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Preparation of Poly(2,5-diheptyl-1,4-phenylenevinylene) by Sulfonium Salt Pyrolysis

Yoriko Sonoda* and Kyoji Kaeriyama
Research Institute for Polymers and Textiles, Higashi 1-1-4, Tsukuba, Ibaraki 305

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Poly(2,5-diheptyl-1,4-phenylenevinylene) (**1**) was prepared by the sulfonium salt pyrolysis procedure. Tough films of **1** were obtained by pyrolysis of its sulfonium salt precursor film. Due to flexible side chains, **1** was soluble in organic solvents such as chloroform. The molecular weights were M_n=3.8—4.7×10^4 and M_w=1.4—1.8×10^5. The ratio of trans to cis olefinic units was found to be 93:7 from the ^{1}H NMR spectrum. Two arylmethylene peaks suggested that there were two kinds of stereochemically different methylene groups. Although the peak energy in the absorption spectra was almost identical to those of poly(1,4-phenylenevinylene) (PPV), the electrical conductivity of **1** was much lower than that of PPV.

Conjugated polymers have been attracting intensive attention as conducting polymers, nonlinear optical materials and backbones of organic ferromagnets. Among these polymers, poly(1,4-phenylenevinylene) (PPV) is one of the most interesting polymers from scientific and technological points of view.[1-5] PPV is not only highly conducting but also processible into a high-quality film at the stage of its soluble sulfonium salt precursor. However, PPV has high oxidation potential and can not be doped with such mild dopants as iodine. Such hazardous dopants as sulfuric acid and arsenic pentafluoride are necessary to enhance electrical conductivity. Although the precursor is soluble, PPV is neither soluble nor fusible, thus intractable.

In order to overcome these undesirable properties, some derivatives of PPV have been prepared. The introduction of the electron-donating alkoxyl group reduced the oxidation potential of PPV and improved its solubility in organic solvents remarkably.[6,7] Poly[2,5-bis(hexyloxy)-1,4-phenylenevinylene] was soluble in 1,2,4-trichlorobenzene and showed conductivity as high as 200 S cm^{-1} after stretching and doping with iodine.[8] The replacement of the vinylene units with 1,3,5-hexatrienylene units also increased affinity to dopants. Poly(1,4-phenylene-1,3,5-hexatrienylene) can be doped with iodine.[9]

Only a few works on alkylated PPV derivatives have been reported. Poly(2,5-dimethyl-1,4-phenylenevinylene) was insoluble in organic solvents and its conductivity was low.[10,11] As for soluble PPV derivatives bearing long alkyl chains, Rehahn et al. prepared poly(2,5-dihexyl-1,4-phenylenevinylene) by the condensation of 1,4-diformyl-2,5-dihexylbenzene in the presence of a titanium catalyst.[12] This procedure is a new interesting method for preparation of PPV. We prepared poly(2,5-diheptyl-1,4-phenylenevinylene) (**1**) according to the sulfonium salt pyrolysis procedure, since this method gave high-quality films of PPV and poly(2,5-dialkoxy-1,4-phenylenevinylene). The present polymer is soluble in chloroform and its diluted solution emits strong green fluorescence. Its structure is clarified by ^{1}H NMR, ^{13}C NMR, and C–H COSY NMR spectra.

Results and Discussion

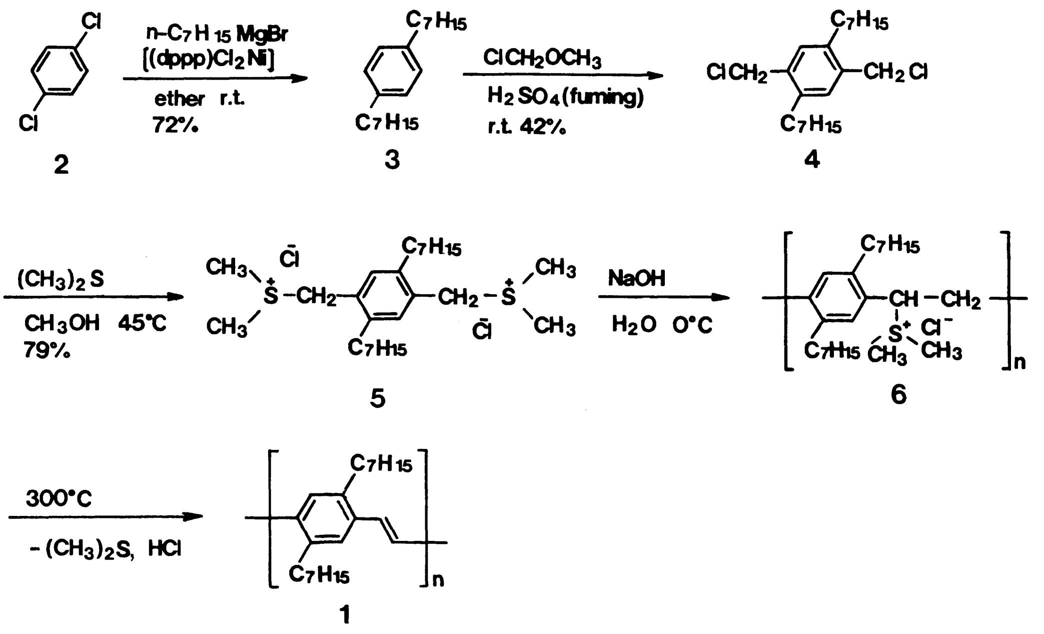
Preparation Procedure. The reaction of **4** with dimethyl sulfide afforded **5** in a considerably high yield. This monomeric electrolyte having a sharp melting point was identified by NMR and IR spectra. The polymerization of **5** took place in an aqueous alkaline solution. After dialysis of the reaction mixture in a neutralized solution, precipitate **6** was separated from the solution. It was used for the pyrolysis without drying completely, due to instability in the dry state. The solution of **6** in 1-butanol was cast into a film. After pyrolysis, a high-quality freestanding film was obtained (Scheme 1).

In the preparation of PPV, tetrahydrothiophene (THT) gives a higher polymerization rate and polymer yield than dimethyl sulfide.[13] Thus, instead of dimethyl sulfide, THT was also used for the preparation of a bis(sulfonium salt) monomer. However, the bis(sulfonium salt) from THT was unstable and gradually decomposed into **4** and THT at room temperature. Dimethyl sulfide afforded the stable bis(sulfonium salt). This is attributable to steric hindrance between bulky THT and heptyl groups.

The pyrolysis was accomplished at 200 or 300 °C. The products obtained at both temperatures showed completely identical NMR and IR spectra. The products were purified by reprecipitation into methanol. This process caused no change in the NMR and IR spectra of the polymers.

Elemental analysis indicates that **1** contains a small amount of sulfur. Since sulfur content was almost identical for **1** obtained at 200 and 300 °C, residual sulfur should be due to the elimination of methane instead of dimethyl sulfide from **5** rather than incomplete decomposition of **5**.

Solubility. Since **1** bears flexible side chains, it is soluble in chloroform, dichloromethane, 1,1,2,2-tetrachloroethane and toluene. Solubility of **1** prepared at 200 °C was 50 mg per ml chloroform. The product obtained by pyrolysis at 200 °C was more soluble than that obtained at 300 °C. While almost all of the product



Scheme 1.

at 200 °C was soluble in chloroform, only 70—75% of the product at 300 °C was soluble. The 25—30% residue was yellow-brown solid emitting no fluorescence. Since it was insoluble in chloroform even at elevated temperatures, crosslinking possibly took place during pyrolysis. However, IR spectra showed no clear difference between the soluble and insoluble parts.

Molecular Weight. The molecular weight of **1** was measured in chloroform with gel permeation chromatography. Calibration with polystyrene standards indicated that the soluble part of **1** prepared at 200 °C had M_n=3.8×10^4, M_w=1.4×10^5, and M_w/M_n=3.7. The molecular weights of **1** prepared at 300 °C were M_n=4.7×10^4, M_w=1.8×10^5 and M_w/M_n=3.8. These molecular weights are 4.5—5.5 times higher than those by the McMurry process.[12] The molecular weight should be controlled at the condensation of **5** into **6** and independent of pyrolysis temperatures. In fact, the molecular weights are higher for **1** obtained at 300 °C than at 200 °C, suggesting crossliking reactions take place more frequently at a higher pyrolysis temperature.

IR Spectra. Figure 1 shows the IR spectrum of a film of **1**. The peaks at 2800—3000 cm^{-1} are assigned to the C–H stretching vibration of the methyl and methylene groups. The peaks at 1378, 1467, and 1498 cm^{-1} are due to the skeletal vibration of a 1,2,4,5-tetrasubstituted benzene ring. The corresponding C–H out-of-plane vibration is observed at 892 cm^{-1}. The strong peak at 963 cm^{-1} is assigned to trans double bonds. The peak due to cis double bonds would be expected to appear around 730 cm^{-1}.[14] Since a peak appeared at 722 cm^{-1} due to the wagging vibration of the methylene groups, it is not clear from the IR spectrum whether cis double bonds are present in **1**.

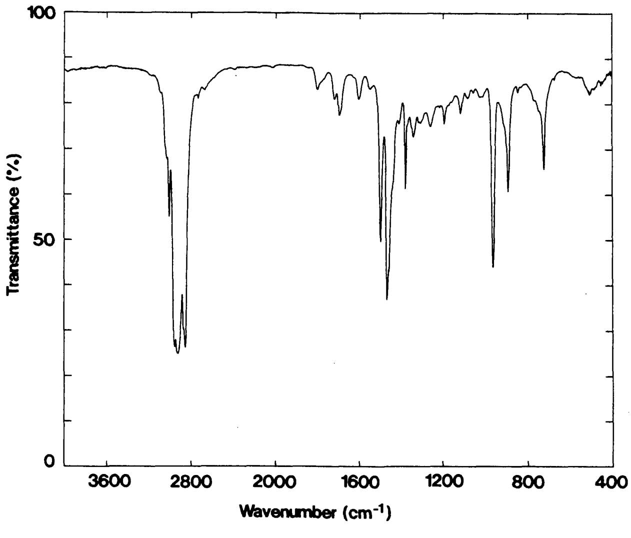


Fig. 1. Infrared spectrum of a film of **1**.

NMR Spectra. Figure 2 shows the ^{1}H NMR spectrum of **1** in deuterated chloroform. The peaks at δ=7.42 and 6.86 are assigned to the aromatic hydrogens of the trans and cis repeating units, respectively. The peaks at δ=7.25 and 6.75 are assigned to the olefinic hydrogens of the trans and cis repeating units, respectively. These assignments are consistent with previously reported ones for *trans*- and *cis*-stilbene, 1,4-distyrylbenzene, and oligo-PPV.[12,15] The ratio of trans to cis olefinic units is found to be 93 : 7 from the integrals of the peaks at δ=7.25 and 6.75. In PPV prepared by the sulfonium salt decomposition, its main chain was

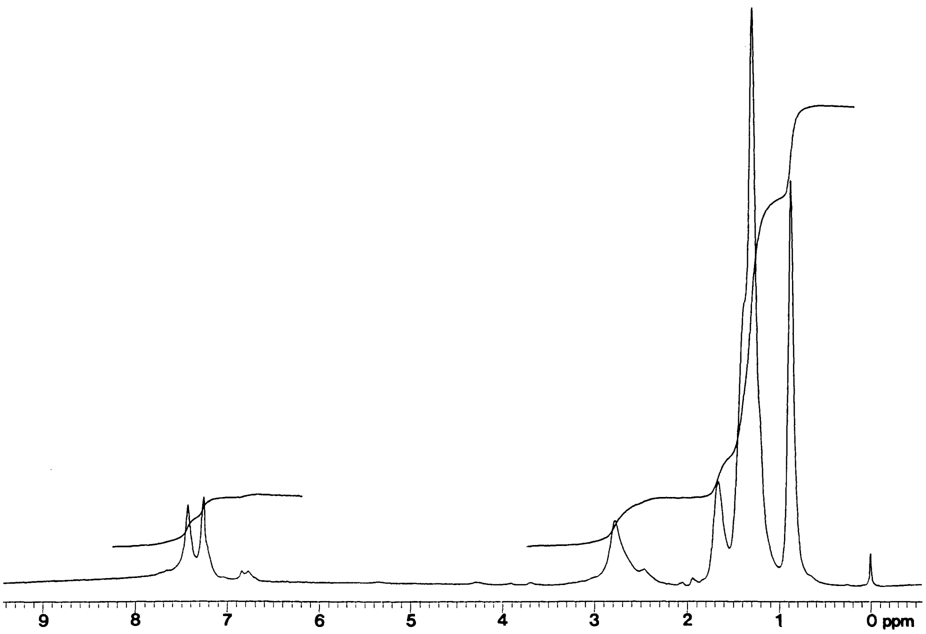


Fig. 2. ^{1}H NMR spectrum of **1**.

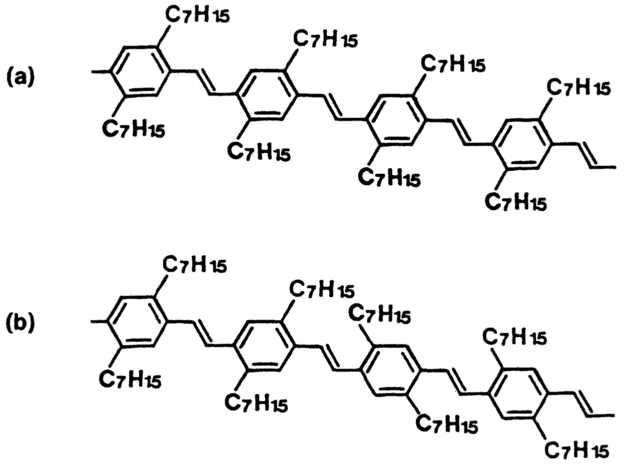


Fig. 3. Two structures of **1**.

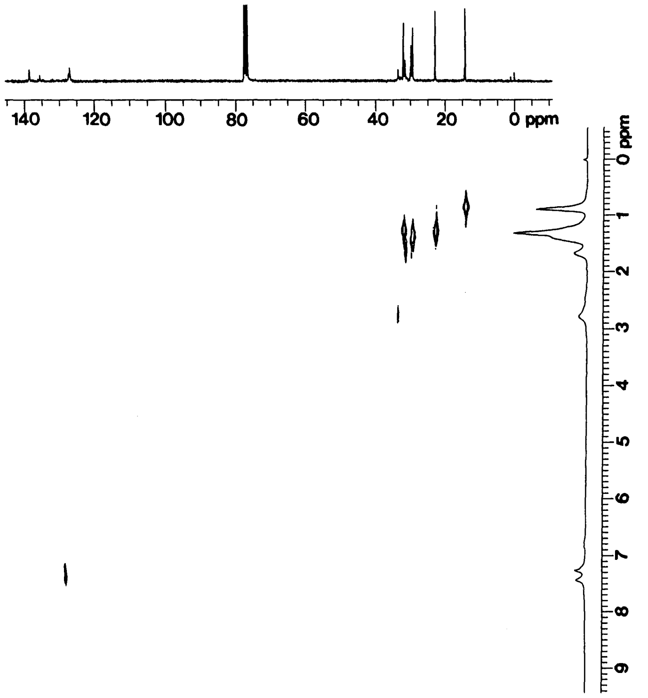


Fig. 4. ^{1}H-^{13}C cosy NMR spectrum of **1**.

assumed to consist predominantly of trans olefinic units from the olefinic peak at 965 cm^{-1} in its IR spectra.[2)] Now the ratio of trans to cis olefinic units is quantitatively estimated. This ratio is 71 : 29 for poly(2,5-dihexyl-1,4-phenylenevinylene) prepared by the McMurry's method.[12)] The present data clearly indicate the sulfonium salt decomposition process is suitable for the preparation of trans PPV derivatives.

The peak at δ=2.77 and the smaller one at δ=2.43 are assigned to the arylmethylenes. The ratio of their integrals is found to be 9 : 1. These two peaks should be due to two kinds of stereochemically different arylmethylenes. The possible structures are shown in Fig. 3. While the peak at δ=2.77 is due to the regular structure(a), the peak at δ=2.43 can assigned to the more crowded structure(b). Two similar peaks due to arylmethylenes were observed in ^{1}H NMR spectra of poly(3-alkyl-2,5-thiophenediyl).[16,17)] The smaller peaks at higher magnetic fields are assigned to the more crowded arylmethylenes associated with the head-to-head bondings of thiophene rings.

The ^{1}H- ^{13}C COSY spectrum of **1** in deuterated chloroform is shown in Fig. 4. It is evident that the peak

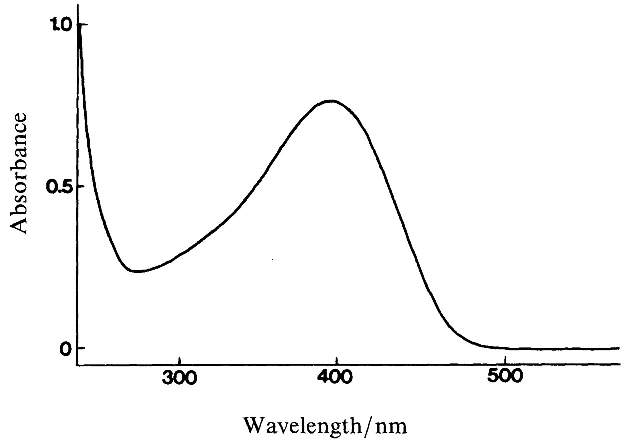


Fig. 5. UV-vis spectrum of **1**. Pyrolysis temperature: 300 °C. Solvent: chloroform.

at δ=126.90 is assigned to the carbons in positions 3 and 6 of the benzene ring. The peak at δ=127.18 is due to the trans olefinic carbons. The assignments of the peaks at δ=135.61 and 138.52 are not clear from this spectrum. Comparison with ^{13}C NMR spectra of **4**, **5**, and **6** indicates that the peak at δ=135.61 is due to the carbons in positions 2 and 5. The other peak at δ=138.52 must be due to the carbons in positions 1 and 4. The peak at δ=33.37 corresponds to the arylmethylene peak at δ=2.77. The ^{13}C peak corresponding to the ^{1}H peak at δ=2.43 would be so weak that it could not be observed.

UV-vis Spectra. Figure 5 shows the UV-vis spectrum of **1**. The maximum was located at 397 nm. It was observed at 404 nm for **1** prepared at 200 °C. These values are almost identical to 402 nm for PPV.[18] The conjugated system would deviate from the coplanar configuration due to the steric effect of the heptyl groups. This effect causes a blue shift but is balanced with their electron-donating one which causes a red shift.

Electrical Conductivity. The electrical conductivities of **1** prepared at 300 °C were measured after vapor-phase doping with sulfur trioxide and antimony pentafluoride. They were 2.7×10^{-3} S cm^{-1} for sulfur trioxide and 2.8×10^{-4} S cm^{-1} for antimony pentafluoride. Although **1** has the large insulating moieties, its conductivities are a little higher than those for the corresponding methyl derivatives, but much lower than those for PPV prepared via the sulfonium chloride precursor.[11,13]

Experimental

Materials. 1,4-Diheptylbenzene(3). Heptylmagnesium bromide was prepared by adding 91.3 g (0.51 mol) of heptyl bromide in 180 ml of dry ether to 13.6 g (0.56 mol) of magnesium in 10 ml of ether under mild refluxing. The mixture was heated at a refluxing temperature for 3 h. This Grignard reagent was added dropwise to 30 g (0.204 mol) of 1,4-dichlorobenzene (**2**) and 0.24 g of dichloro[1,3-(diphenylphosphino)propane]nickel(II) in 150 ml of dry ether at room temperature over a period of 60 min. After stirring for 20 h, the usual work-up and distillation under a reduced pressure gave 40 g (72%) of **3**. Bp 148 °C (0.4 mmHg).

2,5-Bis(chloromethyl)-1,4-diheptylbenzene(4). A solution of 20 g (0.104 mol) of **3** and 23.3 g (0.289 mol) of chloromethyl methyl ether was cooled below 10 °C. To this solution was added 15.8 g of 60% fuming sulfuric acid over a period of 20 min. After stirring at room temperature for 22 h, the reaction mixture was poured into 200 ml of ice water. Resulting crystals were separated and purified by silica-gel column chromatography (hexane eluent). Subsequent recrystallization from hexane gave 19 g (49%) of **4**. Mp 78.0—79.5 °C. ^{1}H NMR (CDCl$_3$) δ=0.88 (6H, t, J=6.6 Hz), 1.18—1.46 (16H, m), 1.52—1.68 (4H, m), 2.66 (4H, t, J=7.9 Hz), 4.56 (4H, s), 7.15 (2H, s). ^{13}C NMR (CDCl$_3$) δ=14.03, 22.60, 29.10, 29.61, 31.07, 31.74, 31.79, 43.77, 131.40, 135.54, 139.50. IR (KBr) 3009, 2952, 2923, 2850, 1511, 1497, 1468, 1406, 1376, 1341, 1260, 1198, 1127, 1119, 1032, 922, 908, 901, 835, 809, 766, 751, 723, 701, 607, 500 cm^{-1}.

Bis(sulfonium Salt) Monomer(5). To a solution of 2.05 g (5.53 mmol) of **4** in 20 ml methanol was added 1.6 ml (1.35 g, 21.8 mmol) of dimethyl sulfide. After stirring the mixture at 45 °C for 23 h, methanol and excess dimethyl sulfide were distilled off. Upon adding acetone to the residue, crystals were separated. After washing with ether and drying at room temperature, 2.17 g (79%) of white crystals were obtained. Mp 187.0 °C. ^{1}H NMR (D$_2$O) δ=0.64 (6H, t, J=7.0 Hz), 0.99—1.16 (16H, m), 1.36—1.50 (4H, m), 2.54 (4H, t, J=7.8 Hz), 2.67 (12H, s), 4.48 (4H, s), 7.21 (2H, s). ^{13}C NMR (CD$_3$OD) δ=15.25, 24.50, 25.94, 31.21, 31.31, 33.30, 33.60, 33.80, 48.49, 130.06, 135.93, 143.74. IR (KBr) 2923, 2853, 1653, 1506, 1467, 1450, 1420, 1395, 1379, 1333, 1307, 1260, 1203, 1179, 1148, 1061, 1022, 951, 907, 835, 763, 724, 701, 672, 607, 464 cm^{-1}.

Monosulfonium Salt Polymer (6). To a solution of 5.00 g (10.0 mmol) of **5** in 50 ml of water was added 55 ml of 0.20 M (1 M=1 mol dm^{-3}) sodium hydroxide solution (11.0 mmol) at 0 °C for 40 min. After stirring the mixture for 2 h, pH was adjusted to 7 with a dilute hydrogen chloride solution. After this solution was subjected to dialysis for 4 d, **5** was separated from the solution as faint yellow-green powder. The dialysis was continued until no chloride ion was detected with silver nitrate.

Poly(2,5-diheptyl-1,4-phenylenevinylene) (1). A saturated solution of **6** in 1-butanol was cast on a glass plate and dried at ambient temperature overnight. The film on the glass plate was heated at 200 or 300 °C for 4 h under dynamic vacuum. The resulting film of **1** was dissolved in chloroform and purified by reprecipitation with methanol. The yield based on **5** was 77%. Mp 355—365 °C (decomp) ^{1}H NMR (CDCl$_3$) δ=0.88 (6H, bs), 1.00—1.51 (16H, m), 1.66 (4H, bs), 2.30—2.95 (4H, m), 7.25 (2H, s), 7.42 (2H, s). ^{13}C NMR (CDCl$_3$) δ=14.06, 22.65, 29.23, 29.67, 31.39, 31.87, 33.37, 126.90, 127.18, 135.61, 138.52. IR (film) 3008, 2921, 2854, 1802, 1695, 1603, 1498, 1467, 1378, 1340, 1259, 1193, 1118, 963, 892, 722, 504 cm^{-1}. Found (for **1** pyrolyzed at 300 °C): C, 88.34; H, 11.56; S, 1.50%. (For **1** pyrolyzed at 200 °C): C, 86.78; H, 10.98; S, 1.40%. Calcd for C$_{22}$H$_{34}$: C, 88.52; H, 11.48; S, 0%.

Conclusions

Poly(2,5-diheptyl-1,4-phenylenevinylene) (**1**) has been prepared accoding to the sulfonium salt pyrolysis procedure. Its molecular weight is high enough to make a freestanding film and its conjugation length is comparable to that of PPV. Elemental analysis indicates that **1** contains a small amount of sulfur. Since **1** has interesting properties, it is desirable to find a method for preparing **1** with more regular structure.

References

1) G. E. Wnek, J. C. W. Chien, F. E. Karasz, and C. P. Lillya, *Polym. Commun.,* **20**, 1441 (1979).

2) I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, *Polym. Commun.,* **25**, 327 (1984).

3) D. R. Gagnon, J. D. Capistran, F. E. Karasz, and R. W. Lenz, *Polym. Bull.,* **12**, 293 (1984).

4) S. Iwatsuki, M. Kubo, and T. Kumeuchi, *Chem. Lett.,* **1991**, 1071.

5) T. Kaino, K.-I. Kubodera, S. Tomaru, T. Kurihara, S. Saito, T. Tsutsui, and S. Tokito, *Electron. Lett.,* **23**, 1095 (1987).

6) M. Onoda, Y. Manda, T. Iwasa, H. Nakayama, K. Amakawa, and K. Yoshino, *Phys. Rev. B: Condens. Matter,* **42**, 11826 (1990).

7) S. Tokito, P. Smith, and A. J. Heeger, *Polymer,* **32**, 464 (1991).

8) S. H. Askari, S. D. Rughooputh, and F. Wudl, *Synth. Met.,* **29**, E129 (1989).

9) Y. Sonoda and K. Kaeriyama, *Polymer,* in press.

10) I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, *Synth. Met.,* **17**, 639 (1987).

11) S. Antoun, F. E. Karasz, and R. W. Lenz, *J. Polym. Sci., Part A: Polym. Chem.,* **26**, 1809 (1988).

12) M. Rehahn and A-D. Schluter, *Makromol. Chem., Rapid Commun.,* **11**, 375 (1990).

13) R. W. Lenz, C-C. Han, J. Stenger-Smith, and F. E. Karasz, *J. Polym. Sci., Part A: Polym. Chem.,* **26**, 3241 (1988).

14) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Chapman and Hall, London (1975), pp. 54.

15) R. Schenk, H. Gregorius, K. Meerholz, J. Heinze, and K. Mullen, *J. Am. Chem. Soc.,* **113**, 2634 (1991).

16) R. L. Elsenbaumer, K. Y. Jen, G. G. Miller, H. Eckhardt, L. W. Shacklette, and R. Jow, *Springer Ser. Solid-State Sci.,* **76**, 400 (1987).

17) M. Leclerc, F. M. Diaz, and G. Wegner, *Makromol. Chem.,* **190**, 3105 (1989).

18) J. Obrzut and F. E. Karasz, *J. Chem. Phys.,* **87**, 2349 (1987).