S0032-3861(96)00628-3

Polymer Vol. 38 No. 5, pp. 1221–1226, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00 + 0.00

Substituted poly(*p*-phenylene)s prepared from 2,5-diheptylbenzene-1,4-bis(trimethylene boronate)

Nobutaka Tanigaki
National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba, Ibaraki 305, Japan

and Hideyuki Masuda
Cooperative Research and Development Center, Yokohama National University, Tokiwadai, Yokohama 240, Japan

and Kyoji Kaeriyama*
Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyoku, Kyoto 606, Japan

(Received 2 February 1996; revised 1 May 1996)

Copolymers were prepared by the Suzuki reaction of 2,5-diheptylbenzene-1,4-bis(trimethylene boronate) with dibromobenzenes or dibromothiophene. From n.m.r. spectra, these copolymers turned out to be alternative copolymers of diheptylbenzene with benzenes or thiophene. The degree of polymerization of poly(2,5-diheptylbenzene) prepared according to the present method was 57, nearly five times as high as that for polymers prepared by Grignard coupling. The copolymer with thiophene had a degree of polymerization as high as 100 and was electrochemically active. Microscopic observation under crossed nicols conditions revealed that spherulite was formed on a film of this copolymer prepared by casting a xylene solution on a glass plate. On an oriented poly(*p*-phenylene) substrate, poly(*p*-phenylene-*alt*-2,5-diheptyl-*p*-phenylene) chains were aligned along the direction of orientation of the substrate. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: 2,5-diheptylbenzene-1,4-bis(trimethylene boronate); poly(2,5-diheptyl-*p*-phenylene-*alt*-2,5-thienylene); poly(*p*-phenylene-*alt*-2,5-diheptyl-*p*-phenylene))

INTRODUCTION

It was in 1886 that Goldschmiedt reported preparation of linear polymers from dibromobenzenes by the Wurz–Fittig reaction[1]. Since then, many chemists have studied the preparation of polyphenylenes. Busch *et al.* obtained polyphenylene consisting of 16 monomer units by heating *p*-dibromobenzene and potassium hydroxide at 150°C in the presence of iodine[2]. Cassidy *et al.* polymerized cyclohexadiene with *n*-butyllithium and converted the resulting polymer to poly(*p*-phenylene) (PPP) by dehydrogenation with chloranil[3]. However, the dehydrogenation was incomplete and aliphatic moieties remained in main chains. Kovacic and Kryakis oxidized benzene and aluminum chloride complex with copper (II) chloride to produce powdery PPP[4]. This method used to be adopted for the preparation of PPP, but this material contained polycyclic defects, detected by an intense e.s.r. signal[5]. Yamamoto *et al.* prepared PPP and poly(*m*-phenylene) by the nickel-catalysed Grignard coupling and PPP by dehalogenative coupling of 1,4-dibromobenzene with a mixture of bis(cyclooctadiene)-nickel(0) and 2,2′-bipyridyl[6,7].

Recently, Gin *et al.* prepared PPP by thermal conversion of precursor polymers from the acetyl derivative of 5,6-dihydroxy-1,3-cyclohexadiene. The molecular weight and structural regularity of the resulting PPP were dependent on the stereochemistry of the precursor polymer and the presence of an aromatization catalyst[8]. Lamba and Tour reported preparation of PPP which was bridged by imine groups to force the consecutive rings into planarity[9]. This polymer had a long conjugation length. Schlüter *et al.* applied the Suzuki reaction to the preparation of alkylated PPP[10]. Percec *et al.* synthesized functional PPP by nickel-catalysed coupling of hydroquinone bis(triflate)[11]. Chaturvedi *et al.* produced PPP by Cu(I)-catalysed decarboxylation of poly(benzoic acid), which was obtained by hydrolysis of poly(methyl benzoate)[12]. Thus, the preparation of PPP and its derivatives is still of current interest.

PPP and its derivatives show useful properties. They are some of the most thermally resistant organic materials. PPP was stable up to 500°C[13]. Poly(benzoyl-*p*-phenylene) could be cast into films which showed tensile moduli higher than 7000 GPa, and which were resistant up to 500°C[14]. Poly(methoxycarbonyl-*p*-phenylene) was also soluble and thermally resistant[15].

---

* To whom correspondence should be addressed

The electrical conductivity of PPP pellet was as high as 500 S cm^{-1} after doping with arsenic pentafluoride[16]. In this study, powdery PPP was pressed into pellets. If a high quality PPP film was obtained, it would show much higher conductivity.

Much attention is attracted to fabricating light emitting diodes (LEDs) with conjugated polymers. Especially, Blue electroluminescence, which is energetically higher than the bandgaps of inorganic semiconductors, is expected for organic LEDs. Grem *et al.* reported blue emission from polymeric LED fabricated from PPP[17]. A multilayer LED was constructed from a copolymer of dihexyloxybenzene with benzene using calcium as the negative contact[18]. Halls *et al.* constructed efficient LEDs from interpenetrating polymer networks formed from a phase-segregated mixture of two semiconductive polymers[19]. Thus, PPP and its derivatives are very promising materials, but it is still necessary to look for high quality materials.

It is possible to prepare copolymers by the Suzuki reaction of 2,5-diheptylbenzene-1,4-bis(boronic acid) but this material is an intractable hygroscopic mass. On the other hand, 2,5-diheptylbenzene-1,4-bis (trimethylene boronate) (HBTB) is crystalline material and not hygroscopic. Copolymerization of HBTB proceeded smoothly and gave high molecular weight polymers. The quality of copolymer with thiophene was high.

EXPERIMENTAL

Materials

Preparation of HBTB. This monomer was prepared according to *Scheme 1*. In a three-necked flask were charged 22 g (0.051 mol) of 1,4-dibromo-2,5-diheptylbenzene and 170 ml of toluene under argon. At room temperature, 85 ml (0.138 mol) of 1.6 M *n*-butyllithium in hexane was dropped to this solution and the mixture was refluxed for 24 h. After cooling to −70°C, 48 ml of trimethyl borate was dropped. This reaction mixture was stirred at room temperature for 24 h, followed by adding 200 ml of 2 N hydrogen chloride under ice-cooling, and stirring for 24 h. The precipitated product was recrystallized from acetone by adding 20 ml of hydrogen chloride. The yield was 3.6 g.

In a three-necked flask were placed 2.91 g (8.1×10^{-3} mol) of 2,5-diheptylbenzene-1,4-bis(boronic acid), 1.45 ml (1.91×10^{-2} mol) of trimethylene glycol and 83 ml of toluene, and the mixture was refluxed for 2.5 h. The solvent was distilled. The residue was dissolved in chloroform and dried over magnesium sulfate. The solvent was distilled and the residue was recrystallized from *n*-hexane. The yield was 2.84 g (80%). M.p. was 87.7–88.3°C.

^{1}H nuclear magnetic resonance (n.m.r., $CDCl_3$): 0.881 (3H, t), 1.29 (8H, m), 1.52 (2H, m), 2.77 (2H, t), 4.14 (4H, t), 7.44 (1H, s). ^{13}C n.m.r. ($CDCl_3$): 14.13, 22.70, 27.35, 29.22, 29.85, 31.89, 33.43, 35.42, 61.84, 135.52 (C_3), 144.99 (C_1, C_2).

I.r. (KBr): 2924 (s), 2853 (m), 1484 (m), 1420 (m), 1394 (m), 1371 (m), 1279 (s), 1209 (m), 1153 (s), 1128 (m), 929 (w), 853 (w), 726 (m), 596 (w).

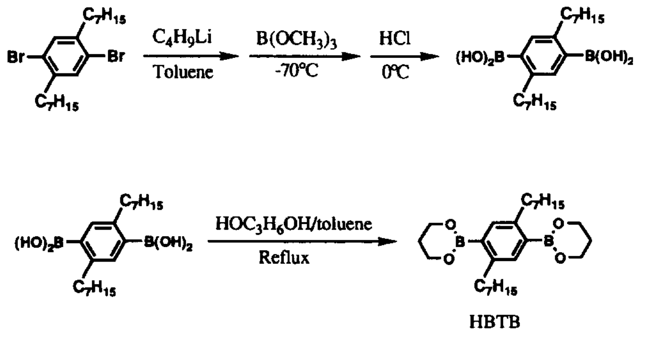
Copolymerization of HBTB. Under argon atmosphere, 0.559 g (2.31 mmol) of 2,5-dibromothiophene, 1.022 g (2.31 mmol) of HBTB, 0.026 g (0.023 mmol) of tetrakis(triphenylphosphine)palladium, 18 ml toluene and 20 ml of 1 M sodium carbonate were placed in a three-necked flask and heated at 95°C for 72 h. The polymerization mixture was poured in methanol. A blackish polymer was recovered and washed with magic solvent[20]. After washing with methanolic hydrazine and acetone, a yellow polymer was obtained. The yield was 0.774 g (91%). Magic solvent consists of quaternary ammonium bromide or iodide, bromine or iodine and organic solvent. The number of moles of halogen must not exceed half of those of the ammonium salt. This solvent dissolves noble metals but does not cause bromination to any organic compounds except a terminal olefinic group. An example of recipes: 25 g (0.119 mol) of tetraethylammonium bromide, 3.06 ml (0.0594 mol) of bromine and 600 ml of methanol.

Elemental analysis: Calcd for $C_{24}H_{34}S$; C 81.29, H 9.66, S 9.04. Found; C 81.69, H 9.58, S 8.73.

The other copolymers were prepared in a similar way. Elemental analysis: P-*p*-H, Calcd for $C_{26}H_{36}$; C, 89.59, H 10.41. Found; C 89.66, H 10.34. P-*p*-OP, Calcd for $C_{36}H_{56}O_2$; C 83.02, H 10.84. Found; C 83.13, H 10.73. P-*p*-HP, Calcd for $C_{20}H_{32}$; C 88.16, H 11.84. Found; C 88.03, H 11.96.

Measurement

U.v.–vis absorption spectra of polymer films, prepared by casting chloroform solution, were measured using a Shimadzu MPS 2000 spectrophotometer on transmission mode. ^{1}H and ^{13}C n.m.r. spectra were measured in $CDCl_3$ on a JEOL JNM-EX 270 n.m.r. spectrometer. Cyclic voltammograms were measured at room temperature in acetonitrile containing 0.1 mol l^{-1} electrolytes on a Hokuto Denko HA-501 potentiostat and HB-104 function generator. The reference electrode was a silver wire.



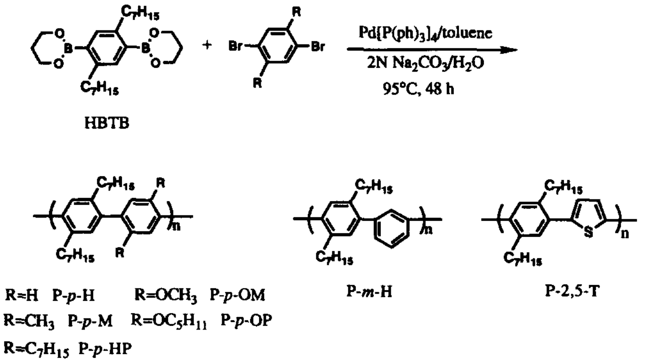
Scheme 1

RESULTS AND DISCUSSION

Preparation of copolymers

Copolymers were prepared according to *Scheme 2*. The monomers and the palladium complex in toluene were vigorously stirred with aqueous sodium carbonate. The aqueous phase absorbed hydrogen bromide and the boronic moiety. Polymerization was carried out smoothly. Recovered copolymers were off-white and washed with solvent to remove residual palladium[20]. After this treatment, the polymers were white or yellow. The polymers are abbreviated in the following part of this paper as shown in *Scheme 2*. P-*p*-HP is poly(2,5-diheptyl-*p*-phenylene). The others were alternative copolymers of diheptylbenzene with aromatic compounds.

Miyaura *et al.* showed that phenylboronic acid was coupled with aromatic bromides in the presence of tetrakis(triphenylphosphine)palladium[21]. Rehahn *et al.* prepared poly(2,5-dihexyl-*p*-phenylene) by the polymerization of 4-bromo-2,5-dihexylbenzeneboronic acid[22]. In the present study, 2,5-diheptylbenzene-1,4-bis(boronic acid) was converted to HBTB before polycondensation. While the former was a hygroscopic mass, the latter was crystalline material stable in a laboratory environment. HBTB could be highly purified by recrystallization. Thus, the copolymerization with HBTB could be performed more accurately than that with 2,5-diheptylbenzene-1,4-bis(boronic acid). A similar method was adopted by Wallow and Novak. They prepared a copolymer by the reaction of biphenyl-4,4′-bis(ethylene boronate) with 4,4′-dibromo-2,2′-dicarboxybiphenyl in the presence of a water-soluble palladium catalyst[23].



Scheme 2

Copolymers were moderately soluble in organic solvents. P-*p*-HP and P-*p*-OP were soluble in chloroform. P-2,5-T was easily soluble in organic solvents such as chloroform, chlorobenzene and toluene but P-*p*-H was only soluble in hot chloroform. P-*p*-H has a straight main chain. On the other hand, the main chain of P-2,5-T is bent with an angle of 32.4° at a thienylene unit, giving flexibility to this copolymer[24]. Thus, P-2,5-T is more soluble than the other copolymers.

The molecular weight was determined in comparison with polystyrene standards. All polymers had monomodal molecular weight distribution. The P-2,5-T had the highest molecular weight and P-*p*-HP the second highest.

The results of copolymerization are summarized in *Table 1*. The copolymers were obtained at high yield. Pn denotes the number of aromatic rings per polymer. While the nickel-catalysed Grignard coupling of 1,4-dibromo-2,5-dihexylbenzene gave oligomers with Pn of 11–13[25],

Table 1 Copolymerization of HBTB with aromatic compound

Polymer	Ring	Substituent	Yield (%)	Pn[a]	$M_n(\times10^3)$	$M_w(\times10^3)$
P-*p*-H	*p*-Phenylene	H	90	47	8.2	19
P-*p*-M	*p*-Phenylene	CH_3	94	17	3.3	5.8
P-*p*-HP	*p*-Phenylene	C_7H_{15}	93	57	15.5	40
P-*p*-HP	*p*-Phenylene	C_7H_{15}[b]	87	29	8.0	16
P-*p*-OM	*p*-Phenylene	OCH_3	94	–[c]	–[c]	–[c]
P-*p*-OP	*p*-Phenylene	OC_5H_{11}	76	11	2.7	4.2
P-*m*-H	*m*-Phenylene	H	90	21	3.6	5.1
P-2,5-T	2,5-Thienylene	H	91	104	18	45

[a] Number of aromatic rings per polymer
[b] Feed ratio of monomers = 0.94
[c] Polymer was insoluble

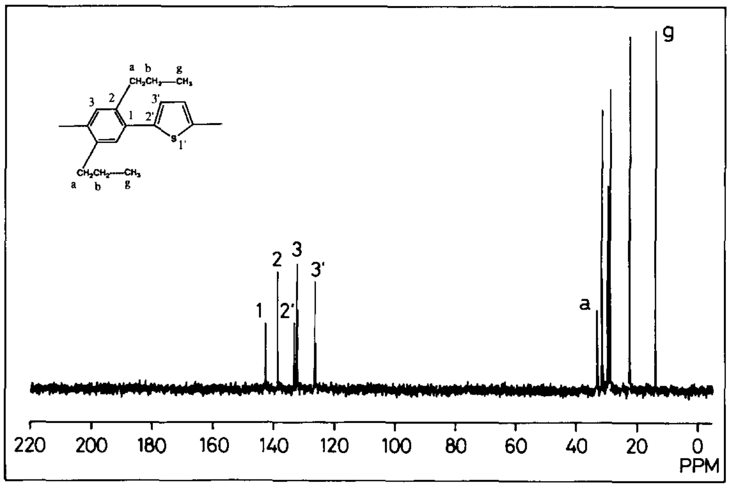


Figure 1 ^{13}C n.m.r. spectrum of P-2,5-T

the Pn of the P-*p*-HP obtained in this study was 57, indicating that the present methodology is reasonable.

The electron-donating ether group decreases the reactivity of bromine atoms on a benzene ring and the bromine atoms on the 2 and 5 positions of a thiophene ring are highly reactive. While Pn of P-2,5-T was as high as 104, P-*p*-OP showed the Pn as low as 11, showing that the Pn of the copolymers is largely dependent on the reactivity of comonomers.

Figure 1 presents ^{13}C n.m.r. spectrum of P-2,5-T. The assignments of signals were shown on the figures. No other signals were appreciable in this spectrum. The ^{1}H n.m.r. spectrum indicates that P-2,5-T is an equimolar copolymer of the two monomers. Taking into account that each monomer cannot be coupled with itself, it is clear that the P-2,5-T is an alternative copolymer expected from *Scheme 2*. P-*p*-HP exhibited identical n.m.r. spectrum to those previously reported by Rehahn *et al.*[22].

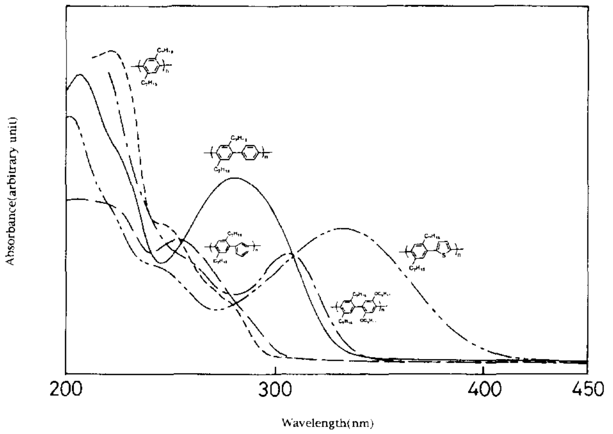


Figure 2 Absorption spectra of copolymer films: -----, P-*p*-HP; ——, P-*p*-H; — —, P-*m*-H; - - -, P-*p*-OP; · - - -, P-2,5-T

Properties of copolymers

Figure 2 shows electronic absorption spectra of copolymer films on quartz plates. P-*p*-HP exhibited a peak at 223 nm and two shoulders at about 247 and 280 nm. The shape of this spectrum was very similar to that previously reported for poly(2,5-dihexyl-*p*-phenylene)[26]. In the spectrum of P-*p*-H, a peak occurred at 281 nm, indicating that steric interaction was less in the P-*p*-H than the P-*p*-HP. The spectrum of P-*p*-OP shifted to the longer wavelength side and an absorption peak occurred at 306 nm. The calculation of the density-of-valence electronic-states for ring-substituted poly(*p*-phenylenevinylene)s has shown that ring torsions caused by lateral alkyl groups decrease the bandwidth of the highest occupied π band and increase the ionization potential and bandgap[27]. On the other hand, the alkoxy groups destabilize the highest two occupied bands, which is explained by the antibonding character of the interaction between the phenyl ring and alkoxy wave functions for the two bands. *Figure 2* indicates that this is also the case for substituted PPPs.

A peak occurred at 253 nm in the spectrum of P-*m*-H, indicating that conjugation along main chains was interrupted at *m*-phenylene units. The peak of P-2,5-T was located at 337 nm, indicating that effective conjugation along the polymer chain was long.

Figure 3 shows cyclic voltammograms of P-*p*-OP. In the first cycle, a peak occurred at 1.0 V vs Ag/Ag$^+$ and a shoulder at 0.89 V. The height of the peak decreased rapidly as the number of the cycle increased. In the seventh cycle, the peak almost disappeared, indicating that this polymer rapidly deteriorated during the electrochemical cycling.

Figure 4 shows cyclic voltammograms of P-2,5-T. This polymer could be cycled between oxidized and reduced states without appreciable decomposition. Two anodic peaks are located at 0.96 and 1.06 V and two cathodic ones at 1.04 and 0.95 V. From cyclic voltammograms of oligophenylene, Meerholz and Heinze have indicated

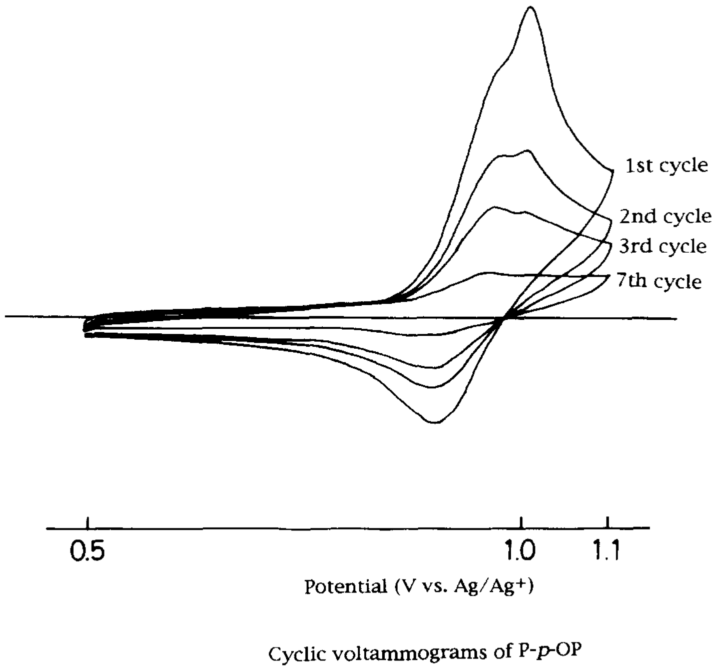


Figure 3 Cyclic voltammograms of P-*p*-OP: electrolyte, $(C_2H_5)_4NBF_4$; solvent, acetonitrile

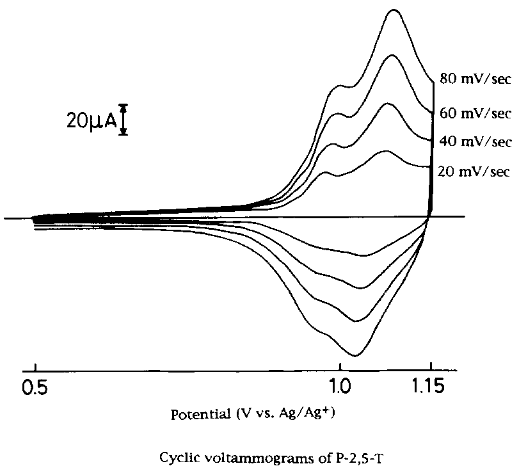


Figure 4 Cyclic voltammograms of P-2,5-T: electrolyte, $(C_2H_5)_4NBF_4$; solvent, acetonitrile

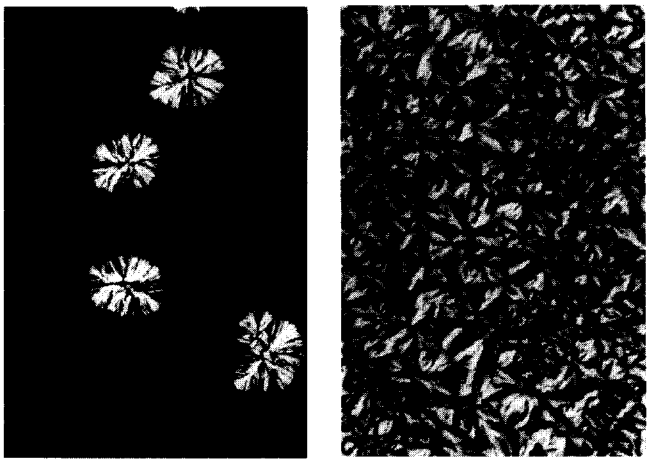


Figure 5 Microscopic photograph of P-2,5-T film under crossed nicols conditions. Film was cast from a xylene solution

that the difference of the potentials between the anodic and cathodic peaks depends on an energetic stabilization of the charged state[28]. This stabilization would be associated with a change from a twisted benzoid structure into a planar quinoid structure. The potential difference is 410 mV for the oxidation of sexiphenyl. The potential difference for P-2,5-T is as low as 10–20 mV, suggesting that this polymer assumes a twisted conformation even in the oxidized state.

The cyclic voltammograms of polythiophene and poly[1,4-bis(2-thienyl)benzene] showed anodic peaks at 0.67 and 0.79 V, respectively[29,30]. The anodic peaks occurred at appreciably higher potential in P-2,5-T than in these polymers.

Two anodic peaks occurred in the cyclic voltammograms of P-2,5-T. Recently Child *et al.* indicated that two anodic peaks in cyclic voltammograms corresponded to the formation of the polaron and bipolaron from spectroscopic and magnetic measurements[31]. This explanation might be true for other cyclic voltammograms of conjugated polymers with two anodic peaks. In *Figure 4*, the peak at 0.96 V is due to the formation of the polaron, followed by oxidation to the bipolaron at 1.06 V. However, only one peak often occurs in cyclic voltammograms of conjugated polymers. These polymers must be oxidized to the polaron and decomposed before the oxidation to the bipolaron. Alternatively, immediately after the formation of the polarons, they are recombined to the bipolaron. Thus, the polaron is not observed. This process is often the case for highly ordered conjugated polymers. In electrochemically prepared poly(3-dodecylthiophene), an as-grown film and a film cast from a solution of the neutral polymer showed two anodic peaks, while a film cast from a solution of the doped polymer exhibited one peak, which corresponded to a peak at a higher potential[32]. These data indicate that poly(3-dodecylthiophene) films were in differently ordered states depending on casting conditions.

Figure 6 Microscopic photograph of P-*p*-H film on oriented poly(*p*-phenylene) under crossed nicols conditions. Thin film was cast from a chloroform solution

Thin polymer films on glass plates were observed under crossed nicols conditions. *Figure 5* shows photographs of P-2,5-T film cast from a xylene solution. These photographs indicate isolated spherulites and overlapping spherulites. Similar pictures were observed for films obtained from a chlorobenzene solution.

A P-*p*-H film was prepared by casting a chloroform solution on oriented PPP and drying. The oriented PPP layer was made by the friction-deposition procedure previously reported[33]. *Figure 6* is a photograph of P-*p*-H on the oriented PPP layer which was taken under crossed nicols conditions. The bright lines in the picture are ridges of PPP chains. All areas of the film, including the ridges of PPP, changed alternately between bright and dark for every 45° rotation of the film, indicating that the overall film was oriented. It was reported that P-*p*-HP was arranged perpendicularly to oriented poly(tetrafluoroethylene) chains[34]. In the present case, the alignment of P-*p*-H chains was possibly caused by a template of oriented PPP chains. This orienting behaviour is being investigated in more detail.

CONCLUSIONS

HBTB was successfully copolymerized with aromatic dibromides, and higher molecular weight polymers were obtained by the present method than by the Grignard coupling. The quality of P-2,5-T was high. While P-*p*-OP was electrochemically decomposed, P-2,5-T was electrochemically active. P-2,5-T formed spherulites from a xylene solution and P-*p*-H aligned along the direction of an oriented substrate.

REFERENCES

1 Goldschmidt, G. *Monatsh.* 1886, **7,** 40

2 Busch, M., Weber, W., Darboven, C., Renner, W., Hahn, H. J., Mathauser, G., Stärtz, F., Zitzmann, K. and Engelhardt, H. *J. Prakt. Chem.* 1936, **146,** 1

3 Cassidy, P. E., Marvel, C. S. and Ray, S. *J. Polym. Sci.* 1965, **A3,** 1553

4 Kovacic, P. and Kryakis, A. *Tetrahedron Letter* 1962, 467

5 Froyer, G., Maurice, F., Bernier, P. and McAndrew, P. *Polym. Commun.* 1982, **23,** 1103

6 Yamamoto, T., Hayashi, Y. and Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1978, **51,** 2091

7 Yamamoto, T., Morita, A., Mayazaki, Y., Maruyama, T., Wakayama, H., Zhou, Z., Nakamura, Y. and Kanbara, T. *Macromolecules* 1992, **25,** 1214

8 Gin, D. L., Vincent, V. P., Conticello, P. and Grubbs, R. H. *J. Am. Chem. Soc.* 1994, **116,** 10934

9 Lamba, J. J. S. and Tour, J. M. *J. Am. Chem. Soc.* 1994, **116,** 11723

10 Schlüter, A.-D. and Wegner, G. *Acta Polym.* 1993, **44,** 59

11 Percec, V., Okita, S. and Weiss, R. *Macromolecules* 1992, **25,** 1816

12 Chaturvedi, V., Tanaka, S. and Kaeriyama, K. *Macromolecules* 1993, **26,** 2607

13 Stille, J. K. *Makromol. Chem.* 1972, **154,** 49

14 Wang, Y. and Quirk, R. P. *Macromolecules* 1995, **28,** 3495

15 Kaeriyama, K., Mehta, M. A., Chaturvedi, V. and Masuda, H. *Polymer* 1995, **36,** 3027

16 Shacklette, L. W., Chance, R. R., Ivory, D. M., Miller, G. G. and Baughman, R. H. *Synth. Met.* 1979, **1,** 307

17 Grem, D., Leditzky, G., Ullrich, B. and Leising, G. *Adv. Mater.* 1992, **4,** 36

18 Jing, W.-X., Kraft, A., Moratti, S. C., Grüner, J., Cacialli, F., Hamer, P. J., Hilmes, A. B. and Friend, R. H. *Synth. Met.* 1994, **67,** 161

19 Halls, J. J., Walsh, C. A., Greenham, N. C., Marseglia, E. A., Friend, R. H., Moratti, S. C. and Holmes, A. B. *Nature* 1995, **376,** 498

20 Nakao, Y. and Kaeriyama, K. US Patent 5,139,752 (1992)

21 Miyaura, N., Yanagi, T. and Suzuki, A. *Synth. Commun.* 1981, **11,** 513

22 Rehahn, M., Schlüter, A.-D., Wegner, G. and Feast, W. J. *Polymer* 1989, **30,** 1060

23 Wallow, T. I. and Novak, B. M. *J. Am. Chem. Soc.* 1991, **113,** 7411

24 Garnier, F., Tourillon, G., Barraud, J. Y. and Dexpert, H. *J. Mater. Sci.* 1985, **20,** 2687

25 Rehahn, M., Schlüter, A.-D., Wegner, G. and Feast, W. J. *Polymer* 1989, **30,** 1054

26 Rehahn, M., Schlüter, A.-D. and Wegner, G. *Makromol. Chem.* 1990, **191,** 1991

27 Fahlman, M., Lögdlund, M., Stafström, S., Salaneck, W. L., Friend, R. H., Burn, P. L., Holmes, A. B., Kaeriyama, K., Sonoda, Y., Lhost, O., Meyers, F. and Bredas, J. L. *Macromolecules* 1985, **28,** 1959

28 Meerholz, K. and Heinze, J. *Angew. Chem. Int. Ed. Engl.* 1990, **29,** 692

29 Sato, M., Tanaka, S. and Kaeriyama, K. *Synth Met.* 1986, **14,** 279

30 Mitsuhara, T., Tanaka, S. and Kaeriyama, K. *Makromol. Chem.* 1988, **189,** 1755

31 Child, A. D., Sankaran, B., Larmat, S. and Reynolds, J. R. *Macromolecules* 1995, **28,** 6571

32 Sato, M., Tanaka, S. and Kaeriyama, K. *Makromol. Chem.* 1987, **188,** 1771

33 Tanigaki, N., Yase, K. and Kaito, A. *Mol. Cryst. Liq. Cryst.* 1995, **267,** 335

34 Fahlman, M., Rasmusson, J., Kaeriyama, K., Clark, D. T., Beamson, G. and Salaneck, W. R. *Synth. Met.* 1994, **66,** 123