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Conjugated Liquid Crystalline Polymers—Soluble and Fusible Poly(phenylenevinylene) by the Heck Coupling Reaction

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ABSTRACT: The Heck coupling reaction between organic halides and vinylbenzene compounds was utilized to synthesize soluble and fusible conjugated polymers. Compared to other approaches, the Heck reaction offers an easier way to prepare processible poly(phenylenevinylenes). The fusibility of the alkoxy substituted poly(phenylenevinylene) enables us to observe the nematic liquid crystalline phase above the melting temperature.

Introduction

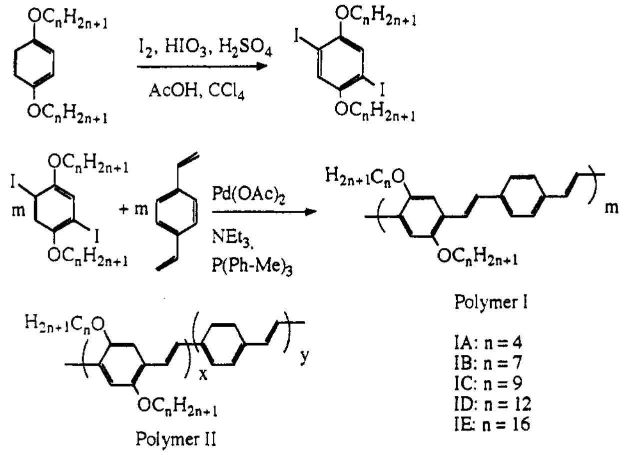
Poly(phenylenevinylene) (PPV) is one of the most interesting electroactive polymers which has demonstrated high conductivity,[1] relatively large third order nonlinear optical activity,[3] and electroluminescent activity.[4] Different approaches have been developed to synthesize PPV,[1] such as the Wittig reaction[2a] and the McMurry condensation.[2b] However, because of the problems associated with these approaches, such as oligomerization and insolubility, PPV was normally synthesized with a water soluble precursor approach via bis(sulfonium salt) polymerization or through a metathesis polymerization of proper cyclic compounds, all followed by a thermal elimination step.[5–7] The main disadvantage of these two-step approaches is that they inevitably introduce defects into the final polymers and the electroactivity of the materials is reduced.[8] Recently, the Heck reaction has been utilized to prepare PPV from dibromobenzene and ethylene and other poly(arene vinylenes).[9]

In the Heck reaction, organic halides and vinylbenzene compounds are coupled to generate a carbon–carbon bond.[10] We have research interests in exploring the feasibility of applying palladium compounds as the catalysts for the polymerization. In our previous work, we demonstrated the feasibility of the Stille coupling reaction to synthesize new conjugated polymers, poly(phenylenethiophenes), which were shown to be liquid crystal materials.[11] Both the Heck reaction and the Stille reaction utilize palladium compounds as catalysts. To compare the nature of the Stille reaction with that of the Heck reaction on the polymerization, we investigated the synthesis of new soluble PPV, as indicated in Scheme I. Although random copolymers with the structure shown in Scheme I (polymer II) have been synthesized,[1b,12] the polymers synthesized by the Heck reaction have the defined alternating structures. We also found that these polymers are soluble and fusible; they form a reversible nematic liquid crystal phase when they are heated to above the melting temperature. This paper describes the synthesis and characterization of these polymers.

Experimental Section

DMF was purified by distillation over phosphorus pentoxide. All of the other chemicals were purchased from the Aldrich Chemical Co. and were used as received unless otherwise stated. The *p*-divinylbenzene was separated from a mixture of *p*-divinylbenzene and *m*-divinylbenzene according to the literature procedure.[13] The triethylamine was distilled over CaH_2 and stored with a 3-Å molecular sieve.

Scheme I. Synthesis of Poly(phenylenevinylene) by the Heck Reaction



Synthesis of Monomers 2. Monomers 2, with different lengths of alkyl chains (n = 16, 12, 9, 7, 4) were synthesized according to the literature procedures shown in Scheme I.[10] In a typical procedure, the mixture of dialkyl ether of hydroquinone[14] (4 mmol), I_2 (0.91 g, 3.6 mmol), HIO_3 (0.42 g, 2.4 mmol), 30% H_2SO_4 (1.2 mL), and CCl_4 (1.6 mL) in AcOH (7 mL) was heated 3 h at 75 °C. Cooled with an ice bath, the crystals were filtered out and washed with a large amount of methanol and then recrystallized twice from ethanol. All of the compounds gave a satisfactory elemental analysis and NMR results. For example, monomer 2B (mp = 32–34 °C): ^1H NMR ($CDCl_3$, ppm) δ 0.9 (t, $-CH_3$, J = 6.88 Hz, 6 H), 1.32 (m, $(CH_2)_3$, 12 H), 1.51 (m, CH_2, 4 H), 1.80 (m, CH_2, 4 H), 3.93 (t, OCH_2-, J = 6.46 Hz, 4 H), 7.17 (s, aromatic, 2 H). Anal. Calcd for $C_{20}H_{32}IO_2$: C, 43.03; H, 5.78. Found: C, 43.18; H, 5.89.

Polymerization. A typical polymerization procedure is as follows: Triethylamine (0.35 mL, 2.5 mmol) was added to a solution of *p*-divinylbenzene (130 mg, 1 mmol), monomer 2A (474 mg, 1 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), and tri-*o*-tolylphosphine (60.9 mg, 0.2 mmol) in 5 mL of DMF. The reaction mixture was heated at 100 °C for 5 h under a nitrogen atmosphere and then poured into 20 mL of methanol. The precipitated polymer was collected by filtration and further purified by redissolving in a minimum amount of hot chloroform and precipitating into acetone. The resulting polymer was extracted with methanol for 24 h and was then dried under a vacuum at 40 °C for 2 days (yield 87%). The same procedure was applied to the synthesis of other polymers. The analytical results are summarized below.

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Polymer IA. ^{1}H NMR (CDCl$_3$): δ 1.05 (t, $J = 7.76$ Hz, $-CH_3$, 6 H), 1.65 (m, $-CH_2-$, 4 H), 1.9 (m, $-CH_2-$, 4 H), 4.05 (broad, $-OCH_2-$, 4 H), 7.15 (broad, vinyl proton, 4 H), 7.5 (broad, aromatic protons, 6 H). Anal. Calcd for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 80.47; H, 8.33.

Polymer IB. ^{1}H NMR (CDCl$_3$): δ 0.95 (broad, $-CH_3$, 6 H), 1.35 (broad, $-(CH_2)_2-$, 8 H), 1.42 (broad, $-CH_2-$, 4 H), 1.55 (broad, $-CH_2-$, 4 H), 1.85 (broad, $-CH_2-$, 4 H), 4.05 (broad, $-OCH_2-$, 4 H), 7.10 (broad, vinyl proton, 4 H), 7.5 (broad, aromatic protons, 6 H). Anal. Calcd for $C_{30}H_{40}O_2$: C, 83.28; H, 9.32. Found: C, 82.55; H, 9.67.

Polymer IC. ^{1}H NMR (CDCl$_3$): δ 0.90 (broad, $-CH_3$, 6 H), 1.35 (broad, $-(CH_2)_4-$, 16 H), 1.4 (broad, $-CH_2-$, 4 H), 1.58 (broad, $-CH_2-$, 4 H), 1.8 (broad, $-CH_2-$, 4 H), 4.05 (broad, $-OCH_2-$, 4 H), 7.10 (broad, vinyl proton, 4 H), 7.4 (broad, aromatic protons, 6 H). Anal. Calcd for $C_{34}H_{48}O_2$: C, 83.55; H, 9.90. Found: C, 83.66; H, 10.72.

Polymer ID. ^{1}H NMR (CDCl$_3$): δ 0.86 (broad, $-CH_3$, 6 H), 1.3 (broad, $-(CH_2)_7-$, 28 H), 1.38 (broad, $-CH_2-$, 4 H), 1.55 (broad, $-CH_2-$, 4 H), 1.86 (broad, $-CH_2-$, 4 H), 4.05 (broad, $-OCH_2-$, 4 H), 7.15 (broad, vinyl proton, 4 H), 7.45 (broad, aromatic protons, 6 H). Anal. Calcd for $C_{40}H_{60}O_2$: C, 83.86; H, 10.56. Found: C, 83.18; H, 10.31.

Polymer IE. ^{1}H NMR (CDCl$_3$): δ 0.85 (broad, $-CH_3$, 6 H), 1.25 (broad, $-(CH_2)_{11}-$, 44 H), 1.35 (broad, $-CH_2-$, 4 H), 1.53 (broad, $-CH_2-$, 4 H), 1.85 (broad, $-CH_2-$, 4 H), 4.05 (broad, $-OCH_2-$, 4 H), 7.15 (broad, vinyl proton, 4 H), 7.47 (broad, aromatic protons, 6 H). Anal. Calcd for $C_{48}H_{76}O_2$: C, 84.15; H, 11.18. Found: C, 83.45; H, 11.79.

Polymer Characterization. The GPC measurements were performed on a Waters RI system equipped with a UV detector, a differential refractometer detector, and an Ultrastyragel linear column at 35 °C using THF (HPLC grade; Aldrich) as an eluant. The molecular weight and the molecular weight distribution were calculated on the basis of monodispersed polystyrene standards. The ^{1}H NMR spectra were collected on a Varian 400-MHz FT NMR spectrometer. The ^{13}C NMR spectra were collected from a GE QE 300-MHz spectrometer. The FTIR spectra were recorded on a Nicolet 20 SXB FTIR spectrometer. A Perkin-Elmer Lambda 6 UV/vis spectrophotometer and a Perkin-Elmer MPR-4 spectrofluorometer were also used. Thermal analyses were performed by using the DSC-10 and TGA-50 systems from TA Instruments with heating rates of 10 and 15 °C/min, respectively, under a nitrogen atmosphere. The polarizing microscopic observation was performed with a Nikon (HFX-IIA) microscope equipped with a Linkam (TMS-90) hot stage. The X-ray diffraction pattern ($4° < 2\theta < 54°$) was collected using Cu Kα radiation on a Noreco diffractometer equipped with a diffracted beam monochromator. The samples for measurements were either a powder or thick films of the pristine polymer. To study the effects of thermal treatment on the X-ray pattern, the powdery polymer sample was annealed at 100 °C for 11 h under nitrogen and was cooled to room temperature at a rate of 0.5 °C/min.

The photoconductivity was studied by measuring the voltage resulting from a photocurrent run through the sample and across a 10-kΩ resistor.[15] A He–Ne laser (623.8 nm) with an intensity of 0.096 mW/cm^2 was used as the light source.

Nonlinear optical measurements were performed using the degenerate four-wave mixing technique (DFWM) developed by Hellwarth and co-workers.[16] A Quantel Model YG471-C Nd:YAG laser, which had been frequency doubled to 532 nm, was used as the laser source with a pulse width of approximately 25 ps.

Results and Discussion

Polymerization. A typical Heck reaction condition was applied to the polymerization, as shown in Scheme I. The polymerization was easily carried out in DMF in the presence of a catalytic amount (2% mol) of Pd(OAc)$_2$ with the tertiary amine and triarylphosphine under a nitrogen atmosphere. The polymerization went on quickly, and the final polymer precipitated out of the reaction medium (DMF as solvents) after 3 h of reaction. The polymerization rate with the Heck reaction is much faster than that with the Stille reaction which took 1 or more days to complete.[10]

Structural Characterizations. Since the final polymers are soluble in many organic solvents, such as THF, chloroform, toluene, and dichloroethane, many physical characterizations can be facilitated. The ^{1}H NMR spectral data are listed in the Experimental Section. The ^{13}C NMR spectrum of polymer B is shown in Figure 1, where the assignments of chemical shifts are indicated. The results of the ^{1}H and ^{13}C NMR spectra clearly indicate that the polymer structures are as proposed and that the major configuration of the vinylene unit is in the trans form. However, as in the observations of the normal Heck reactions, side reactions due to the coupling of aryl halides with the α-vinyl position did happen in a minor way, as evidenced by the weak ^{1}H NMR signals of the end β-vinyl proton (<1% in intensity ratio).

Figure 2 is the FTIR spectrum of polymer B, which shows a strong absorption due to the ether linkage at 1208 cm^{-1}; the C—H stretchings of $-CH_2$ and $-CH_3$ appear at 2853 and 2924 cm^{-1} (see Figure 2), respectively. The typical absorption due to trans >C=C< stretching of the vinylene, at 965 cm^{-1}, is strong, in contrast with Lenz's observation that methoxy substituted PPV derived from sulfonium polymer salts have a very weak *trans*-vinylene C—H absorption.[12] Polymers A, C, D, and E showed spectroscopic features similar to polymer B.

The features of the UV/vis/fluorescence spectra are consistent with the results reported in the literature.[4] A strong absorption in the visible at ca. 459 nm can be observed. It is red-shifted from that of unsubstituted PPV (400 nm) due to the electronic effects of the alkoxy groups (see Figure 3). The emission spectrum showed three main features at 513, 550, and 601 nm, a typical pattern for the PPV.

All of these polymers exhibit high molecular weights, as indicated by the GPC measurements. Table I summarizes the GPC results, which indicate that the Heck reaction is a generic reaction for preparing high molecular weight PPVs.

Thermal Properties. TGA thermograms indicated that these polymers were stable up to 430 °C under nitrogen. DSC thermograms showed the glass transition temperatures (second order transition) to be 46, 44, 38, and 33 °C for polymers B, C, D, and E, respectively. All of the DSC thermograms displayed at least two transitions, both side chain melting and backbone melting, as the temperature increased from 50 to 300 °C. Table II summarizes the thermal properties for these polymers. Compared to the results reported in the literature,[5,6,11] however, the thermal transitions in these polymers are more complicated. For example, the pristine sample of polymer D showed two endothermic transitions, at ca. 69.1 and 152 °C, respectively (see Figure 4). An exothermic transition above the backbone melting transition, at ca. 212 °C, was also observed. Similar endothermic transitions have been observed in polymers A–C, but not in polymer E. If the sample was annealed at 100 °C for 11 h, a sharp new transition at ca. 117 °C appeared together with the other transitions. However, the enthalpy of the exothermic transition was reduced. If this annealed sample was only heated to 170 °C and then cooled down, the reversed endothermic transitions at 117 and 152 °C appeared at 93 and 113 °C, respectively. If this annealed sample was heated to 300 °C, cooled down, and then annealed at 100 °C for another 11 h, the melting transition at ca. 152 °C

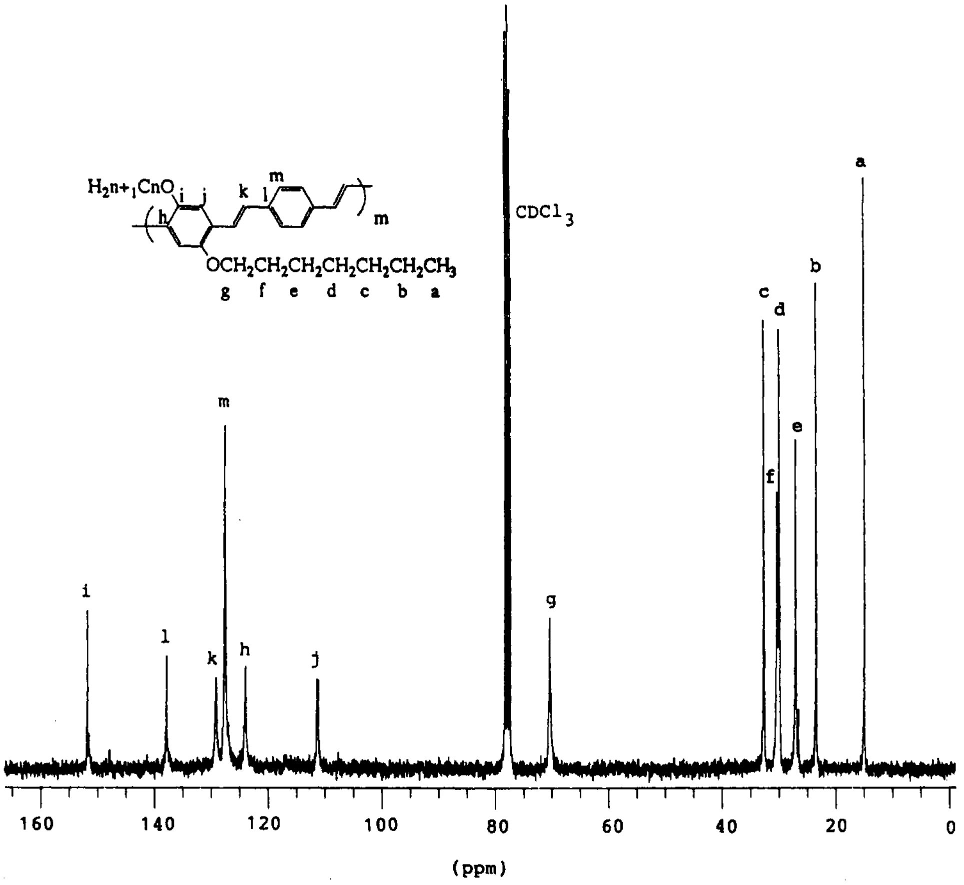

Figure 1. ^{13}C NMR spectrum of polymer B in CDCl$_3$.

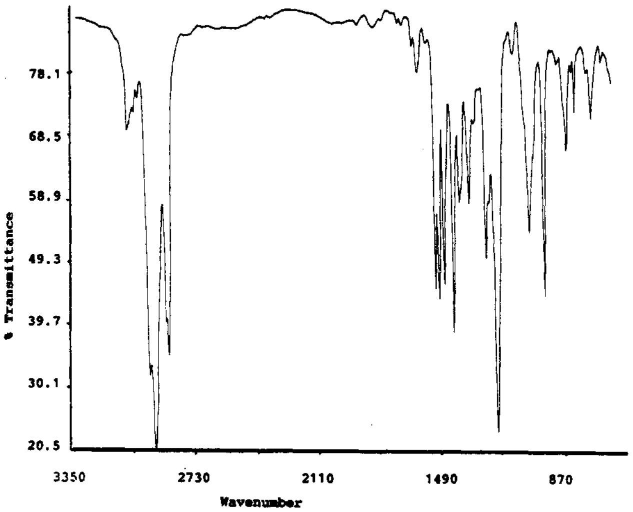

Figure 2. FTIR spectrum of polymer B, taken by using thin films coated on the NaCl crystal plate.

disappeared while the transition at 117 °C remained. The enthalpy of the exothermic transition was further reduced. A tentative interpretation could be that the transition at 68 °C is due to side chain melting; the polymer exhibits two crystalline forms, corresponding to two melting transitions at 117 and 152 °C, respectively. The crystalline form at 117 °C was reversible when it was annealed at 100 °C, while the other one was irreversible, caused by the thermal cross-linking of the main chain. X-ray diffraction studies provide evidence for the assumption of two crystalline structures. Figure 5 shows diffraction lines at 2θ values of 5.0, 7.4, 12.0, 21.5, 40.5, and 47.5°, indicating that the pristine polymers are crystalline materials (see Figure 5). After the polymer was annealed at 100 °C for 11 h, the diffraction pattern clearly changed; the intensities of the lines at 7.4 and 12.0° increased, the lines at 16.0, 23.3, and 25.1° became evident, and the line at 21.5° was split into two clear lines at 19.0 and 22.0°. Additionally, the intensities of the lines at 40.5 and 47.5° were reduced, while the line at 5° had only a slight increase. The detailed structures of these crystalline forms are to be determined by further X-ray diffraction studies which will be reported separately. The evidence for the cross-linking is discussed in the following section.

Polarized Microscopy. The *trans*-poly(phenylenevinylene) backbone is a rigid rod which can act as the mesogenic unit. These side chain substituted conjugated polymers have a mesogenic structure similar to those with rigid rod side chain polyester and polyamide; therefore, they should be able to manifest liquid crystalline properties. From the DSC studies, we could not see the liquid crystalline to isotropic transition because of the small enthalpy. Polarized microscopy provided supplemental observations of the transitions of different samples. All of these polymers showed birefringent fluids above the melting temperature; the typical textures of a nematic phase were observed (see Figure 6). The texture of polymer E was reversible at a cooling rate of 5 °C/min; the textures for other polymers were reversible only at a very slow cooling rate (1 °C/min). Both the DSC studies and the polarizing optical microscopic observations indicated that the melting and the clearing transition temperatures were affected by the lengths of the side chains. Figure 7 shows a phase diagram of the polymers in which the transition temperatures are plotted against the carbon number, *n*, of the alkyl side chain. As the carbon number, *n*, increases, the melting temperature of the polymer decreases steadily, as does the clearing temperature, T_c.

From these observations, an explanation for the exothermic process observed by the DSC studies can be given. Since the TGA did not detect any weight loss before 430 °C for any of these polymers, the exothermic process must

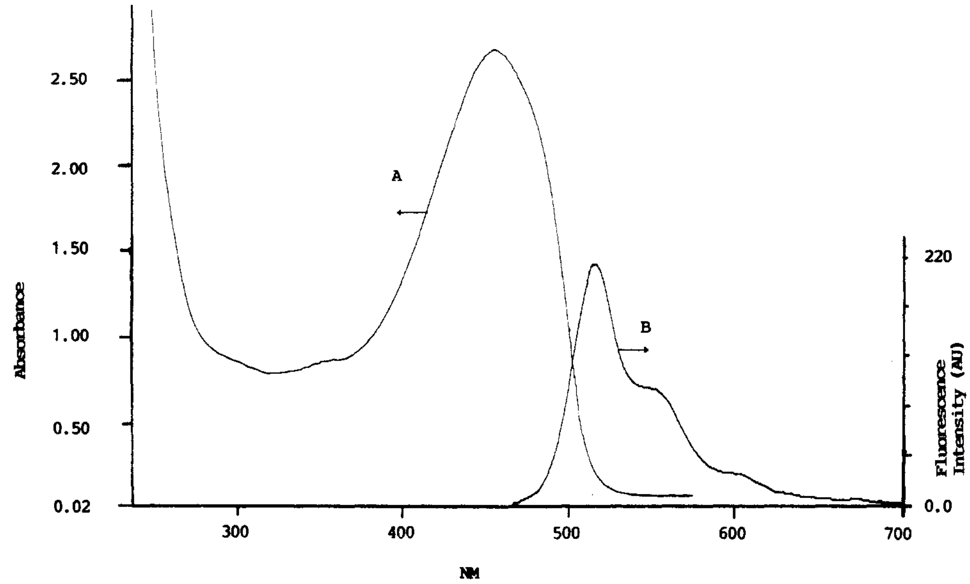

Figure 3. UV/vis and emission spectra of polymer B in chloroform.

Table I. GPC Results for Alkoxy Substituted PPV

polymer	M_n	M_w	polydispersity
A	8 300	32 000	3.85
B	18 500	49 300	2.66
C	15 800	46 900	2.97
D	21 800	62 500	2.87
E	18 700	53 900	2.88

Table II. DSC Results for Alkoxy Substituted PPV[a]

polymer	T_s (°C)	ΔH_s (J/g)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
IA	*b*	*b*	239.0	10.60	325.0	*c*
IB	73.8	2.48	*c*	*c*	*b*	*b*
IC	82.0	2.25	*c*	*c*	*b*	*b*
ID	69.1	4.90	152.0	10.24	*b*	*b*
IE	66.4	2.75	103	8.52	133.0	103

[a] T_s refers to the side chain melting temperature, T_m, to the main chain melting temperature, and T_c, to the liquid crystalline phase to isotropic phase transition temperature. [b] Transition was not observed. [c] T_m and ΔH_m could not be precisely determined due to the cross-linking.

be related to the cross-linking of the polymer backbone. Polymer E has long alkyl side chains which prevent the vinylene double bonds from being close to each other; the probability of cross-linking is reduced. The DSC trace of polymer E showed almost no exothermic transition and its LC–isotropic transition was reversible. For the other polymers with shorter alkyl chains, the cross-linking was evoked at a high temperature (ca. 200 °C) because the double bonds have a greater possibility of being close to each other. Further evidence for cross-linking comes from the UV/vis spectroscopic study; a dramatic decrease in the absorption of polymer D at λ_{max} = 456 nm was observed after annealing the sample at 208 °C for 1 h under a nitrogen atmosphere (see Figure 8).

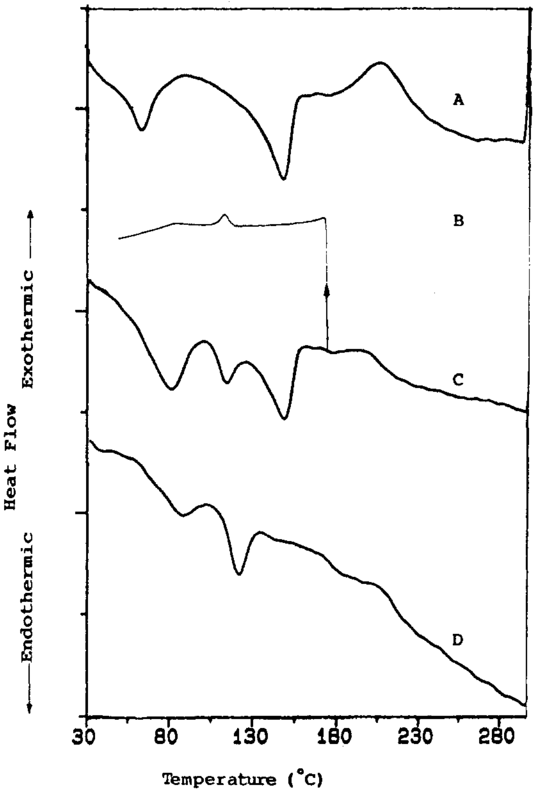

Figure 4. DSC diagrams of polymer D at various conditions: (A) heating curve of pristine polymer with a heating rate of 10 °C/min; (B) cooling curve after the sample is heated to 170 °C at a cooling rate of 2 °C/min; (C) heating curve of polymer after being annealed at 100 °C for 11 h; (D) second heating of the sample from curve C after being further annealed for 11 h.

Photoconductivity. It is known that PPV is an interesting class of photoconductive materials. We performed photoconductivity measurements on our polymers by using a He–Ne laser (λ = 632 nm). The photocurrent of polymer D as a function of the electric field strength is shown in Figure 9. A maximum photoconductivity of $6.43 \times 10^{-13}\ \Omega^{-1}\ cm^{-1}$ was obtained with a field strength of 66.7 kV/cm and the laser intensity of 0.115 mW/cm^2, while the dark current was very small and difficult to measure. However, the photoconductivity of our polymer was very small at the measuring conditions, for which there are two possible reasons: (1) the exciting laser wavelength is far away from the sensitive region of the polymers (see Figure 2), and (2) the polymer chain was not oriented.

Third Order Optical Nonlinearity. The PPV was shown to exhibit relatively large third order optical nonlinearity.[3] We performed the DFWM measurements at λ = 532 nm; Figure 10 shows the plot of the DFWM signal of polymer D, $\chi^{(3)}/\alpha$, as a function of the backward laser beam delay time. It can be estimated that polymer D has a $\chi^{(3)}/\alpha$ value of 1.7×10^{-13} esu cm. The absorption coefficient value, α, of this polymer was determined to be ca. $2.7 \times 10^4\ cm^{-1}$, resulting in a $\chi^{(3)}$ value of ca. 4.6×10^{-9} esu. Since the measurements were performed in the region

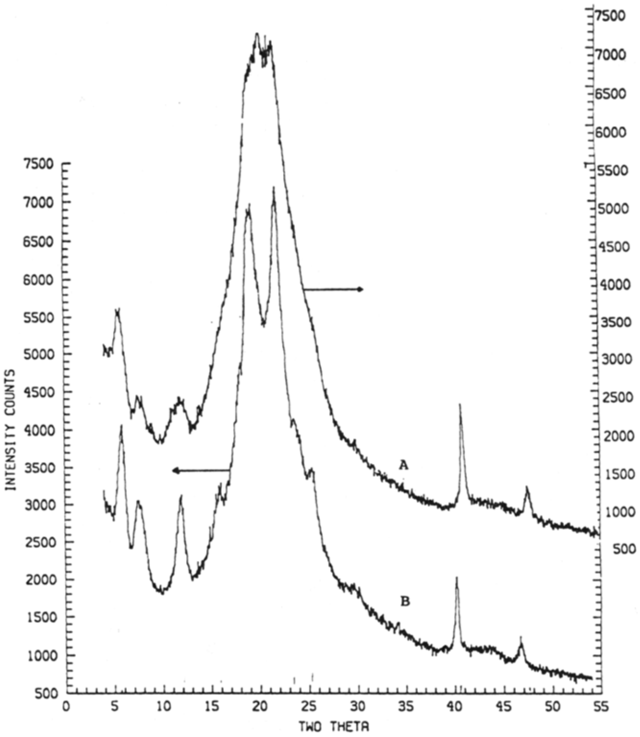

Figure 5. X-ray diffraction patterns: (A) pristine polymer D; (B) polymer D after annealing at 100 °C for 11 h.

Figure 6. Polarized micrography of polymer E at 129 °C (×85).

of absorption, this value contains a large resonant contribution.

Conclusion

In summary, it is clear from our results that the Heck reaction can be used to synthesize different soluble and fusible poly(phenylenevinylenes). Compared to the other approaches to poly(phenylenevinylene), this approach is relatively easy in access to monomers and in the preparation of polymers. Since these alkoxy substituted poly(phenylenevinylenes) exhibit excellent solubility and fusibility, they demonstrated the nematic liquid crystalline

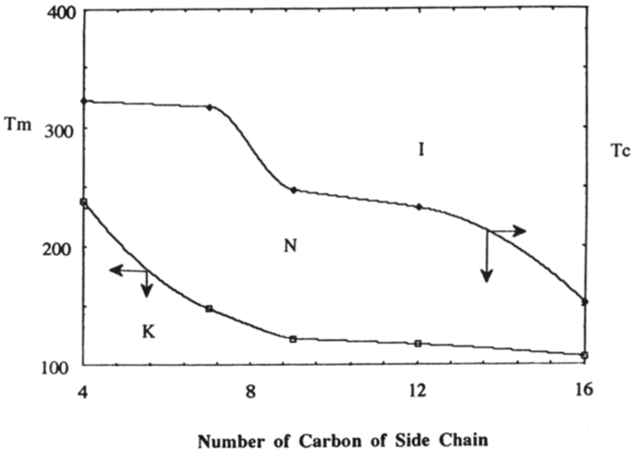

Figure 7. Phase diagram of the melting transition and clearing temperature (liquid crystal phase–isotropic phase) as a function of the length of side chains.

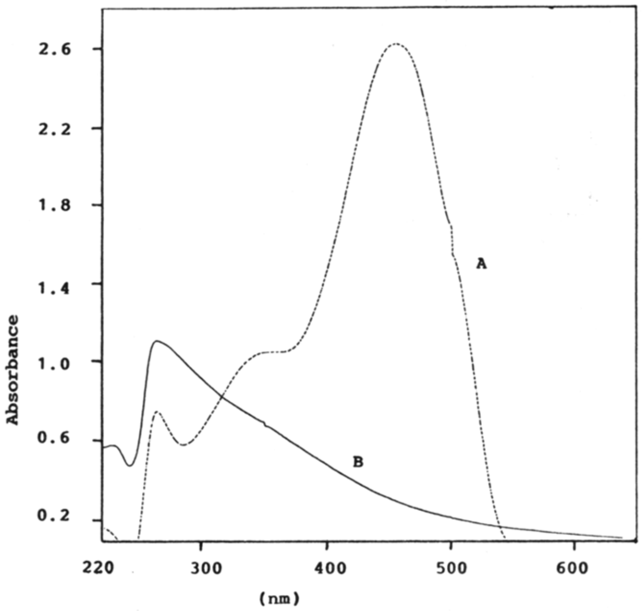

Figure 8. Absorption change of polymer D: (A) pristine polymer film; (B) after annealing at 208 °C for 1 h.

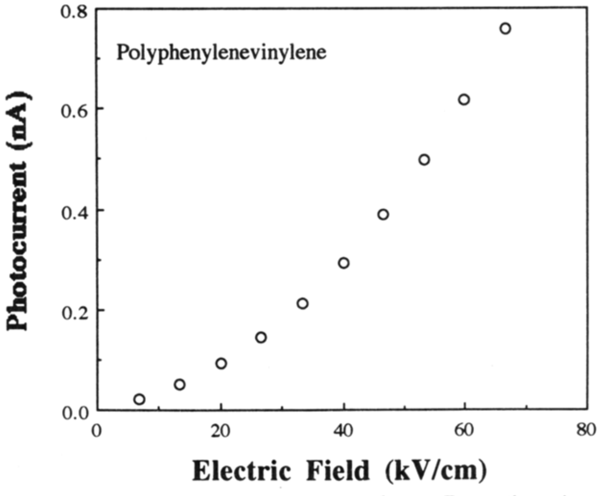

Figure 9. Photocurrent response of polymer B as a function of the external applied electric field.

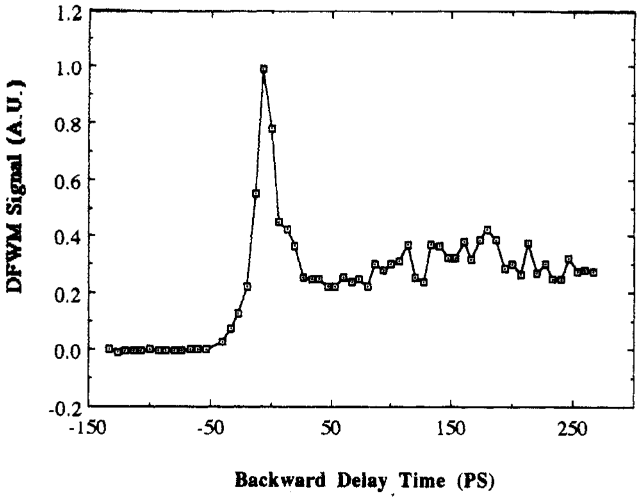

Figure 10. DFWM signal of polymer B, $\chi^{(3)}/\alpha$, as a function of laser beam (backward beam) delay time. All of the beams are parallel to each other.

phase above the melting temperature. Although other physical properties of these PPV are identical with the PPV obtained from other approaches, further extension of the Heck reaction for synthesizing different conjugated polymers with vinylene linkage is highly possible. Thus, we can easily tune the electronic properties of the polymers by structural modification; thereby, new properties can be expected.

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