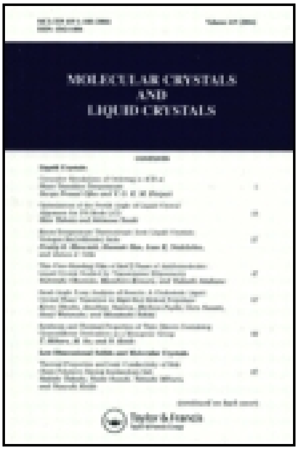

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Synthesis and Electrical Properties of Crosslinked Poly(1,2,4,5-Phenylenedivinylene) and Copolymers

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SYNTHESIS AND ELECTRICAL PROPERTIES OF CROSSLINKED POLY(1,2,4,5-PHENYLENEDIVINYLENE) AND COPOLYMERS

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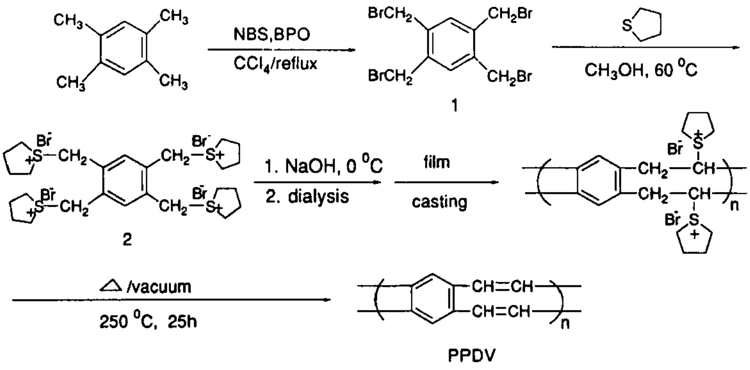
Abstract Crosslinked conjugated conducting polymer, poly(1,2,4,5-penylene divinylene)(PPDV) and its copolymers were prepared by the water-soluble precursor method. The spectral characteristics of these materials have been investigated by using UV-visible and FT-IR spectroscopy. PPDV homopolymer film could not be stretched due to its crosslinked structure, so this homopolymer could slightly be doped with strong oxidant, $FeCl_3$, to produce a very low conductivity value of 3 x 10^{-6} Scm^{-1}. However, copolymers containing PDV units and DMPV units showed considerably high conductivities ranging from 3 x 10^{-2} to 68 Scm^{-1}, when doped with $FeCl_3$, depending upon the copolymer composition.

Keywords: crosslinked conjugated, water-soluble precursor, conductivity, copolymer composition

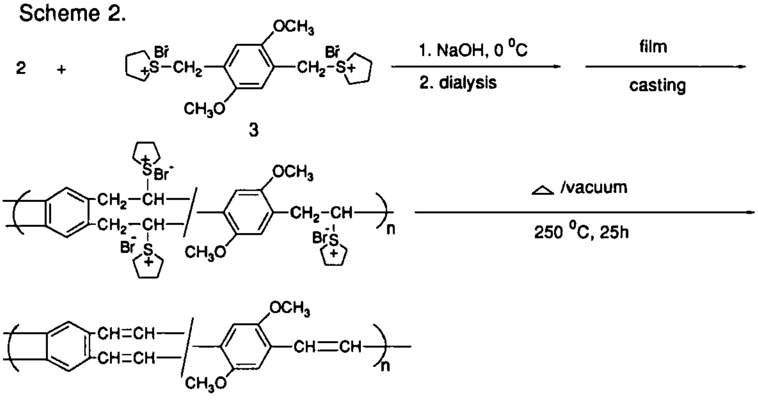
INTRODUCTION

Conjugated polymers are currently considerable interest as materials for a wide variety of application and the present concern is in polymers which are potentially conductive.[1-3] Poly(1,4-phenylenevinylene)(PPV) and its derivatives are of interest for their electrooptical properties, especially for their ability to be doped with either oxidizing or reducing agents to form films with unusually high electrical conductivities.[4-5] PPV and its derivatives can be easily prepared in high molecular weight through the water-soluble method.[6-8] The precursor sulfonium salt polymers are converted into extended π-conjugated structures by thermal elimination reaction. The PPV films can be easily doped with strong oxidizing agent such as AsF_5 to produce highly conducting materials, but they can not be doped with weak oxidant like I_2. Such highly stretched films show a significantly enhanced conductivity on doping along the draw direction.[9-10] Interestingly enough, there has not been any report on the synthesis and electrical properties of poly(1,2,4,5-phenylenedivinylene)(PPDV) which is a chemically crosslinked PPV. We prepared PPDV by the water-soluble precursor method. A series of copolymers was also prepared to study the dependence of electrical conductivity on polymer composition. It is our purpose to learn more about the effect of morphological change on the electrical properties of crosslinked PPDV and its copolymers. The structures of PPDV and copolymers prepared and characterized in this study are shown below.

Scheme 1.



Scheme 2.



EXPERIMENTAL

1. Monomer Synthesis

1,2,4,5-Tetrakis(bromomethyl)benzene(1) was prepared by reacting 1,2,4,5-tetramethylbenzene with N-bromosuccinimide(NBS). NBS(35.7g; 0.20mol) and 1.0 g of benzoyl peroxide were dissolved in 150 ml of CCl_4. This suspension solution was mixed with 1,2,4,5-tetramethylbenzene(6.0g; 0.075mol). The mixture was refluxed for 1 hr at 77℃ under nitrogen atmosphere. The solution was concentrated and then poured into petroleum ether. After filtration, pure 1,2,4,5-tetrakis(bromomethyl)benzene was obtained by recrystallizing the crude product from ethanol. Yield was 9.7 g(49%). The compound(1) and excess tetrahydrothiophene(11.0g; 0.12mol) were reacted for 5 hrs at 60℃ in 70ml of methanol. The momomer salt, 1,2,4,5-phenylenetetramethylenetetrakis(tetrahydrothiophenium bromide)(2), was obtained by concentration of the reaction solution, precipitation in cold acetone, filtration and vacuum drying. Yield was 10.5 g (74%). ^{1}H-NMR(D_2O) ; δ 8.0(s,2H), 4.8(s,8H), 3.7~3.5(m,16H), 2.7~2.4(m,16H) and 4.7(HDO from solvent) ; See Figure 1. The compound(3) was prepared similarly from 2,5-dimethoxy-1,4-bis(chloromethyl) benzene following the literature method.[1-4]

2. Polymerization

The procedure used for the preparation of homopolymer and copolymers was the same as reported by us and others[1-4]. The monomer sulfonium salt solution(0.3M) was polymerized by dropping 1 N NaOH solution under a nitrogen atmosphere at 0℃. The base solution was very slowly added to the monomer sulfonium salt solution to avoid the powder forming during polymerization. For the copolymers, the total moles of the two sulfonium salt monomers were kept constant(0.3M), but their mole ratio was varied. After the reaction was quenched by neutralization with standard 1.0 N HCl solution, the resulting polyelectrolyte precursor solution was dialyzed against deionized water for 3 days using a dialysis tube(Sigma) with a molecular cut-off at 12,000 to remove the low molecular weight species. The films cast from this precursor polymer solution were subjected to thermal elimination in vacuo(10^{-2} torr) at 250℃ for 25 hrs to transform into the final polyconjugated polymer. If desired, the precursor polymer films were uniaxially drawn at 120℃ using a zone-heating apparatus.

3. Analysis

Elemental analyses were performed by the Analytical Department of the Korea Research Institute of Chemical Technology. ^{1}H-NMR spectra were recorded on a Brucker AM 300 spectrometer and IR spectra were obtained on a Bomem Michelson series FT-IR spectrometer. The differential scanning calorimetry(DSC) and thermogravimetry(TGA) thermograms were recorded on a Dupont 9900 analyzer. A heating rate of 10℃ was utilized for both analyses. Conductivities were measured using a four-in-line probe configuration on which resistance measurements were performed using a Keithley 197 digital multimeter.

RESULTS AND DISCUSSION

The final polyconjugated films had a golden brown to light brown color depending on the elimination condition and copolymer composition. Typical film thickness was 10~27 μm. The ^{1}H-NMR spectrum shown in Figure 1 agrees with the anticipated spectrum of the salt monomer(2). Table 1 summarizes the data for the monomer conversions to the precursor polymers and polymer yields. Data for conversion were obtained by titration of the precursor polymer solution with standard 1.0 N HCl. Polymer yields were calculated from the weight of the remaining polymer after evaporating the solvent. The degrees of monomer conversion(75~94%) to precursor polymers are slightly higher than those reported for other similar polymerization systems, but the polymer yields(12~28%) after dialysis are slightly lower than those of other systems.[2,6] These results are very interesting. The reaction sites of our salt monomer(2) which has tetrafunctionality are twice as many as other typical salt monomers. Therefore, the degrees of conversion are very high. As the contents of tetrasulfonium salt units(PDV) in the precursor polymer increased, the degree of conversion increased. However, the polymer yield is decreased with increasing the content of tetrasulfonium salt units(DMPV) in polymer. It is explained that crosslinking reaction gave the low molecular weight polymers, and these low molecular weight polymers were removed through the dialysis process. As shown in Table 1, the contents of tetrasulfonium salt units incorporated into copolymers are significantly higher than those in the monomer feed mixtures, suggesting that the reactivity of tetrasulfonium salt monomer is greater than that of the dimethoxy-contained monomer.

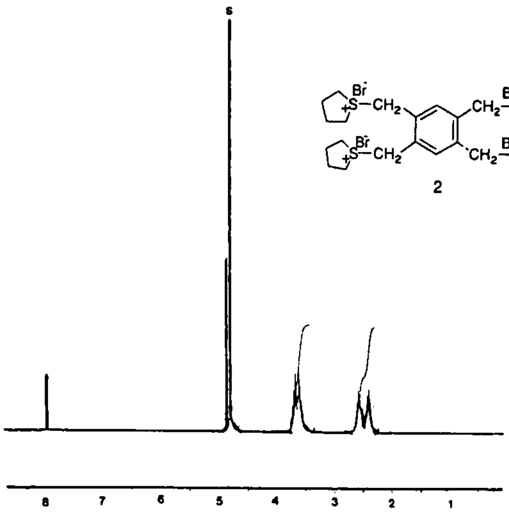


FIGURE 1. ^{1}H-NMR spectrum of the salt monomer(2)

TABLE 1. Monomer conversions and polymer yields

Polymers[a)]	Feed mole ratio	Monomer conversion in %	Polymer yield in wt.%
PPDV	0:100	94	12
54-Poly(DMPV-co-PDV)	83:17	85	22
28-Poly(DMPV-co-PDV)	91:9	87	28
7-Poly(DMPV-co-PDV)	95:5	75	26

[a)] The numerical values stand for mole % of PDV units in the final copolymers, and these numbers were calculated from the results of the elemental analyses.

Thermal analyses of the elimination reaction of the precursor polymer were studied by DSC and TGA with a heating rate of 10℃/min. As shown in Figure 2, the low temperature(about 100℃) endotherm in the DSC curve corresponds to the loss of water, and the higher temperature(about 150℃) one to the elimination of HCl and tetrahydrothiophene.

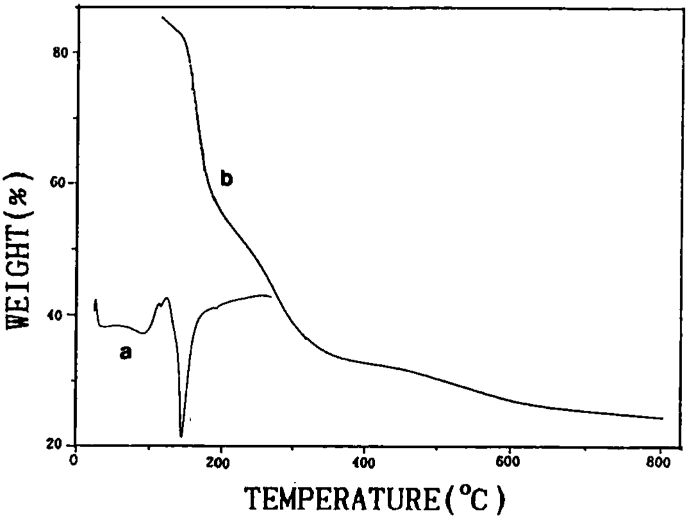


FIGURE 2. DSC(a) and TGA(b) thermograms for the precursor polymer of PPDV

FT-IR spectrum of PPDV film is compared with that of the precursor polymer film in Figure 3(a) and 3(b). The precursor polymer film exhibited a broad and strong absorption at 3125~3650 cm^{-1} due to the presence of absorbed water, which disappears in the spectrum of the eliminated film. This polymer reveals strong absorption at 962 cm^{-1} due to out-of-plane bending vibration of trans-vinylene C-H bond, and another absorption at 892 cm^{-1} which is known to be due to the cis-vinylene C-H out-of-plane bending mode.[11-12] Generally, it is well known that trans-vinylene structure was formed through thermal isomerization during the elimination process, but crosslinking formed by the tetrafunctionality of our tetrasulfonium salt monomer certainly restricts conformational rotation around C-C bonds of incipient vinylene groups and thus brings about the formation of trans- as well as cis-vinylene groups.

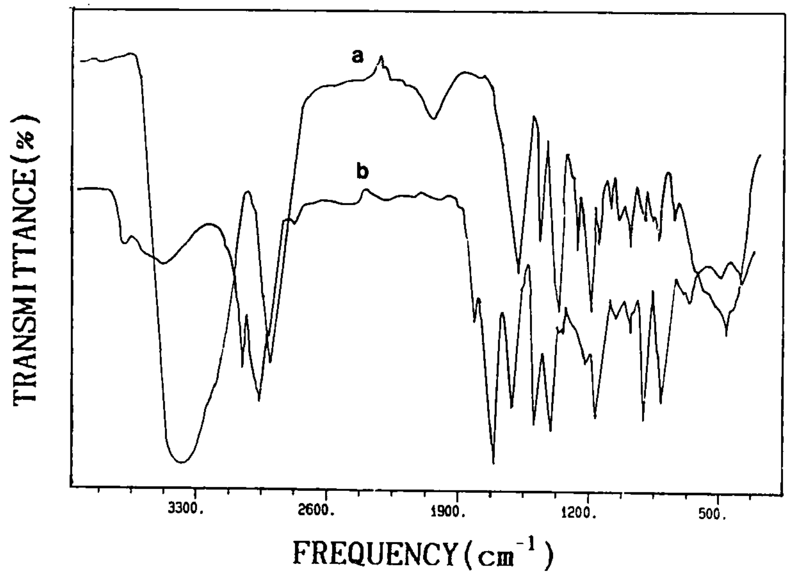


FIGURE 3. FT-IR spectra of precursor polymer(a) and PPDV(b) film

Figure 4. shows UV-visible spectra of thin films of PPDV and copolymers. The maximum absorptions and absorption edges of PPDV and its copolymers are shifted to the shorter wavelength relative to poly(2,5-dimethoxy-1,4-phenylene vinylene) (PDMPV). Particularly, the maximum absorption of PPDV homopolymer is appeared at very shorter wavelength region compared with those of the copolymers. Cross linking would diminish the effective π-delocalization resulting in blue-shift in UV-visible spectrum, and the structural characteristics of the present polymers containing both trans- and cis-vinylene geometry also can be attributed to the diminished effectiveness in π-delocalization.

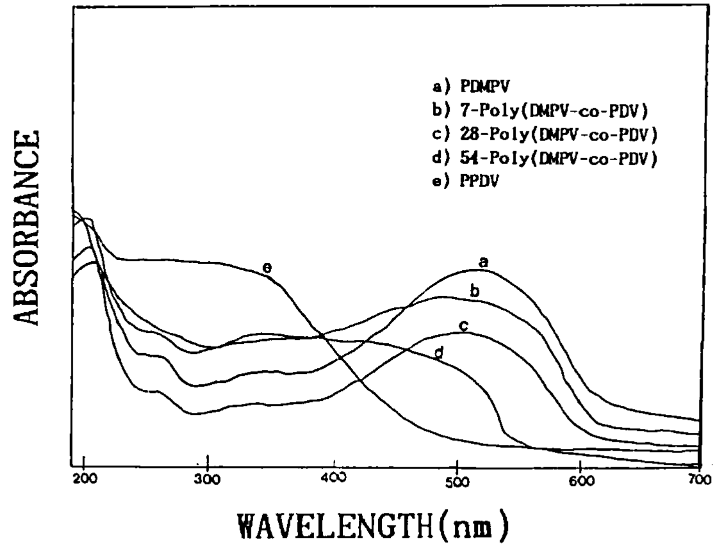


FIGURE 4. UV-visible spectra of eliminated PPDV and copolymers

Table 2 summarizes draw ratio, degree of doping, the maximum conductivities of PPDV and its copolymers. Doping with I_2 was performed in a vacuum chamber at a pressure of 10^{-3} torr and doping with $FeCl_3$ was performed by soaking the polymer films in nitromethane solution of $FeCl_3$ for 10~30 sec depending on the thickness and copolymer composition. As shown in Table 2, all of the polymer films could not be stretched due to their crosslinked structures. PPDV homopolymer could not be doped with I_2, but could very slightly be doped with strong oxidant, $FeCl_3$, to produce a very low conductivity of 2.9×10^{-6} Scm^{-1}. Conductivity of copolymers constituted of PDV units and DMPV units decreased rapidly with increasing content of PDV units. This observation is well coincided with the UV-visible absorption behavior of the copolymers. As described above, λ_{max} and λ_{edge} values(Figure 4) of the copolymers gradually shift to shorter wavelength relative to the PDMPV as the content of PDV unit increases, which suggests that increasing content of PDV unit increases the band gap, Eg. The maximum conductivities of the copolymer containing 7 mole % of PDV units, when doped with I_2 and $FeCl_3$, were 33 and 68 Scm^{-1} respectively.

TABLE 2. Maximum conductivity of the polymers

Polymers	Draw ratio L/L_0	Conductivity(Scm^{-1}) I_2-doped	$FeCl_3$-doped
PPDV	1		$2.9x10^{-6}$
54-Poly(DMPV-co-PDV)	1	$2.6x10^{-4}$	$2.5x10^{-2}$
28-Poly(DMPV-co-PDV)	1	2.1	13
7-Poly(DMPV-co-PDV)	1	33	68

Copolymers consisting of PDV units and 1,4-phenylenevinylene(PV) units were also prepared, and their conductivities were measured. These copolymer films could be easily stretched up to draw ratio of 3 and showed various conductivity values ranging from 4.5 x 10^{-2} to 11 Scm^{-1}, when doped with $FeCl_3$, depending upon the copolymer composition.

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REFERENCES

1. I. Murase, J. D. Capistran, D. R. Gagnon, and R.W. Lenz, MOL. Cryst. Liq. Cryst., 118, 327 (1985)
2. J. I. Jin, C. K. Park and H. K. Shim, J. Polym. Sci. Part A : Polym. Chem., 29, 93 (1991)
3. C. C. Han. R. W. Lenz and F. E. Karasz, Polm. Commun., 28, 261 (1987)
4. H. K. Shim, D. H. Hwang and K. S. Lee, Makromol. Chem., 194, 1115 (1993)
5. T. Kaino, k. Kubodera, S. Tomaru, T. Kurihara, S. Saito, T. Tsutsui, and S. Tokito, Electron. Lett., 23, 1095 (1987)
6. J. I. Jin, H. K. Shim and R. W. Lenz, Synth. Met., 29(1), E 53 (1989)
7. D. R. Gagnon, J. D. Capistran, F. E. Karasz and R. W. Lenz, Polymer, 28, 567 (1987)
8. J. I. Jin, H. J. Kang and H. K. Shim, Bull. Korean Chem. Soc., 11(5), 415 (1990)
9. J. I. Jin, C. K. Park, H. K. Shim and Y. W. Park, J. Chem. Soc. Chem. Commun., 17, 1205 (1989)
10. J. I. Jin, J. C. Kim and H. K. Shim, Macromolecules, 25, 5519, (1992)
11. H. H. Horhold and J. Opfermann, Makromol. Chem., 131, 105 (1970)
12. J. I. Jin, C. K. Park and H. K. Shim, Macromolecules, 26(8), 1793 (1993)