductivity, 10^1 - 10^3 S/cm. Applications are thought to be possible for these materials if problems of stability and fabrication can be overcome.

Publications about oxidatively or electrochemically generated "Aniline Black," which may partially possess a polyquinonediimine structure, extensive-

ly discuss the conductive properties of this polymer. We thought that polyquinonediiimines prepared by polycondensation methods might lead to well-defined structures showing conductive properties.

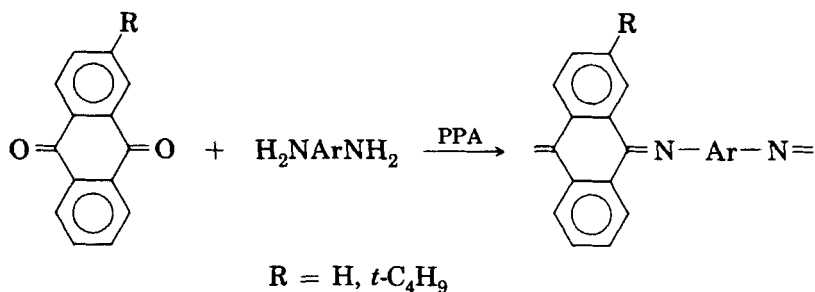
Results

Despite a report to the contrary by Uehara and Kunugi, condensations of aromatic diamines with 1,4-benzoquinone in polyphosphoric acid gave unsatisfactory results. The black, insoluble powders contained covalently bonded phosphate and, indeed, 1,4-benzoquinone itself reacts with polyphosphoric acid, probably by Michael addition.

Cyclohexane-1,4-dione reacted with *p*-phenylenediamine with dehydration and dehydrogenation to give black metallic-looking films. However, these did not conduct well or analyze correctly, and they appear to have involved aldol condensation. Very recently, Wudl and his colleagues at Santa Barbara have found that use of cyclohexane-1,4-dione-2,5-dicarboxylic acid avoids these difficulties and gives successful polycondensations with aromatic diamines.

We turned to anthraquinone as an example of a quinone which cannot undergo unwanted Michael addition.

Polymer Synthesis. The polycondensation of a wide variety of aromatic diamines with anthraquinone or with 2-*t*-butylanthraquinone gave a new family of polymers, the aromatic polyquinonediiimines:



Copolymers from diamine pairs were also synthesized. Yields were generally high (>70%). The reaction temperature was generally 250°C for several hours. This temperature was necessary in order to obtain reasonable molecular weights.

Thermal Properties. Attempts to melt press these polymers in a Carver press, heated to 200°C, with or without plasticizers, did not succeed. Glass

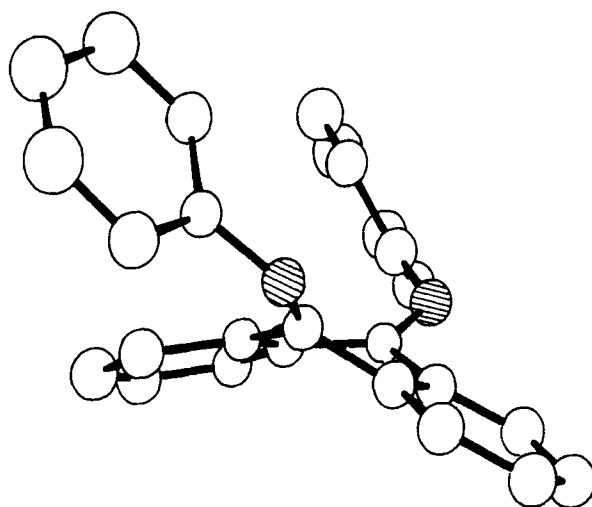


FIG. 1. X-ray crystal structure of 9,10-dianilinoanthraquinone.

transition temperatures by DSC were very high, ranging from $>500^{\circ}\text{C}$ to a minimum of 350°C . Nevertheless, even at 500°C , none of the polymers appeared to fuse.

Solubility. The solubility of the polymers and copolymers is extremely low. Even strong solvents like sulfuric acid, methanesulfonic acid, hexafluoroisopropanol, etc., gave negligible solubility.

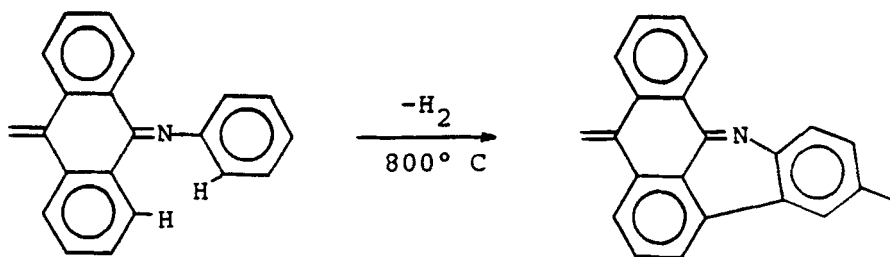
Conductivity. The conductivities, as measured on compacted pellets of these polymers, ranged from 10^{-9} to 10^{-4} S/cm, from the insulating to the semiconducting range. Attempted doping with I_2 , etc., did not lead to substantial increases.

Following literature procedures, anthraquinone was condensed with two equivalents of aniline to form a model compound for our aromatic polyquinondiimines. It was subjected to x-ray crystal structure determination.

A Model Compound: 9,10-Dianilinoanthraquinone. The study proved that the molecule is the *syn*-isomer, with the two arylimino groups on the same side of the molecule. The representation of the molecule in Fig. 1 shows that the anthraquinone ring in the model compound is not planar but

is "butterfly-shaped." Also, the torsion angles around the N2-C21 and N1-C31 are 57° and 61° , respectively, so that the *N*-aryl groups are not in the same plane. This is ascribed to the repulsive interactions between the other hydrogens of the aromatic amine fragment and the *peri* hydrogens of the anthraquinone unit. This lack of planarity explains the low electrical conductivities observed.

Thermolysis. Accordingly, several polymers were subjected to thermolysis at 800°C under vacuum for 10 h. The resulting fused black polymers displayed high conductivities in the range of 1 S/cm (Table 1). We ascribe this to the formation of flat, planar, highly conjugated structures via *ortho* dehydrogenation.



Status and Conclusions. Polycondensation of anthraquinones with aromatic diamines in polyphosphoric acid gave intractable polymers. Their conductivity was low because, as shown by x-ray determination, the structure was far from planar. Efforts to synthesize planar polyquinonediimines are in progress.

Starburst Aromatic Polyamines [2]

Introduction

Oxidation ("doping") of electron-rich aromatic compounds such as triaryl amines has led to ion-radical conducting salts. Linear arylamines have been reported by Honzl and coworkers through nucleophilic aromatic substitution on *p*-nitrochlorobenzene by aniline, followed by reduction or by oxidative condensation. They prepared linear oligoaryl amines up to tetramers. The iodine and perchlorate complexes of these amines had conductivities in the semiconducting region (10^{-7} to 10^{-1} S/cm).

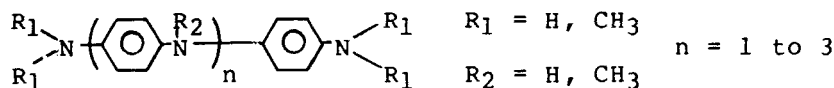
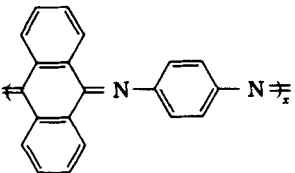
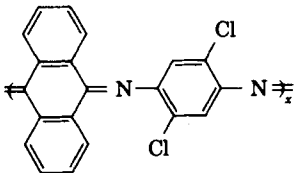
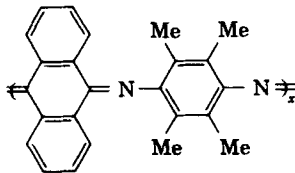
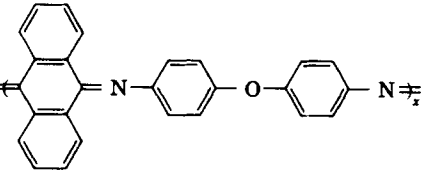
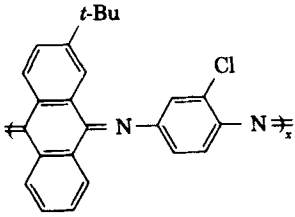


TABLE 1. Semiconducting Polyanthraquinonediimines

Polymer	Conductivity, S/cm	
	Unheated	Heated (800°C)
	3.00×10^{-6}	0.39
	1.32×10^{-5}	1.10
	3.14×10^{-5}	0.48
	9.80×10^{-5}	1.25
	3.50×10^{-6}	0.87

Tomalia and coworkers recently offered the novel concept of the "starburst" polymer. Here progressive dendritic branching leads by stepwise reactions to highly branched polymer molecules. Tomalia's report was confined to polyamides and to polyethyleneimines.

Honzl's synthesis had been difficult because *p*-nitrohalobenzenes are not highly reactive with aryl amines, and cooxidation routes led to mixtures of products. In contrast, 2,4-dinitroaryl halides, especially the fluoride, are far more reactive. Moreover, dimethylsulfoxide (DMSO) is a particularly effective solvent for these reactions. Accordingly, it seemed appropriate to build starburst aromatic amines through stepwise condensations of 2,4-dinitrofluorobenzene with aniline derivatives, followed by reduction, and to investigate the electrical properties of the derived complexes.

Results and Discussion

As the nuclear aromatic amine, four aniline derivatives were selected. An example is shown on page 736.

The condensations proceeded well in DMSO at room temperature. Some reactions were exothermic. Overall yields were high.

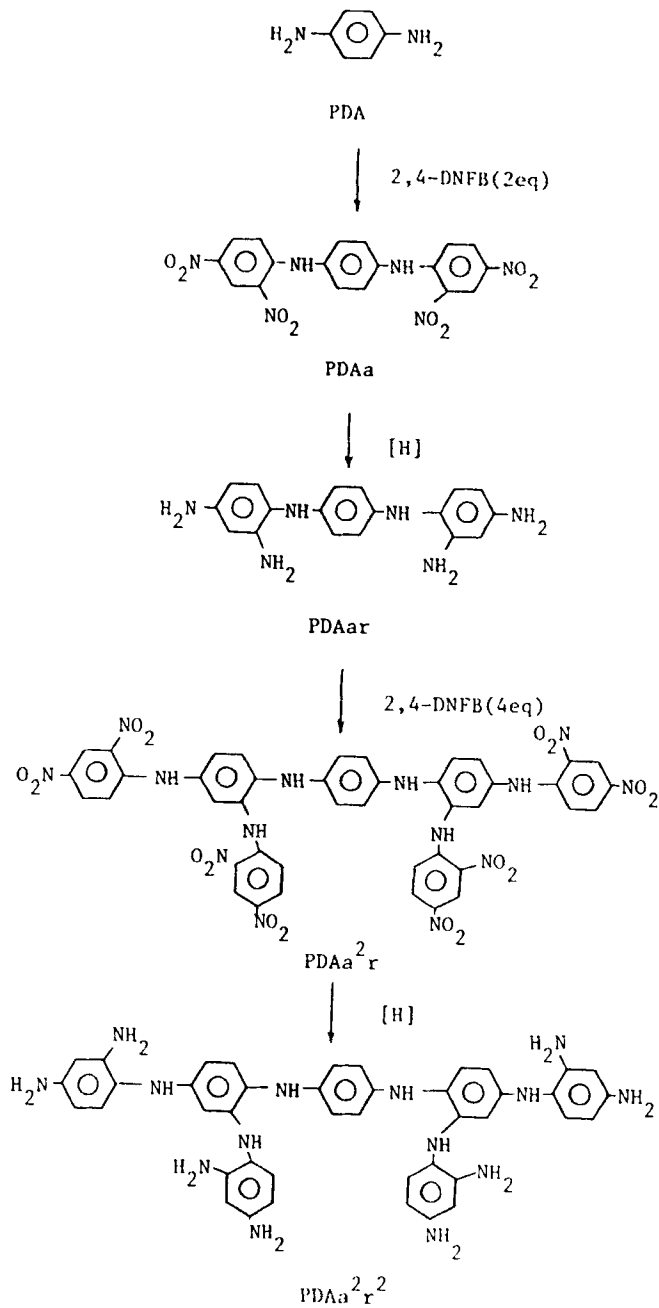
The multinitro amines were insoluble in water or ethanol but soluble in DMSO. At the second round of addition they became less soluble and difficult to crystallize, owing perhaps to their increasingly disordered structures. Their internal donor-acceptor character may contribute to insolubility.

The polyamines were insoluble in water but soluble in alcohol, acetonitrile, or DMSO. At the second round of reductions they were very sensitive to autoxidation and were not crystalline. Finally, the polyamines became unstable toward air or light oxidation. For these reasons, we terminated our growth at the third stage of monomer additions. This contrasts with the compounds studied by Tomalia, which remained tractable during the structural build-up.

The complexes were difficult, if not impossible, to crystallize. Conductivity of pressed pellets up to 10^{-5} S/cm was observed.

Status and Conclusions

The idea that "starburst" arylamines would yield highly semiconductive redox complexes was tested. The trend of longer chain length giving higher conductivity as found by Honzl does not apply, due to the complexity of the aromatic structures and resulting inability to form crystalline complexes. Probably Honzl's linear compounds "pack" better as crystals, so that they conduct better.



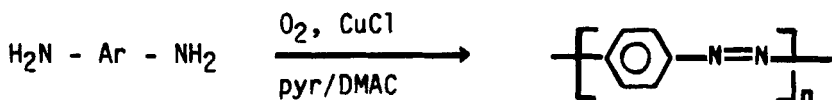
Polyazoarylenes [3]

Introduction

Conjugated polymers based on stilbene derivatives, such as poly(*p*-phenylenevinylene) ($-\text{C}=\text{C}-$ bonds), and on aromatic polyimines, such as poly-aniline ($-\text{C}=\text{N}-$ bonds), have been shown to be highly conducting upon doping. However, although polymers containing *p*-phenyleneazo links ($-\text{N}=\text{N}-$ bonds) were reported long ago, their electrical properties have just begun to be examined. The conductivity of such polymers was mostly investigated in the form of compressed pellets, owing to the intractability of the polymers. In this work, we have prepared films of polyazo polymers and copolymers, and investigated their electrical conductivities.

Results

Polymerization. Various azopolymers were synthesized by the oxidative coupling of the aromatic diamines according to the literature:



The azo structure predominates, but direct elemental analysis (not reported previously) shows the presence of oxygen. Presumably some of the azo links were further oxidized to azoxy groups. Polymerization under milder conditions lessened, but did not completely remove, oxygen. The presence of azoxy groups was evidenced in the IR spectra which showed peaks at $\sim 1300 \text{ cm}^{-1}$.

Solubility. When the polymerizations were performed at room temperature, the polymers were soluble in strong acids, such as trifluoroacetic, sulfuric, and methanesulfonic, after several days.

Film Casting. Selected polyazoarylenes were cast into films both from the polymerization solution and from the solutions obtained by dissolving the isolated polymer powders in trifluoroacetic or methanesulfonic acids. The solvent was evaporated at room temperature or slightly elevated temperature. The films were purified by extracting with acetonitrile and ethanol for several days. The films were black with a metallic luster. Several films of copolymers were flexible and strong, and could be drawn (5%) and oriented on a hot bar.

Doping. The polymer films were *n*-doped by sodium naphthalide in THF or *p*-doped by iodine vapor. After doping, the films became black with a metallic luster, and the weight increased.

Electrical Conductivity. The undoped films are insulators. Upon doping, the films became semiconducting, generally showing conductivities of 10^{-4} to 10^{-5} S/cm (either *p*-type or *n*-type). When exposed to air, the conductivity decreased to 10^{-6} to 10^{-7} S/cm in several days for *n*-doped films and in several hours for *p*-doped films. The observation that the *n*-doped films were more stable than the *p*-doped films may be due to the fact that reduction is easier than oxidation for these azopolymers.

Status and Conclusions

We prepared films of polyesters and polyformals, as well as small molecules, containing multiple azoarylene units. For reference, we examined their doping and conductivity. According to our results from the doping of these polyazoarylene polyesters, polyformals, and small molecules, a long conjugated system is required for an azo compound to be even moderately conducting.

Liquid Crystalline Multiazo Polyesters and Polyformals [4]

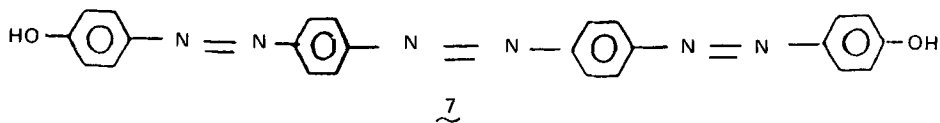
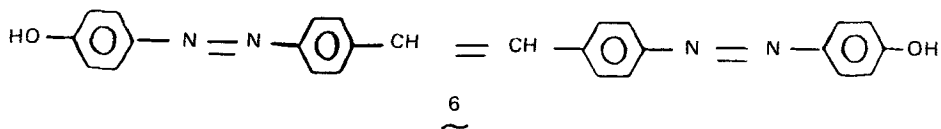
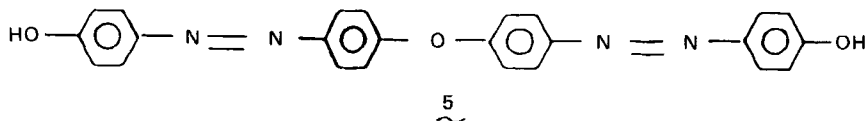
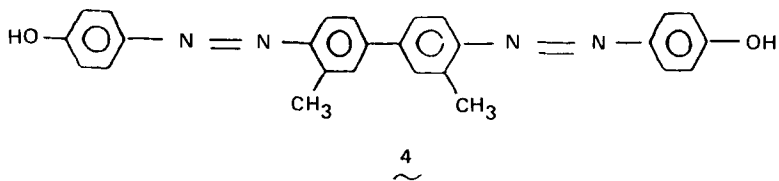
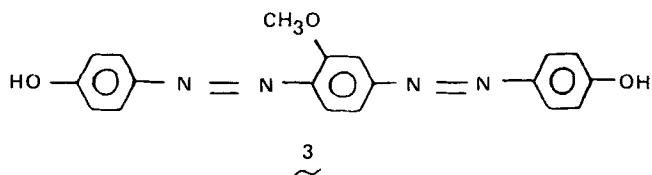
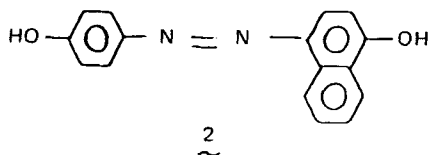
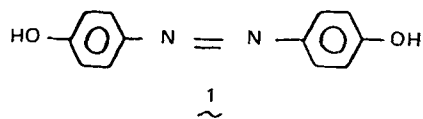
Introduction

Liquid crystal (LC) polymers have been of great interest in recent years. LC polymers come in several types: 1) The entire chain is mesogenic; 2) mesogenic groups are in the side chain; 3) mesogenic groups are in the main chain. Our study will be confined to polymers in the third class. Polymers based on stilbene derivatives, tolanes, and aromatic polyimines have been reported to display LC properties. However, although the *p*-phenyleneazo link is known to favor LC behavior in small molecules, it has only recently been briefly reported to cause LC polymer formation.

Polyesters have been the most popular type of thermotropic LC polymer. Accordingly, in this work we have synthesized a number of aromatic and aliphatic polyesters from bisphenols containing one to three *p*-phenyleneazo groups. The polymers have been examined for their LC properties. Aromatic formals have come to attention recently, and we also synthesized them from our multiazobisphenols.

Results and Discussion

Monomers. The bisphenol monomers in this study are as follows:



They were obtained as indicated by the literature or were synthesized by standard procedures involving aryldiazonium ion couplings.

The monomers were examined for their LC behavior. Moreover, they were converted to their diacetates, diisobutyrate, or dimethyl ethers, mostly new compounds, which were also examined for LC behavior as models of the polymers.

An important factor in these studies was the tractability of the polymers. We wanted to avoid intractable, infusible "brick dust." Inasmuch as the *p*-phenylene azo group tends to form intractable polymers, we used relatively "soft" diacyl halides to offset the "hard" bisphenol. Because the "soft" diacid components possessed *m*-aromatic or aliphatic structures, the resulting combinations represent a trade-off between LC character and tractability. Isophthaloyl chloride and 5-*t*-butylisophthaloyl chloride were the aromatic acid chlorides employed. Sebacic acid was used as an aliphatic diacid.

Polymerizations. All of the polyesters were synthesized by interfacial polycondensation. Polyformals were synthesized by use of excess dichloromethane and base in *N*-methylpyrrolidone solution, as described in the literature.

Properties of Polymers. Data were obtained on polymer melting behavior, inherent viscosities, film-forming ability, color, and LC behavior. Polymer solubility was increased by the 5-*t*-butyl group in isophthalic acid and the methoxy group in 3. Derivatives of the bisphenols 2 and 5 had the greatest solubility. This factor helped us to achieve higher molecular weight by keeping the polymer in solution longer. Films were cast from the polymer solutions.

LC Behavior. The occurrence of LC behavior depended strongly on the bisphenol monomer and on the diacid. Both small molecules and polysebacates based on 4 and 7 uniformly showed LC characteristic melting point behavior. Polysebacates based on 2, 3, and 5 showed LC properties. On the other hand, monomer or derivatives of 5 showed no LC behavior. All the liquid crystalline compounds and polymers showed nematic textures.

The results agree with the generally accepted idea that extended rodlike character is required for LC behavior. Only the sebacate group, with its ability to adopt the *trans* planar extended zigzag form, meets this criterion. The isophthalate residue, as well as the methylene formal units, lead to kinks in the chain. These disrupt the propensity for LC character shown by the monomeric bisphenols and their simple derivatives.

Status and Conclusions

The arylazo link, in combination with sebacate units, has been shown to form thermotropic liquid crystalline polyesters.

PIEZOELECTRIC POLYMERS

Introduction

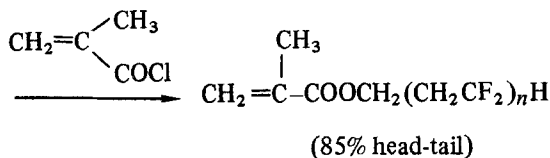
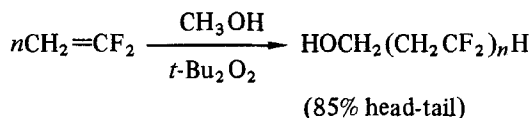
Piezoelectric polymers are of current interest. The best-known polymer is crystalline poly(vinylidene fluoride). Other crystalline polymers such as the odd nylons and polyhydroxybutyrate also exhibit piezoelectricity. However, glassy polymers with high concentration of dipoles can also exhibit it. The copolymer of vinylidene cyanide and vinyl acetate represents such a case.

Macromonomer of Poly(Vinylidene Fluoride) [5]

The new field of macromonomer chemistry has expanded rapidly in recent years. Macromonomers derived from many of the common monomers are now available, and research continues to make more such useful intermediates. In this work we describe the synthesis of a macromonomer of poly(vinylidene fluoride) (PVDF).

Results

Hydroxy-ended poly(vinylidene fluoride) was prepared by telomerization of vinylidene fluoride with methanol and di-*t*-butyl peroxide, analogous to the procedure reported for tetrafluoroethylene. Reaction on a 1.47 mol scale gave 41% yield. The molecular weight of the methanol-insoluble part was 3600, based on polystyrene standards. NMR, especially ^{13}C NMR of the polymer, supports the structure $\text{HOCH}_2(\text{CH}_2\text{CF}_2)_n\text{H}$.



Conversion to the methacrylate was readily carried out. The resulting macromonomer was characterized by SEC, IR, and ^1H NMR.

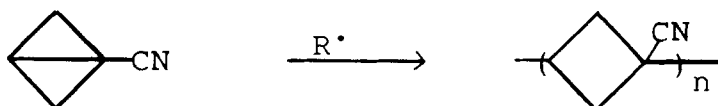
^1H NMR of the copolymer between the macromonomer and methyl methacrylate did not show the methylene protons of the main chain. This is explained by the broadness of that peak due to the restricted mobility of methylene protons of the main chain in the graft-type copolymer. After extraction of homopolymer, the copolymer showed high molecular weight, as shown by size exclusion chromatography. This result indicates that the macromonomer copolymerized well with methyl methacrylate.

Status and Conclusions

A macromonomer of poly(vinylidene fluoride) has been synthesized. It copolymerized well with methyl methacrylate. The copolymer will be studied more thoroughly. Copolymerization with other monomers can now be carried out.

Polybicyclobutane-1-carbonitrile [6]

Polyacrylonitrile and polymethacrylonitrile have high concentrations of nitrile dipoles. However, the helical structure of the polymer chains causes the radiating dipoles to cancel each other. This cannot be the case for poly(1-bicyclobutanecarbonitrile), as the rigid structure prevents helix formation. Accordingly, we prepared films of this polymer, and determined that they showed piezoelectric activity.



The polymer in film form was poled by applying an electric field across the film thickness at an elevated temperature to orient the $-\text{CN}$ groups in the film along an axis normal to the plane of the film. Samples of film ($25\ \mu\text{m}$ thick) were coated with a conductive Ag paste composition and poled at 205°C with an applied field strength of $50\ \text{kV/mm}$ of film thickness.

Key piezoelectric coefficients of the poled film demonstrated its piezoelectric activity. The transverse piezoelectric coefficient (d_{31}) was $0.3\ \text{pC/N}$ and the hydrostatic piezoelectric coefficient (d_h) was $1.4\ \text{pC/N}$ ($\text{pC/N} = \text{pico-coulombs/newton}$). The dielectric constant of the film was 4.34 at $3\ \text{Hz}$. The dynamic mechanical modulus (c_{11}) was $2.2 \times 10^{10}\ \text{dyne/cm}^2$, also at $3\ \text{Hz}$.

Results and Discussion

The results of our piezoelectric measurements show significant activity. This shows that even modest concentrations of dipoles in a glassy polymer can be effective if they are unable to cancel each other within a polymer molecule. The superior physical properties of poly(1-bicyclobutanecarbonitrile) offer advantages over those of poly(vinylidene cyanide-co-vinyl acetate). The high T_g of the polymer assures that the poled orientation will be locked over a wide range of lower temperatures. It has the highest T_g of any polymer that exhibits piezoelectric activity. This will permit its use as a transducer material up to higher temperatures than heretofore possible.

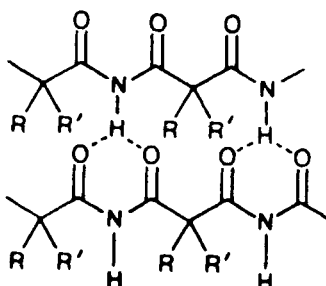
Status and Conclusions

Rigid polymer structures containing nitrile groups offer strong possibilities as piezoactive materials.

Polymalonimides [7]

Introduction

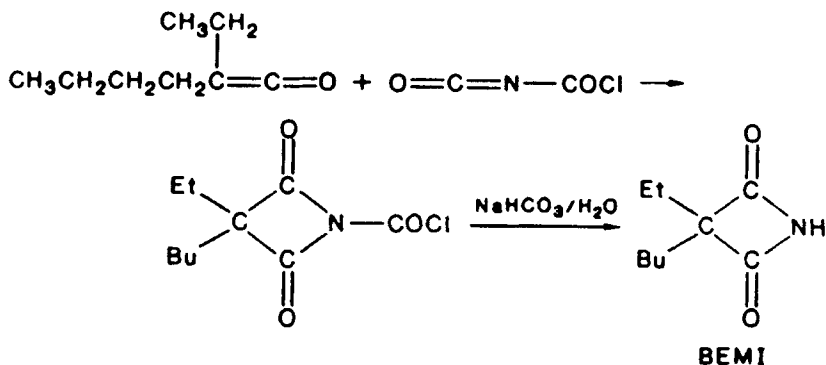
Polymalonimides have not been described in the literature even though interesting properties can be expected from these polymers, such as very efficient hydrogen-bonding between the chains.



The method of choice to obtain these polymers should be ring-opening polymerization of the malonimide ring, a four-membered ring that is expected to be highly strained. For anionic or hydrolytic ring-opening polymerization, the monomer should be unsubstituted at nitrogen.

Results and Discussion

3-Butyl-3-ethylmalonimide (BEMI) was synthesized in good yield via cycloaddition of butyl ethyl ketene and *N*-chlorocarbonyl isocyanate at room temperature.



The hydrolysis and decarbonylation of the chlorocarbonyl substituent proceeded at room temperature under heterogeneous conditions in good yield. BEMI is stable at room temperature for short periods of time but can be kept at -45°C indefinitely.

BEMI was polymerized using anionic initiators. The best results were obtained with potassium butoxide as initiator in bulk, giving a 58% yield of polymer with an inherent viscosity of 0.37 dL/g.

Status and Conclusions

The first member of a new family of cyclic monomers has been synthesized and polymerized. The polymer will be studied more thoroughly for higher molecular weight and film-forming ability. Piezoelectric evaluation will be carried out.

POLYMERS CONTAINING NLO-ACTIVE GROUPS IN THE MAIN CHAIN

Polyesters Containing Donor-Acceptor Quinodimethane Units [8]

Introduction

Second-order nonlinear optical (NLO) processes, including harmonic generation and the electrooptic effect, are the result of a nonlinear response in the polarization P of a dielectric, which is quadratic in the applied electric field of the light beams E :

$$P = \chi^{(2)} \cdot EE$$

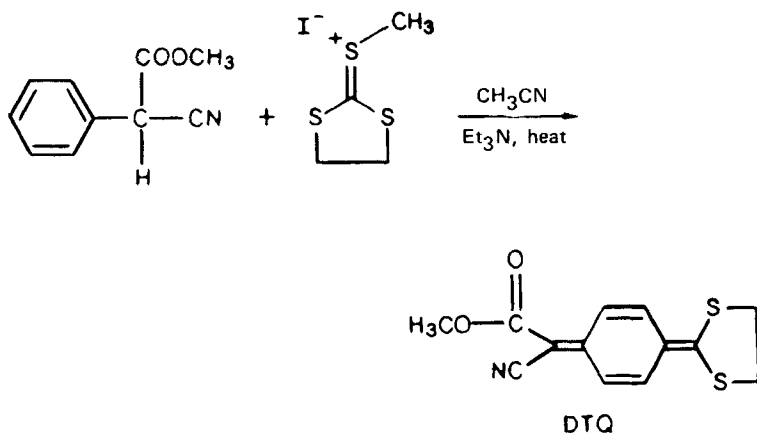
Understanding the origins of $\chi^{(2)}$ often requires examination of these interactions on the microscopic level. Here, the process can be viewed by the molecular polarization P which is induced by an electric field e local to the molecular environment:

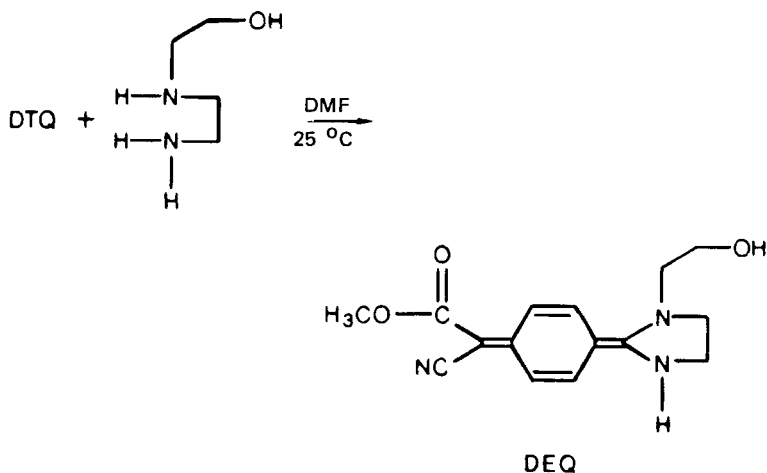
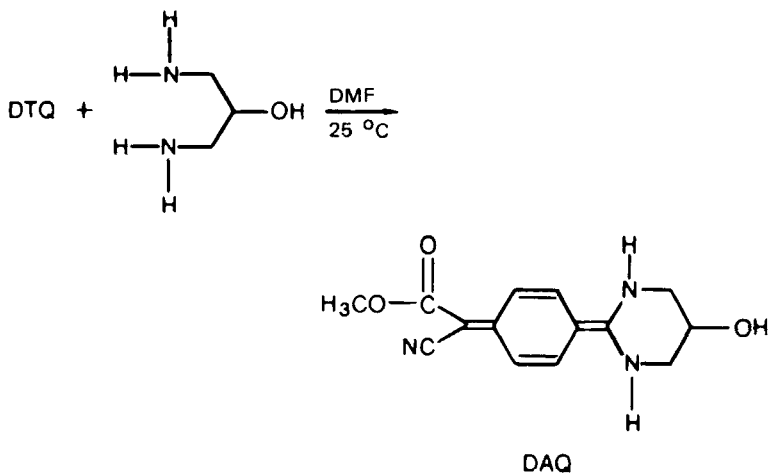
$$P = \beta : ee$$

where β is referred to as the second-order molecular hyperpolarizability. Much theoretical and experimental research in the past has been directed toward understanding the molecular origins of β . Of particular importance has been the discovery of the contributions of intramolecular charge-transfer in conjugated systems to the hyperpolarizability. This finding has resulted in the discovery of numerous molecules with large hyperpolarizabilities. We wished to prepare polyesters containing highly polarizable dipolar units, with all dipoles pointing in the same direction. The quinodimethane unit presented itself as a suitable choice for this purpose.

Results and Discussion

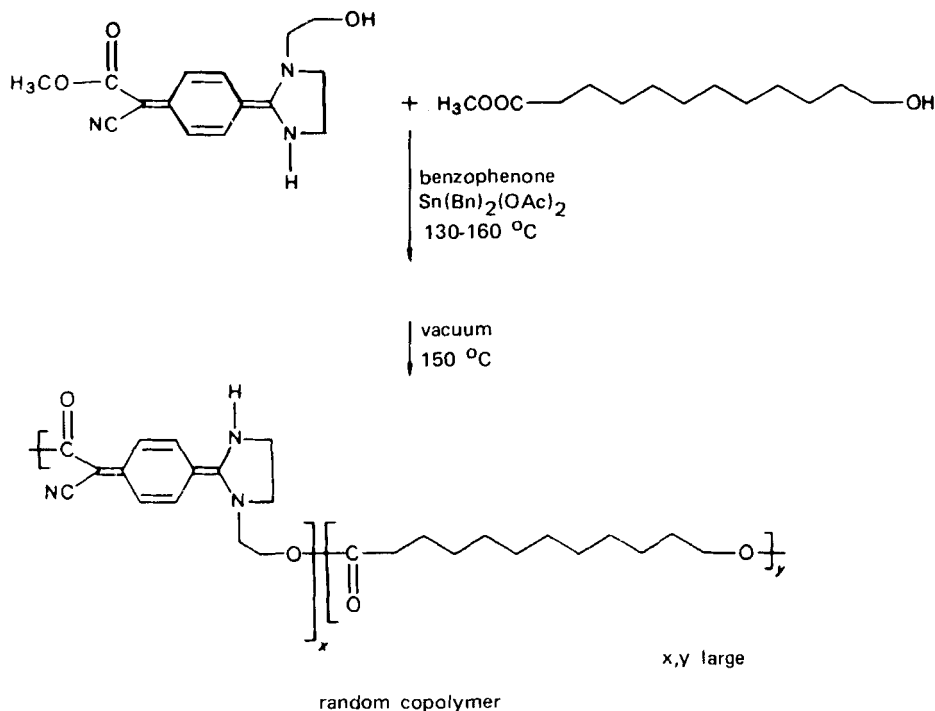
Monomer Synthesis. The donor-acceptor quinodimethane monomers were synthesized by condensation of 7,7-(ethylenedithio)-8-carbomethoxy-8-cyanoquinodimethane and a hydroxy diamine.





Polymer Preparation and Characterization. Attempted homopolymerizations of DEQ or DAQ established that the relative insolubility of these monomers creates an intractable homopolymer. Therefore, we investigated copolymer systems to lead to soluble polymers. A specialized polymerization process was needed to achieve high molecular weight polymers without decomposition of the quinoid structure. Utilizing the synthetic strategy outlined by Kantor, we performed the copolymerizations in benzophenone. Heating a mixture of DEQ and 12-hydroxydecanoic ester (1:1) in benzophenone (35 wt%) with di-

butyltin diacetate catalyst to 150°C under nitrogen resulted in the formation of a slurry. A second-stage polymerization process, application of high vacuum, allowed the formation of a high polymer from the slurry. Benzophenone was removed from the resulting copolymer by extraction with methanol. The copolymer obtained with this procedure was soluble in phenol/chlorobenzene (1:1) and hexafluoro-2-propanol (HFIP) at room temperature and dipolar aprotic solvents (DMF, DMSO, and *N*-methylpyrrolidone) at elevated temperatures. Inherent polymer viscosities ranged from 0.16 to 0.45 dL/g. The polymers all had crystalline melting ranges at 86°C. Glass transition temperatures were not detectable down to -40°C.



Status and Conclusions

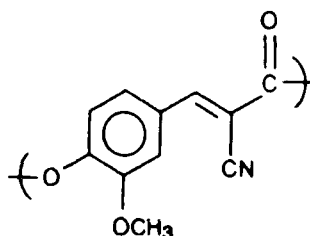
We successfully incorporated donor-acceptor quinodimethane monomers in condensation copolymers with more flexible α -hydroxy- ω -ester monomers. A procedure using benzophenone for the polyesterification led to 1:1 copolymers with moderate to high viscosities. In these polymers, as well as in the monomers, IR data indicate that a high degree of electron delocalization occurs from the donor moiety to the acceptor moiety. This proves that the

highly dipolar character observed in the monomeric quinodimethanes is preserved in the polymer chain, and all these dipoles point in the same direction. However, these polyesters containing donor-acceptor quinodimethane units were too polar, high-melting, and insoluble to permit spin casting from useful solvents.

Polyesters Containing *p*-Oxy- α -Cyanocinnamate Units [9]

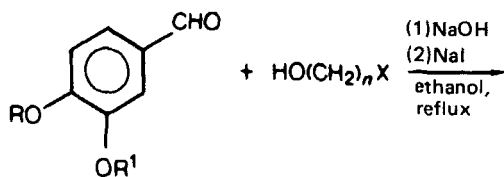
Introduction

In this work we have synthesized copolyesters with somewhat less dipolar repeats units than before in order to achieve processability. The group we selected is the *p*-oxy- α -cyanocinnamate unit.

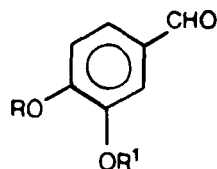


UV data for model compounds indicate that they are highly delocalized, but the dramatic shifts observed in the infrared spectra of the donor-acceptor quinodimethane monomers are not present here. This indicates that the *p*-oxy- α -cyanocinnamate derivatives are not as highly polarized, yet are more soluble and processable.

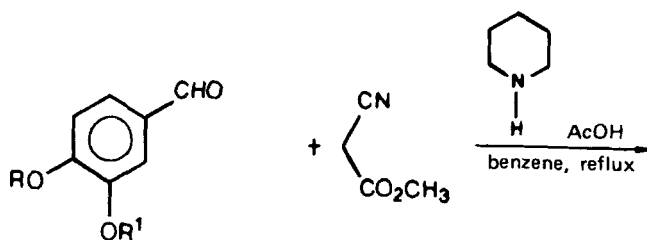
Synthesis of Monomers. In order to incorporate the above dipolar moiety into a polymer chain in a nonrandom fashion, an AB-type functionality is required, such as an ω -hydroxyester. Because the model studies proved that an ester substituent on the phenyl group greatly decreased the dipolar character of the monomer and because a long alkyl chain would improve the processability of the polymer, 4-hydroxy-3-methoxybenzaldehyde and 3-hydroxy-4-methoxybenzaldehyde were converted to (ω -hydroxyalkyl)benzaldehyde derivatives and then to the *p*-oxy- α -cyanocinnamate monomers.



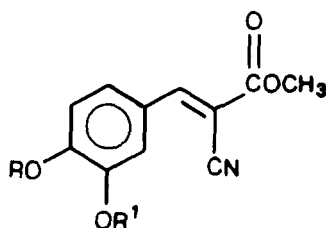
- 8a. $\text{R} = \text{H}; \text{R}^1 = \text{CH}_3$ $n = 3, \text{X} = \text{Br}$
 8b. $\text{R} = \text{H}; \text{R}^1 = \text{CH}_3$ $n = 6, \text{X} = \text{Cl}$
 8c. $\text{R} = \text{CH}_3; \text{R}^1 = \text{H}$ $n = 3, \text{X} = \text{Br}$



- 9a. $\text{R} = (\text{CH}_2)_3\text{OH}; \text{R}^1 = \text{CH}_3$
 9b. $\text{R} = (\text{CH}_2)_6\text{OH}; \text{R}^1 = \text{CH}_3$
 9c. $\text{R} = \text{CH}_3; \text{R}^1 = (\text{CH}_2)_3\text{OH}$



- 9a. $\text{R} = (\text{CH}_2)_3\text{OH}; \text{R}^1 = \text{CH}_3$
 9b. $\text{R} = (\text{CH}_2)_6\text{OH}; \text{R}^1 = \text{CH}_3$
 9c. $\text{R} = \text{CH}_3; \text{R}^1 = (\text{CH}_2)_3\text{OH}$



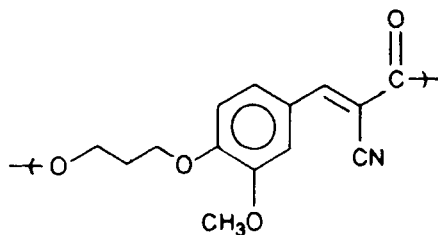
- 10a. $\text{R} = (\text{CH}_2)_3\text{OH}; \text{R}^1 = \text{CH}_3$
 10b. $\text{R} = (\text{CH}_2)_6\text{OH}; \text{R}^1 = \text{CH}_3$
 10c. $\text{R} = \text{CH}_3; \text{R}^1 = (\text{CH}_2)_3\text{OH}$

Polymer Synthesis and Characterization. Formation of polymers was accomplished with the standard two-stage high-temperature polyesterification procedure in the presence of dibutyltin diacetate.

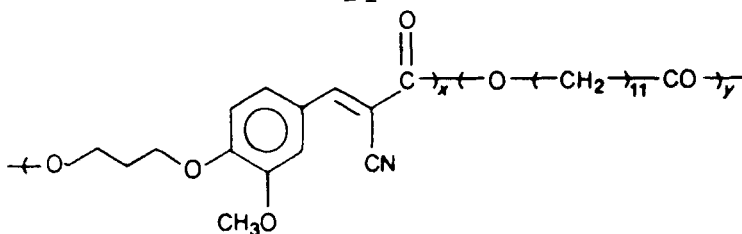
Homopolymerization of **10a** yielded **11**, a hard, yellow, brittle compound that showed only slight solubility in organic solvents such as dichloromethane and acetone, which prevented characterization by size exclusion chromatography. In order to increase polymer solubility in dichloromethane, copolymers of **10a** and methyl 12-hydroxydodecanoate were synthesized. These polymers were quite soluble, and by varying the Stage 2 reaction time, the average molecular weight could be controlled.

To maximize the average number of dipolar moieties per polymer chain, various monomer ratios were studied. A 2:1 copolymer (**10a** to methyl 12-hydroxydodecanoate) was easily soluble in dichloromethane and, therefore, easily characterizable. However, the 3.67:1 copolymer was insoluble.

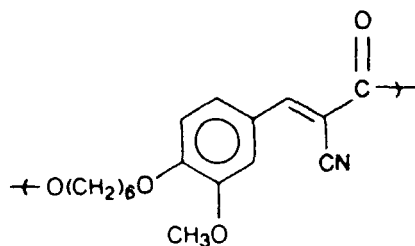
The desire to synthesize a soluble homopolymer led to the synthesis of **10c**, a monomer with a six-carbon alkyl chain. We hoped that the increase in alkyl chain length would result in a less crystalline polymer, which would therefore be more soluble. Unfortunately, homopolymer (**13**) of **10c** was insoluble in dichloromethane. A 3:1 copolymer (**14**) of **10c** and methyl 12-hydroxydodecanoate was also dichloromethane-insoluble.



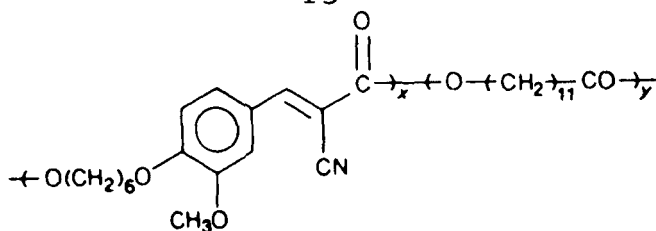
11



12



13



14

Solution-cast thin films were made from all of the soluble copolymers. These yellow, transparent films were flexible and amorphous. Upon heating, the films could be stretched to above 300% of their original length, yielding an oriented crystalline polymer. As the polymer was oriented, it became cloudy in appearance. Under the polarizing microscope it was observed that the polymer lacked crystalline domains before orientation and possessed them after orientation.

Discussion

Our presently reported *p*-oxy- α -cyanocinnamate polyesters are tractable, contain dipolar character, and can be cast from dichloromethane solutions into flexible, transparent thin films. Since these polymers can be oriented, causing crystal formation, they potentially possess good mechanical and NLO properties.

Status and Conclusions

Polyesters containing the reasonably dipolar *p*-oxy- α -cyanocinnamate units are soluble in spin-casting solvents. The films are clear and flexible, and undergo uniaxial orientation to give tough, flexible films.

Electric-Field Poling of Nonlinear Optical Polymers [10]

Introduction

The new group of nonlinear optical small molecules and polymers based on *p*-oxy- α -cyanocinnamate would be expected to display moderate second-order NLO properties on the basis of their conjugated electron donor-acceptor structures. In addition, their lowest electronic transitions lie in the ultraviolet region of the spectrum, making them potentially useful for frequency doubling into the visible. Measurements were performed on dilute solutions (<3 wt%) in chloroform.

The flexible main-chain polyesters all contain monomeric units which are oriented in the same direction along the polymer backbone. Homopolymers were found to be only slightly soluble in common organic solvents, but 1:1 random copolymers were readily soluble in chloroform. Absorption spectra for the copolymers and molecule II were nearly identical for the lowest excited, charge-transfer state ($\lambda_{\text{max}} = 363$ nm). Therefore, the chromophore electronic properties critical to the hyperpolarizability are assumed to be unperturbed by the polymerization; changes in the average molecular susceptibility are the result of orientational rather than chemical interactions.

Results and Discussion

Solution Measurements. The experimental data for model compounds are in Table 2, and data for two 1:1 copolymers of different lengths, as well as the NLO chromophore, are given in Table 3. The polymers display enhancements as large as a factor of 20 for the average monomer susceptibility relative to that of the NLO chromophore. This is due to the average polymer chain conformation in solution, which results in an effective chain dipole considerably larger than those of individual monomer units. The electric-field-induced SHG signal is, therefore, considerably larger for these correlated chains than for an equivalent concentration of monomeric units. The fact that the enhancement factor G is substantially less than n indicates that the conformation is far from extended.

Properties of Poled Polymeric Thin Films. An advantage of polymers with regard to poling applications is that they can exist in various viscous and non-viscous states. Molecular orientation can be frozen into polymeric materials by using the following sequence:

fixed isotropic $\xrightarrow{\text{mobilize}}$ mobile isotropic $\xrightarrow{\text{field on}}$ mobile polar $\xrightarrow{\text{freeze}}$ fixed polar

TABLE 2. Electric-Field Induced Second Harmonic Generation Results for *p*-Oxy- α -cyanocinnamate Derivatives

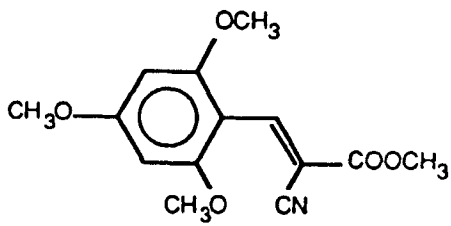
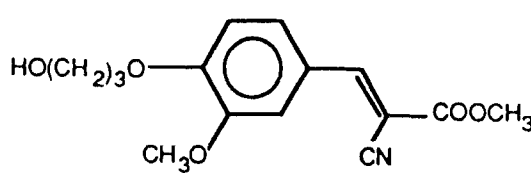
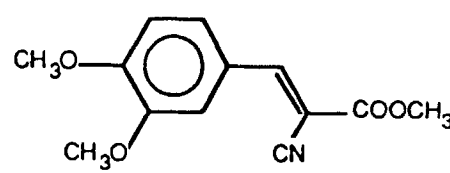
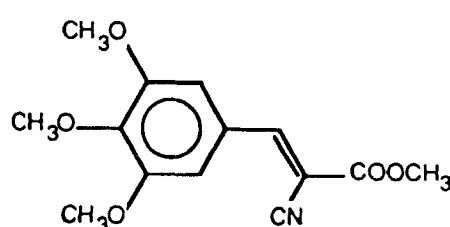
Monomer	$\mu_2\beta_z, 10^{-48}$ esu
I 	113
II 	57
III 	48
IV 	-10

TABLE 3. Average Monomer Susceptibilities for Various Molecular Weight Copolymers in Solution

Molecular weight, ^a \bar{M}_n	Calculated number of monomer units, n	$\mu_z\beta_z/n$, 10^{-48} esu	Enhancement factor, G
NLO chromophore ^b	—	57	—
17 000	37	830	15
70 000	152	1140	20

^aDetermined by GPC relative to polystyrene.

^bStructure II from Table 2.

“Thermal-locking” of a polar orientational distribution can be obtained by heating the polymer above the glass transition temperature T_g (mobilizing the polymer chains) and poling with an electric field. The orientational order is then fixed by cooling to temperatures below T_g before removing the field.

Differential scanning calorimetry (DSC) measurements revealed the glass transition temperature of the film to lie below room temperature. Hence, the sample could be poled at ambient temperature. The maximum electric field strength used in our experiments was 0.2 MV/cm. At room temperature, the SH intensity from the poled film was found to increase and decrease by at least one order of magnitude when the static field was turned on and off, respectively. In addition, a subsecond time response of the molecular orientation was encountered with no slow processes occurring over a period of 1 to 2 h. Next, the sample was cooled to approximately 220 K (well below T_g) before removal of the field. Here, the SH intensity from the poled sample appeared to be independent of the presence of the electric field. The signal was therefore assumed to be the result of a field-induced molecular reorientation with negligible contribution from third-order NLO mixing processes. In addition, the signal at 220 K was constant over a period of hours, indicating the fixed polar molecular alignment to be stable.

Next, the sample was slowly heated to room temperature with the field off. Two distinct transition temperatures in the SH signal were found (see Fig. 2). At ~ 250 K, a slow decline of the signal was noted, followed by a steeper decline beginning at ~ 285 K. The heat capacity, as measured by DSC, for the copolymer is also displayed in Fig. 2. There appears to be excellent overlap in the glass transition region of the heat capacity curve, i.e., T_g , and the steepest declining region of the SH intensity curve. In this region, one would expect to observe large-scale segmental motions in the polymer chains,

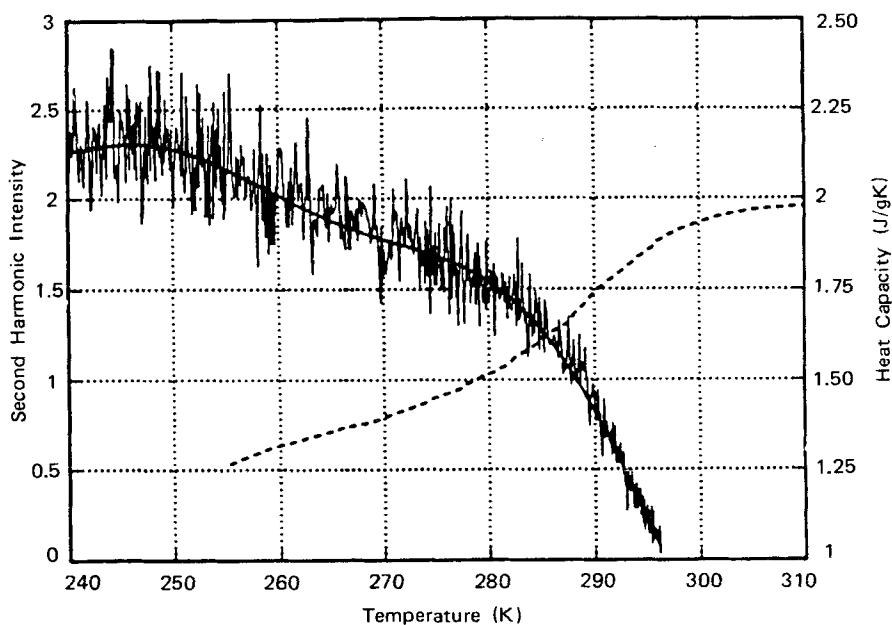


FIG. 2. Heat capacity and second harmonic intensity of the copolymer.

allowing for an orientational relaxation of the poled film and a subsequent loss in SH signal.

Mathematical analysis of our data gives an effective dipole moment for the poling process of $(30 \pm 5 D)f_0$. This value is much less than expected in solution and is the equivalent of segmental alignment over a distance of only 3 or 4 monomer units. Measurements performed at 310 and 360 K gave similar results, suggesting that the polymer motion is constrained even at temperatures well above T_g . This constrained motion leads to a $\mu_z\beta_z/n$ value for the poled polymer film of only 24×10^{-48} esu compared to 1140×10^{-48} esu for the same polymer in solution and 57×10^{-48} esu for the monomer.

Conclusions and Status

The second-order nonlinear optical susceptibilities were examined for a series of model monomer and copolymer compounds in dilute solution and thin film formats. Second harmonic generation experiments on poled solutions revealed that substantial enhancements in the SH conversion efficiency

(up to 20-fold increases) could be attained by incorporating the nonlinear optical chromophores into a polar main-chain polymer. This effect is the manifestation of overall increases in the field-induced molecular alignment through cooperative effects of the separate molecular dipoles. While investigations on thin films of the same copolymers showed that the poled molecular orientation could be frozen and maintained in the absence of the field, the degree of orientation in the thin films was found to be much less than that in the solution, but considerably more than an uncorrelated assembly.

ACKNOWLEDGMENTS

I am deeply indebted to my many able colleagues whose names appear on the cited papers. Cited references will be found in these papers. Generous funding was provided by the Office of Naval Research, the U.S. Army Research Office, the Eastman Kodak Company, the Celanese Company, and PPG Industries.

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