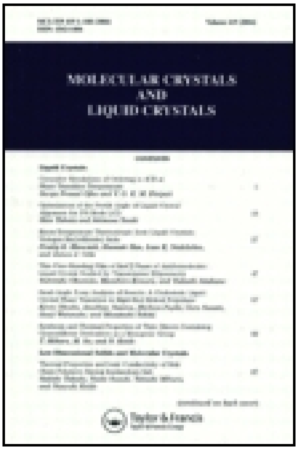

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C.-C. Han [a] & R. L. Elsenbaumer [a]

[a] Corporate Research and Technology, Polymer Sciences Laboratory, Allied-Signal, Inc., Morristown, New Jersey, 07962, USA

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Conveniently Processible Forms of Electrically Conductive Poly(Dibutoxyphenylene Vinylene)†

C.-C. HAN and R. L. ELSENBAUMER

Corporate Research and Technology, Polymer Sciences Laboratory, Allied-Signal, Inc., Morristown, New Jersey 07962 (USA)

Highly versatile conductive polymers have been derived from a variety of readily prepared, conveniently processible precursor polymers to substituted poly(phenylene vinylenes). Key discoveries were made that facilitate processing of these precursor polymers. These include the ability to stabilize solutions of dialkoxyphenylene-vinylene precursor polymers against gel formation by the addition of weak amines, and the preparation of new non-ionic precursor polymers that can be processed from a wide range of solvents. In addition to structurally diverse precursor polymers, our recent discovery that strong protonic acids are generally applicable as dopants for conjugated polymers provides methodologies for directly processing these polymers in their highly conductive forms. Protonic acid doped conductive polymers can be obtained by thermal conversion of polyelectrolyte precursor polymers that contain conjugate bases of relatively non-volatile strong acids. Further, methods have been developed for the conversion of non-ionic precursor polymers into doped conductive materials in solution at room temperature. Conditions can be chosen to prepare either the undoped or doped conjugated polymer. Partial formation of conjugated structures from these precursor polymers gives copolymers that display liquid crystalline behavior.

1. INTRODUCTION

Convenient processibility still remains a serious limitation associated with the application of today's inherently conductive polymers. A breakthrough came with the discovery that certain conductive polymers could be solution processed in liquid AsF_3 at room temperature[1] and liquid I_2 at elevated temperatures.[2] Although not commercially practical, these discoveries demonstrated the feasibility of processing typically rigid-chain, highly conjugated conductive polymers. Incorporating flexible alkyl substituents onto the backbone of thiophene[3] and pyrrole[4] based polymers was found to impart convenient solution and melt processibility to these systems without sacrificing conductivity. In general, these polymer systems are difficult to prepare with high molecular weights, which severely limits their mechanical properties. Recently, progress has been made in preparing high molecular weight

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poly(alkylthiophene)s with good mechanical properties.[5] The thiophene based polymers also suffer from being relatively unstable in ambient environments at temperatures above 90°C.[6]

Very high molecular weight poly(phenylene vinylene)[7] and poly(thienylene vinylene)[8] conductive polymers can be prepared from readily obtainable monomers. Owing to their high degree of conjugation, these polymers are only conveniently processible *via* nonconjugated water soluble precursor polymers. After casting these precursor polymers into films, they can be heat treated to induce an elimination reaction that generates the highly conjugated forms of these polymers. A subsequent doping step (redox process) is then needed to make the polymers highly conductive. Needless to say, from a commercial standpoint, the need for multiple process steps to fabricate a conductive article leaves much to be desired.

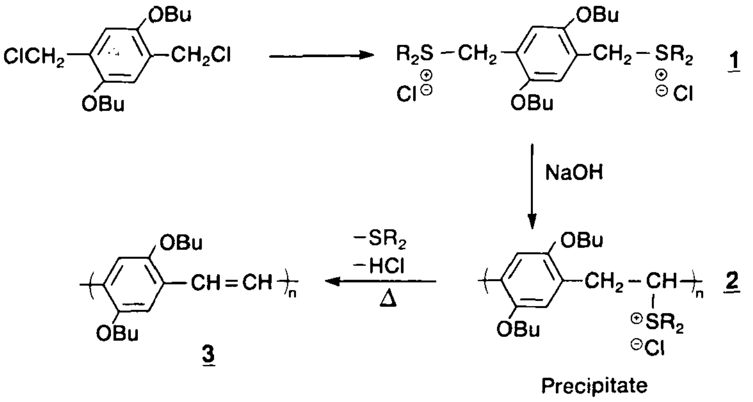
To be generally applicable for a wide range of electronic applications, inherently conductive polymers need to be conveniently melt-processible or solution-processible in their conductive forms. Alternatively, techniques need to be developed for the direct fabrication of conductive polymer articles by one step processes, from either monomers or processible precursor polymers. Herein we report the synthesis and properties of a novel conductive polymer, poly(dibutoxyphenylene vinylene), and the progress we have made toward achieving these processing goals.

2. RESULTS AND DISCUSSION

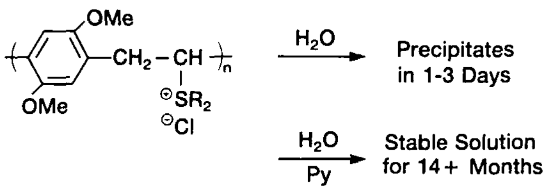
2.1 Preparation of Processible Precursor Polymers to Poly(dibutoxyphenylene vinylene) (PDBPV)

To make a high molecular weight soluble conductive polymers, we chose to introduce long-chain alkoxy substituents into thienylene-vinylene[9] and phenylene-vinylene conjugated polymer systems. Alkoxy substituents were chosen for several reasons. As in the case with poly(alkylthiophenes), the introduction of flexible side chains was expected to reduce interchain interactions and increase chain disorder, thereby giving the polymer solution and possibly melt processibility. In contrast to alkyl substituents, the strong electron donating ability of alkoxy groups was expected to reduce polymer ionization potentials giving rise to conductive compositions with improved environmental and thermal stability. Lastly, it has been shown that methoxy substituted phenylene-vinylene polymers give highly conductive materials (500 S/cm)[10] whereas methyl substituted phenylene-vinylene polymers do not (10^{-5} S/cm).[11]

Poly(dibutoxyphenylene vinylene) (poly(1,4-dibutoxy-2,5-phenylendiyl-1′,2′-vinylendiyl),PDBPV, $\underline{3}$) was prepared in a fashion analogous to that used to make poly(phenylene vinylene)[7,12] and poly(thienylene vinylene)[8] as outlined in Equation 1. 1,4-Dibutoxybenzene was synthesized from hydroquinone and n-butyl bromide by the Williamson ether synthesis.[13] 1,4-Bis(chloromethyl)-2,5-dibutoxybenzene was prepared from 1,4-dibutoxybenzene by chloromethylation according to the procedure of Wood and Gibson.[14] 2,5-Dibutoxyphenylene-1,4-dimethylene bis(tetramethylene sulphonium chloride) was synthesized by reacting 1,4-bis(chloromethyl)-2,5-dibutoxybenzene with an excess of tetrahydrothiophene (three equivalents) in methanol at 50°C.

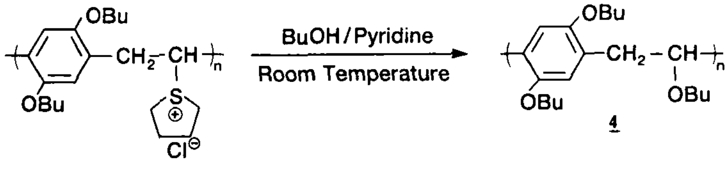


Upon treatment of a degassed aqueous solution (0.4 M) of the bis-sulfonium salt 1 with an equimolar amount of NaOH (0.4 M) at 0°C, a white gummy polymer precipitated, which was then repeatedly washed with water. The solid polyelectrolyte precursor polymer 2 could be dissolved into organic solvents such as methanol, ethanol, ethanol/benzene, ethanol/n-hexane, DMF/toluene, acetonitrile/water, and water at high dilution. All of these polymer solutions, except one, were unstable. Within hours, the polymer reprecipitated or formed a gel that could not be redissolved. However, the solution behavior of the polyelectrolyte precursor polymer 2 in DMF/toluene was found to be unique. In this solvent system, the polymer solution was surprisingly very stable. We surmised that the presence of a weak base in the solvent was responsible for preventing the polyelectrolyte polymer from precipitating or forming gels. Indeed, we discovered that, in general, small amounts of a variety of weak bases, especially pyridine, substantially stabilized aqueous and non-aqueous polyelectrolyte solutions of the precursor polymers to both poly(dialkoxyphenylene vinylenes)[15] and poly(heteroaromatic vinylenes).[16] Stabilized fresh solutions have remained precipitate and gel free for several months to years at room temperature (Equation 2). Polymers obtained from stabilized solutions also exhibit much greater conductivities than those from non-stabilized solutions.[15] Having stabilized solutions of these precursor polymers has greatly facilitated the processing of these important conducting polymer systems.



	Conductivity (S cm^{-1})	
PDMPV	I_2-Doped	$FeCl_3$-Doped
Pyridine-Stabilized	500	300
Unstabilized	50	30

Interesting results were obtained when the precipitated precursor polymer 2 was redissolved in, and dialyzed against (3–5 days), a butanol solution containing a small amount of pyridine (0.5–1 wt%). By casting the butanol solution and evaporating the solvent, a highly elastic new precursor polymer (4) was obtained (Equation 3). This yellow precursor polymer was found to be highly soluble in a variety of common organic solvents. It was also thermally stable; no change was observed on heating to 150°C in vacuum.



This new precursor polymer was established to be poly(1,4-dibutoxyphenylen-2,5-diyl-1′-butoxy-1′,2′-ethylendiyl) (4) as evidenced by elemental and ^1H NMR analyses. Apparently, the substitution of the sulfonium groups by butanol is a relatively facile process.[8b,12,15] The thermogravimetric analysis (TGA) (Figure 1) and pyrolysis-mass spectra of polymer 4 showed that only ca. 2% weight loss occurred on heating up to 150°C in argon, owing to the loss of solvent and a small amount of pyridine. A further 20% weight loss occurred between 150–300°C resulting from the thermal elimination of butanol from the benzylic carbons. A small amount of tetrahydrothiophene was also detected in this temperature range, implying that 4 still contained a small fraction (ca. 4.3%) of undisplaced sulfonium units.

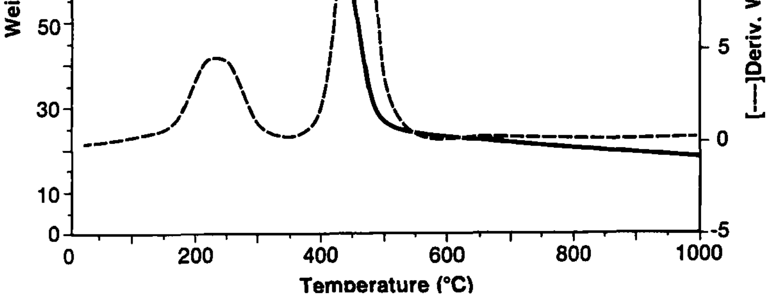


FIGURE 1 Thermogravimetric Analysis of Polymer 4 in Argon (10°C/min).

Differential scanning calorimetry on precursor polymer 4 (Figure 2) showed it had a glass transition temperature at 2.6°C. Gel permeation chromatography indicated that polymer 4 was obtained with a high molecular weight (Mw 2.7 × 10^6; Mn 6.6 × 10^4; Mw/Mn = 40.9).

2.2 Preparation of Poly(dibutoxyphenylene vinylene) by Thermal Methods

Freestanding films of PDBPV (3) were prepared from cast films of polymer 4 by thermal elimination of butanol at 220–250°C in vacuo. Films of the highly conjugated polymer were red in color and readily dopable with acceptor dopants (oxidants) such as ferric chloride (1 wt% $FeCl_3 \cdot 6H_2O$ in CH_3NO_2 at 20°C) and nitrosonium hexafluoroantimonate (1 wt% $NOSbF_6$ in CH_3NO_2 at 20°C). Typical conductivities for doped films are given in Table I. The conductivities of PDBPV prepared from the tributoxy precursor polymer 4 were found to be generally lower than those obtained on doping poly(dimethoxyphenylene vinylene) (PDMPV) prepared from sulfonium-containing precursor polymers. Lower conductivities for PDBPV relative to PDMPV might be expected for at least two reasons. One, the number of conjugation defects in PDBPV is expected to be greater than that in PDMPV because the thermal elimination of benzylic alkoxy fragments from 4 is generally more difficult and therefore probably less complete than the elimination of sulfonium fragments. The presence of uneliminated fragments causes disruption of conjugated conductive pathways along the polymer chain. Longer conjugation lengths usually provide higher conductivity polymers. And two, the greater steric requirements of the butoxy groups relative to methoxy groups may cause a greater inter- and intra-chain impedance to electron transport in PDBPV than in PDMPV. Larger coplanar conjugated chain segments improve effective electron overlap

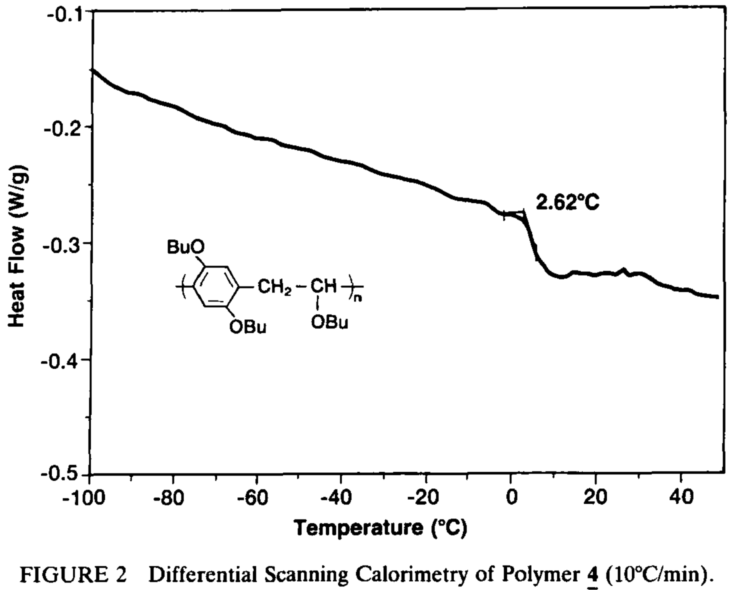


FIGURE 2 Differential Scanning Calorimetry of Polymer 4 (10°C/min).

TABLE I

Conductivities of p-doped PDBPV

Exp.	Dopants	Conductivities (Scm^{-1})
1	I_2	2.1
2	$FeCl_3 \cdot 6H_2O$	2.0
3	$NOSbF_6$	1.5
4	$Fe(OTs)_3$	0.008
5[*a]	I_2	14
6[*b]	I_2	2.2±0.7
7[*c]	I_2	98

[*a] Observed on non-thermally prepared PDBPV

[*b] Average conductivity over three sequent iodine-doping and dedoping cycles on the same sample film.

[*c] Observed on stretch-oriented PDBPV with a stretch ratio (L/Lo) of 7.

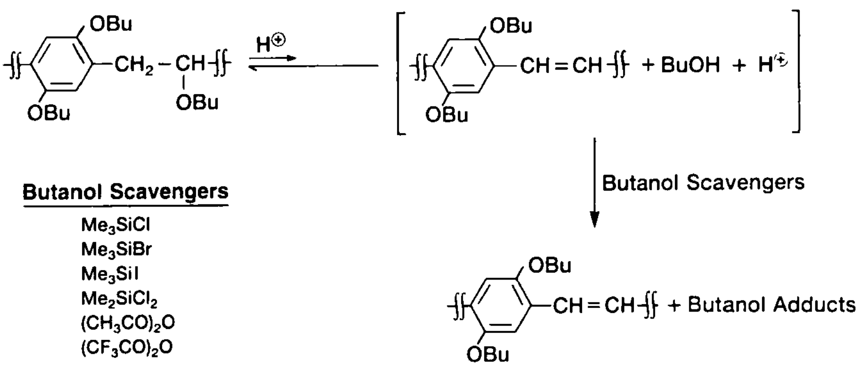
along the polymer chain and closer proximity of neighboring chains improves the probabilities for electron transport between chains. The latter feature is especially important for establishing a three dimensional conductive network within the bulk of a polymer sample.

Thermally prepared PDBPV films could not be redissolved into common organic solvents. Presumably, this insolubility arises from thermally induced crosslinking that takes place along with elimination of butanol. Crosslinking provides another source of conjugation defects that can adversely affect conductivity.

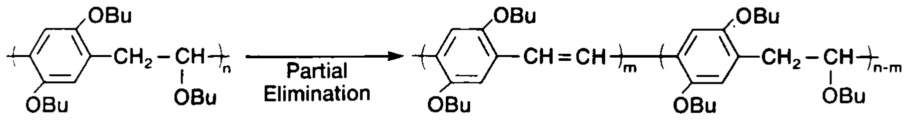
2.3 Preparation of Poly(dibutoxyphenylene vinylene) (3) by Non-Thermal Methods

The high temperatures needed to convert the tributoxy precursor polymer 4 to PDBPV, and the poor solubility and conductivity of the so formed conjugated polymer, necessitated the development of alternative techniques to effect elimination and formation of a higher quality conjugated PDBPV.

We found that a catalytic quantity of a protonic or Lewis acid readily induced loss of butanol from polymer 4 at room temperature.[15,17] Saito and coworkers also observed that at elevated temperatures the presence of protonic acids was necessary to induce nearly complete thermal elimination of methanol from similar phenylene-vinylene non-ionic precursor polymers.[18] It appears that under normal conditions, an equilibrium reaction is established between 4 and PDBPV, where the position of the equilibrium resides largely to side of polymer 4 (Equation 4). We found that with the addition of a butanol scavenger, the equilibrium reaction is driven toward nearly complete formation of PDBPV at room temperature. Our results showed that an acid and a butanol scavenger are needed for effective elimination. Useful butanol scavengers were reagents capable of irreversibly reacting with butanol, such as acetic anhydride, trifluoroacetic anhydride, trimethylsilyl chloride, dimethyl dichlorosilane, and the like. A variety of protonic acids were found useful; even relatively weak acids such as acetic acid were effective.



PDBPV prepared *via* this non-thermal elimination method from precursor polymer 4 is highly conjugated and yet highly soluble in common organic solvents such as chlorobenzene and toluene at concentrations up to at least 2 wt%. The conductivity of an iodine-doped PDBPV film prepared by this non-thermal elimination method (Table I, entry 5) was nearly an order of magnitude higher than that observed on a film prepared by conventional thermal elimination (Table I, entry 1). Non-thermal methods for the formation of soluble conducting polymers provides an important technological advancement for processing these types of conductive polymers. This new method makes it possible to prepare thin conductive coatings onto heat sensitive substrates and low melting polymers.



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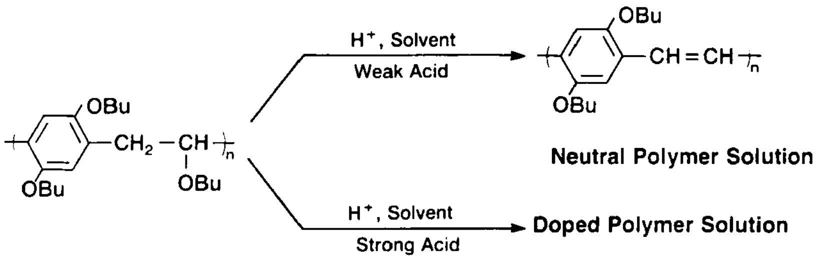
The degree of elimination from the tributoxy precursor polymer can be controlled by using an appropriate amount of alcohol scavenger and short reaction times (Equation 5). Partially eliminated precursor polymers (5) can be cast from solution to give freestanding films having good mechanical properties. Solutions of polymer 4 change gradually from yellow to orange to red as the degree of elimination and length of conjugated segments increase. Films of partially eliminated precursor polymers are less sticky than uneliminated ones. In practice, the partially eliminated precursor polymer films are easier to handle. Highly oriented PDBPV can be easily prepared from these partially eliminated films by first stretch-orienting 5 at room or elevated temperatures, then heating the oriented polymer under vacuum at high temperatures to complete the elimination. The conductivity of stretch-oriented films can be significantly greater than unoriented ones; a sample with an elongation (L/L_0) of 7 exhibited a 47-fold conductivity enhancement in the stretch direction (see entry 7 in Table I).

2.4 Formation of Conductive Polymer Solutions From Solutions of Precursor Polymers by Simultaneous Elimination and Doping

During our development of non-thermal methods to prepare conjugated polymers from precursor polymers, we made a very interesting observation. When polymer 4 in a nonaqueous solvent was subjected to treatment with a butanol scavenger and a protonic acid with a pK_a (aqueous) less than about two, the resulting solution of the conjugated polymer was not the expected red color characteristic of a solution of the undoped polymer. Rather, a deep green, or green-blue solution was obtained. Recognizing that green and green-blue colors are typical for conductive polymers, we suspected that these new solutions were in fact solutions of doped PDBPV (see Equation 6). This speculation was confirmed by ESR and Vis-NIR absorption spectra. Subsequently, we recognized that protonic acids are generally applicable as dopants for a wide range of conductive polymers.[17]



Dilute solutions of protonic acid doped PDBPV in chloroform were transparent and stable for more than 4 weeks at room temperature (23°C). Absorption spectra of these solutions are shown in Figure 3. Three prominent absorption bands for

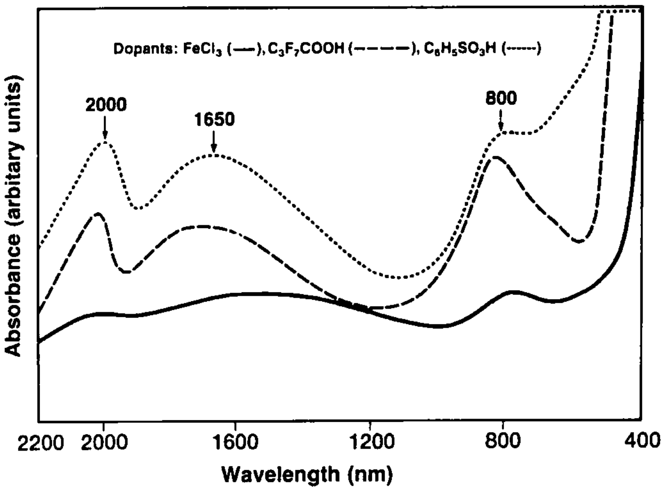
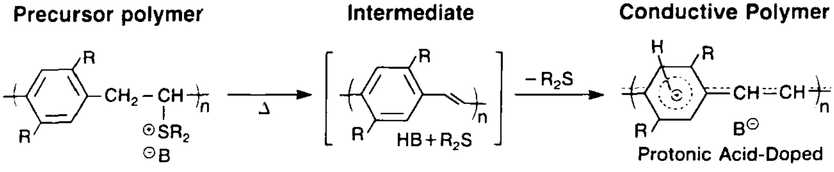


FIGURE 3 Near IR—Visible Spectra of Solutions of Doped Poly(Dibutoxyphenylene Vinylene).

protonic acid doped PDBPV in solution are evident at 0.6, 0.8, and 1.54 eV. These bands are very similar to those observed for conventional redox doped, conductive PDBPV and PDMPV films.[17] ESR spectra of the solutions exhibited a strong signal at a g value of 1.0019 with a ΔHpp of 6.9 Gauss. The observed absorption and ESR spectra are characteristic of polaronic type electronic defects.

To further extend the processibility of dialkoxyphenylene-vinylene polymers, we developed a thermally activated process for the direct conversion of the precursor polymers into doped conjugated polymers in the solid state.[15,17,19] Here, sulfonium-containing precursor polymers (2) of PDBPV were used (Equation 7). Best results were obtained when B^- was a conjugate base of a protonic acid that has an inherently low vapor pressure, and when the transformation was carried out at low to moderate temperatures (20 to 150°C).



$B^{\ominus}$= Halogen, $BF_4^{\ominus}$, $PF_6^{\ominus}$, $SbF_6^{\ominus}$, $RSO_3^{\ominus}$, etc.

2.5 Liquid Crystallinity

Partially eliminated precursor polymer 5 can be viewed as a copolymer of 1,4-dibutoxyphenylene-vinylene units and 1,4-dibutoxyphenylene-1′-butoxyethylene units. One can consider this copolymer to be made up of alternating rigid, highly conjugated block and flexible, non-conjugated block chain segments. Because of the random nature of the elimination process, the length of each segment can vary depending on the overall degree of elimination. Nonetheless, it would be expected that the rigid chain segments would tend to aggregate and align in the solid state. As such, we hoped these partially conjugated polymers would exhibit liquid crystalline behavior. Indeed, liquid crystallinity was observed when polymer 5 was first heated above its softening point (140–150°C) and then sheared between two glass slides. The liquid crystalline properties of 5 were retained on cooling to room temperature. Heating above 160°C caused further elimination of butanol, and when the degree of elimination exceeded a certain limit, the liquid crystallinity disappeared. The liquid crystalline form of polymer 5 exhibited an amorphous x-ray pattern and displayed no indication of a glass transition temperature or melting point. Therefore, polymer 5 might best be described as a glassy liquid crystalline material. Considering that stretch-orientation of polymers provides an alternative method for shearing polymer chains at the molecular level, it came as no surprise that stretched samples of 5 also exhibited liquid crystalline behavior.

3. SUMMARY

The unusual optical, electrical and liquid crystalline properties of PDBPV, coupled with the various techniques developed for its fabrication, makes PDBPV an attractive material for many potential applications.

Acknowledgment

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