

Synthesis and Characterization of Electrically Conducting Copolymers Based on Benzene and Biphenyl

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ABSTRACT: Poly(*p*-phenylene) (H-PPP), which is one of the firstly investigated conducting polymer, has the disadvantage of difficult processability because it is infusible and insoluble. The use of biphenyl instead of benzene leads to *ortho*-, *meta*-, *para*-polyphenylenes (H-PP) which are more soluble and easier to be processed, however their electrical conductivity is lower. Copolymers of polyphenylenes (C₁ and C₂) and corresponding homopolymers (H-PPP and H-PP) were produced by the oxidative cationic polymerization of benzene and/or biphenyl. The soluble (-S) and the insoluble (-I) in chlorobenzene polyphenylenes were separated (H-PP-I, H-PP-S, C₁-I, C₁-S, C₂-I, and C₂-S) and they were doped with a solution of FeCl₃. All polyphenylenes were studied by FTIR, XRD, TGA, and their electrical conductivity with constant current was determined. Pronounced differences between the copolymers

and the homopolymers were observed, indicating the different structure of the former. The values of the electrical conductivity of doped insoluble copolymers (10⁻⁴ and 10⁻⁵ S/cm) are between that of H-PPP (10⁻³ S/cm) and H-PP-I (10⁻⁶ S/cm). The values of the electrical conductivity of doped soluble copolymers (10⁻⁵ S/cm) are considerably higher than that of H-PP-S (10⁻⁹ S/cm). The new electrically conductive polyphenylenes that were produced differ significantly from the corresponding homopolymers and combine good electrical conductivity and solubility. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 356–367, 2008

Key words: poly(*p*-phenylene); conducting polymers; copolymerization; (oxidative) cationic polymerization; electrical conductivity

INTRODUCTION

Since the discovery of conducting polyacetylene in late 1970s,^{1,2} the focus on the research for similar materials based on π -conjugated structures led to the development of the electrically conducting polymers.^{3–6} The latter, due to their low cost, low density, mechanical flexibility, and easy processability,^{7,8} are promising candidates for electronic applications, e.g., electromagnetic interference shielding,^{8–10} flexible "plastic" transistors,^{9–11} for electrooptical applications, e.g., electroluminescent polymer displays,^{5,10,12,13} polymer light-emitting diodes,^{8–12,14–16} photovoltaic solar cells^{9,11,17,18} and for electrochemical applications, e.g., rechargeable batteries,^{5,10,14–16} corrosion inhibitors,^{8–10,19} chemical and biochemical sensors.^{5,8,11,20,21}

Poly(*p*-phenylene), PPP, has attracted much interest among various conducting polymers, because of its high stability in air even at high temperatures,^{4,5,12,14,15,22} due to the aromatic repeat units, which are the simplest organic structures that resist to thermal decomposition and oxidation.²² Further-

more, PPP has high conductivity when it is doped,^{4,23} optoelectronic properties (e.g., as active constituents of blue light emitting diodes^{11,12}) and high strength.^{3,24} Polyphenylenes can be prepared using benzene or other aromatic compounds, such as biphenyl, either chemically in the form of powder or electrochemically as film.^{4,5,21} A principal advantage of chemical polymerization compared with the electrochemical one is the possibility of mass production at a reasonable cost.^{5,21} The different chemical syntheses of PPP are classified into three main reaction families: (1) direct oxidation of benzene with a suitable catalyst-oxidant system, usually referred to as the Kovacic reaction, (2) catalytic and thermal dehydrogenation of poly(1,3-cyclohexadiene), (3) metal-catalyzed coupling reactions (Grignard, Ullmann, Wurtz-Wittig, Yamamoto and Suzuki).^{4,23,25} The *para*-coupling of the benzene ring leads to poly(*p*-phenylene), which is infusible and insoluble.^{3,4,23}

On the other hand, fusible and soluble polyphenylenes can be prepared from several aromatic compounds, such as biphenyl, instead of benzene because the resulting isomeric polyphenylenes have *ortho*-, *meta*-, and *para*-couplings and therefore they are easier to be processed compared with PPP.^{23,25} PPP, as well as other polymers with poly-

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conjugated structure are insulators in the ground state, however, such polymers can be converted into highly conductive materials by doping with either electron acceptors or electron donors.⁴ Specifically, PPP has very wide range of conductivity, starting from 10^{-12} S/cm in the undoped state and up to 10^2 S/cm in the doped state.^{4,5,23,26} To improve the processability of PPP, apart from the isomeric polyphenylenes, other approaches have been developed, including the structural modification of PPP in the directions of solubilizing constituents,¹² functionalization with pendant alkyl groups,²⁴ graft copolymers with complex macromolecular architectures¹⁶ and copolymerization.^{14,15} The latter refers to the incorporation of other monomeric units, such as 3-octylthiophene,^{14,15} with the aryl unit derived from the benzene monomer. The modified polymers may increase the applications of PPP and allow better control of different properties of the materials such as conductivity, processability, stability, and morphology.¹⁵

The copolymerization of aryl derivatives through oxidative cationic polymerization was investigated in the early 1970s from Bilow and coworkers.^{22,27,28} The copolymers produced were studied under the aspect of applying polyphenylenes as ablative polymers suitable for use in erosive hyperthermal environments, although their potential application as conductive materials has not been investigated ever since.^{22,27,28} Moreover, in these reports many copolymers were synthesized using different comonomers, such as *meta*- and *ortho*-terphenyl, however the copolymerization of benzene with biphenyl was not studied.

The aim of this paper is to copolymerize benzene with biphenyl to produce modified polyphenylenes based on aryl units. Specifically, two monomeric units will be included in these copolymers, namely, benzene unit (one aryl) and biphenyl unit (two aryls). New isomeric polyphenylenes are expected to be produced depending on the proportion of the monomers. Their structure, electrical conductivity and thermal stability will be examined in comparison to that of the corresponding homopolymers.

EXPERIMENTAL

The benzene or the biphenyl was polymerized by oxidative cationic polymerization based on Kovacic and coworkers method,²⁵ using copper chloride, CuCl_2 , (Riedel-de Haën, anhydrous) as the oxidizer and aluminum chloride, AlCl_3 , (Fluka, anhydrous) as the catalyst. An 1L vapor reflux reactor was used, including a stirring system, a feed-tube for purified nitrogen stream, a condenser, a thermocouple for controlling the temperature of the reaction mixture and an oil bath for heating the reactor. Poly(*p*-phen-

ylene) (H-PPP) was produced by polymerization of benzene, C_6H_6 , (Merck, p.a.) at room temperature using the molar ratio of raw materials: $[\text{C}_6\text{H}_6]/[\text{CuCl}_2]/[\text{AlCl}_3]/[\text{H}_2\text{O}] = 1/0.497/0.602/0.055$,^{29,30} with water acting as cocatalyst. Initially, benzene, AlCl_3 and water (dropwise) were added in the reactor. Then, 15% w/w of the total amount of CuCl_2 was added and the rest was added in portions of 15% w/w every 5 min. After adding the last portion of the CuCl_2 , the polymerization continued for 150 min. Isomeric *ortho*-, *meta*-, *para*-polyphenylene (H-PP) was produced by polymerization of biphenyl, $\text{C}_{12}\text{H}_{10}$, (Fluka, p.a.), using a stoichiometric ratio of monomer to the oxidizer: $[\text{C}_{12}\text{H}_{10}]/[\text{CuCl}_2]/[\text{AlCl}_3] = 1/2/1.5$.^{29,31,32} The raw materials, biphenyl, AlCl_3 , and CuCl_2 , were added in the reactor simultaneously and the reaction mixture was heated at 100°C for 6 h.

Concerning the copolymerization of benzene with biphenyl, the fact that the polymerization procedure of benzene alone differs significantly from that of biphenyl, was taken into consideration. The main differences between the polymerization of benzene and that of biphenyl are the corresponding molar ratio of raw materials and the polymerization temperature. The feed molar ratio of benzene to biphenyl in the copolymerization may vary, but the sum of their moles should follow the molar ratio: [sum of the monomers]/ $[\text{CuCl}_2]/[\text{AlCl}_3] = 1/2/1.5$. This molar ratio ensures that the oxidant and the catalyst are in enough amounts to polymerize both monomers. Benzene is polymerized at room temperature, however biphenyl at 100°C . A series of preliminary experiments were carried out to define the copolymerization temperature, taking into consideration that this temperature should be below the boiling point of benzene, i.e., 80°C . The evolution of HCl vapors which are the polymerization by-product, started at 55°C , indicating the lowest possible copolymerization temperature. The latter was chosen for the production of two copolymers, C_1 and C_2 , using the molar ratio of benzene to biphenyl, $[\text{C}_6\text{H}_6]/[\text{C}_{12}\text{H}_{10}] = 0.5/0.5$ and $0.7/0.3$, respectively. Initially, benzene, biphenyl and AlCl_3 were added in the reactor and the same procedure as it was previously described for the polymerization of benzene was followed.

All the polymerizations were terminated by adding 400 mL of fuming HCl (37% w/w) and heating the reaction mixture up to boiling for 10 min. The reaction products were washed with dilute solution of HCl (16% w/w), filtrated and washed again with distilled water until the filtrate was free of chloride, to remove the catalyst and the oxidant residues. Since both benzene and biphenyl dissolve in fuming HCl under heating, the unreacted monomers contained in the reaction products were removed during

this washing process. After filtration, the polymers were purified from oligophenylenes or other admixtures by extraction with appropriate solvents in a Soxhlet device. For H-PPP the solvents were methanol, chloroform and *p*-xylene, whereas for the other polymers (i.e., H-PP, C₁, C₂) the solvent was *n*-hexane and the extraction time was 6 h for every solvent. Then, the purified polymers H-PPP, H-PP, C₁ and C₂ were separated in the insoluble (H-PPP, H-PP-I, C₁-I, C₂-I) and the soluble (H-PP-S, C₁-S, C₂-S) in chlorobenzene polyphenylenes by extraction with chlorobenzene for 12 h. After the last extraction, every insoluble polymer was dried in a vacuum oven at 70°C up to constant weight. The soluble in chlorobenzene polyphenylenes were obtained by evaporation of the solvent and subsequent drying of the remaining solid.

The polyphenylenes (i.e., H-PPP, H-PP-I, H-PP-S, C₁-I, C₁-S, C₂-I, C₂-S) were doped using a 10% (w/v) solution of anhydrous ferric chloride, FeCl₃, (Fluka, p.a.) in acetonitrile, CH₃CN, (Merck, LiChrosolv®), at room temperature for 24 h and the doped polymers were dried in a vacuum oven at 35°C up to constant weight.

The undoped and doped polyphenylenes were studied by Fourier Transform infrared spectroscopy (FTIR), X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA) and their electrical conductivity at room temperature with constant current was determined. The FTIR spectra were recorded on a Perkin-Elmer Spectrum GX spectrometer using KBr discs. The XRD diffractograms were recorded on a Siemens D5000 diffractometer using samples in the form of powder, with CuK_α radiation and scan rate of 0.02 degrees per second. TGA measurements were recorded on a Mettler Toledo 815E thermobalance using platinum pans under nitrogen flow, by heating the sample from 25°C up to 1000°C, with a heating rate of 10°C/min. The electrical conductivity of the polyphenylenes with constant current was determined at room temperature by the two-probe technique.³³ The specimens were in the form of discs having a diameter of 20 mm and a thickness of 0.5–0.7 mm, which were prepared from powdered polyphenylenes by exerting pressure (94 MPa for 1 min). The morphology of the undoped polyphenylenes was examined with a FEI Quanta 200 Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

Table I presents the homopolymers and copolymers produced from benzene and/or biphenyl, including their subsequent extractions with proper solvents and their doping. The polymer yield after every

extraction with the proper solvent was calculated from the equation:

$$\text{Polymer yield (\%)} = \frac{P}{M} \times 100$$

where *P* is the mass (g) of the polymer received after a definite extraction and *M* is the mass (g) of the monomer or the sum of monomers fed in the polymerization reactor.

Generally, the yield of the homopolymers after all extractions is sufficient, varying from 54 up to 72%. The polymerization of biphenyl has higher yield compared with that of benzene. The yield of the copolymers is between that of the homopolymers. The weight loss of the polymers after their extraction with methanol, chloroform and *p*-xylene (polymer H-PPP) or *n*-hexane (polymers H-PP, C₁, C₂) is lower than 5% and represents the oligomers formed during the polymerization and removed by extractions. After that, the polymers were extracted with chlorobenzene and the insoluble and soluble polyphenylenes were collected. Apart from H-PPP, all the polyphenylenes have soluble fraction. The inherent viscosity of the undoped soluble in chlorobenzene polyphenylenes was measured in chlorobenzene at 25°C and the values are (in 100 mL/g): [η]_{H-PP-S} = 0.17, [η]_{C₁-S} = 0.23 and [η]_{C₂-S} = 0.44.

Figure 1 shows the FTIR spectra of the undoped homopolymers H-PPP, H-PP-I and H-PP-S, whereas Figure 2 shows the FTIR spectra of the undoped copolymers C₁-I, C₁-S, C₂-I, and C₂-S. It is noticed that the spectra of the doped polyphenylenes exhibit the same absorption bands as those of the corresponding undoped. The various bands of the polyphenylenes were attributed to proper chemical bonds according to the literature^{4,23,29,31,34–37} and the results are summarized in Table II. The bands at 3030, 1600, 1480, and 1400 cm⁻¹ are associated with the aromatic ring. The broad absorption band at 1600 cm⁻¹ is particularly strong if a further conjugation with aromatic rings takes place. The intensity of this band characterizes the degree of condensed aromatic rings in the case of polyphenylenes.^{4,23,29,31,34,38,39} The type of substitution can be obtained from the intense bands below 900 cm⁻¹. The band at ~806 cm⁻¹ is characteristic of the *para*-substitution and the bands at 765 and 695 cm⁻¹ are characteristic of the aromatic rings which are at the end of the macromolecules, i.e., (mono) end-groups. In the case of the presence of the bands at 880–870 cm⁻¹, the stronger bands at 765 and 695 cm⁻¹ can be attributed to *meta*-substitution. The presence of a small band at 740 cm⁻¹ indicates *ortho*-substitution.^{4,23,31,34}

According to Figures 1 and 2, and Table II, the most intense absorption bands of polyphenylenes

TABLE I
Homopolymers and Copolymers Produced From Benzene and/or Biphenyl, Including Their Subsequent Extractions
With Proper Solvents and Their Doping

Code of polymers*	Polymerization				Extractions			Doping With solution of 10 % w/v FeCl ₃ in acetonitrile (-D) *			
	Raw materials (mol)		Catalysts AlCl ₃	With methanol, chloroform and p-xylene (for H-PPP) or n-hexane (for H-PP, C ₁ , C ₂)	With chlorobenzene Insoluble fraction (-I) *	Soluble fraction (-S) *					
	Monomers Benzene	Oxidizer CuCl ₂					With chlorobenzene Soluble fraction (-S) *				
Homopolymers	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
H-PPP	1	-	1	-	0.497	1.603	0.255	54.2	54.2		no
H-PPP-D	-	1	-	1	2	1.5	-	71.6	yes		yes
H-PP	-	1	-	1	2	1.5	-	71.6	→ 36.0		no
H-PP-I	-	1	-	1	2	1.5	-	71.6	→ 36.0		no
H-PP-S	-	1	-	1	2	1.5	-	71.6	→ 36.0		no
H-PP-I-D	-	1	-	1	2	1.5	-	71.6	→ 36.0	→ 35.6	no
H-PP-S-D	-	1	-	1	2	1.5	-	71.6	→ 36.0	→ 35.6	no
Copolymers	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
C ₁	0.5	0.5	0.5	0.5	2	1.5	-	62.5	→ 38.0		no
C ₁ -I	0.5	0.5	0.5	0.5	2	1.5	-	62.5	→ 38.0		no
C ₁ -S	0.5	0.5	0.5	0.5	2	1.5	-	62.5	→ 38.0		no
C ₁ -I-D	0.5	0.5	0.5	0.5	2	1.5	-	62.5	→ 38.0	→ 24.5	yes
C ₁ -S-D	0.5	0.5	0.5	0.5	2	1.5	-	62.5	→ 38.0	→ 24.5	yes
C ₂	0.7	0.3	0.3	0.3	2	1.5	-	57.6	→ 41.5		no
C ₂ -I	0.7	0.3	0.3	0.3	2	1.5	-	57.6	→ 41.5		no
C ₂ -S	0.7	0.3	0.3	0.3	2	1.5	-	57.6	→ 41.5		no
C ₂ -I-D	0.7	0.3	0.3	0.3	2	1.5	-	57.6	→ 41.5	→ 16.1	yes
C ₂ -S-D	0.7	0.3	0.3	0.3	2	1.5	-	57.6	→ 41.5	→ 16.1	yes

*The code of polymer consists of the following parts: a) for homopolymers 1st (H-), 2nd (PPP-) for poly(*p*-phenylene) and (PP-) for ortho-, meta-, para- polyphenylenes, produced from benzene or biphenyl, respectively, and 3rd / 4th the corresponding symbols (I-), (S-), (-D) b) for copolymers 1st (C-), i.e. (C₁-) and (C₂-) depending on the molecular ratio of the two monomers and 2nd / 3rd the corresponding symbols (I-), (S-), (-D)

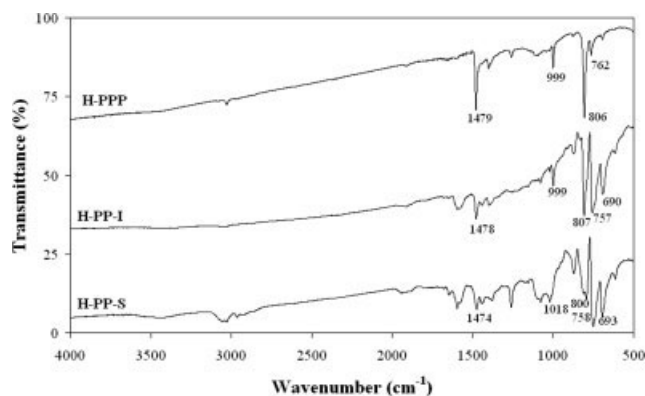


Figure 1 FTIR spectra of undoped homopolymers H-PPP, H-PP-I and H-PP-S (for the codes see Table I).

are at 1480 cm^{-1} and in the region $900\text{--}600\text{ cm}^{-1}$. Apart from H-PPP, the other polyphenylenes (H-PP or copolymers, both insoluble and soluble in chlorobenzene) exhibit *para*- and *meta*-substitution. The main differences between the spectra of H-PPP, H-PP-I and H-PP-S (Fig. 1 and Table II) are the following. The absorption band at 1600 cm^{-1} is negligible for H-PPP contrarily to that of H-PP-I and H-PP-S, where it is significant and the absorption bands at 1440 cm^{-1} (due to CH_2 aliphatic parts) and at 740 cm^{-1} (due to *ortho*-substitution) are not present in the spectrum of H-PPP. Concerning the soluble polyphenylenes H-PP-S, the bands at $2980\text{--}2950$, $2890\text{--}2850\text{ cm}^{-1}$ (due to methylene aliphatic parts) and at 1260 cm^{-1} (probably due to C—O—stretching vibrations) are significant, opposite to that of H-PPP and H-PP-I. In respect to the copolymers (Fig. 2), both the insoluble and the soluble in chlorobenzene polyphenylenes have similar spectra, since they contain both benzene and biphenyl structural units.

The structure of the different polyphenylenes under the aspect of their *para*- and *meta*- linkages can be estimated based on the intensity of the corresponding bands in the FTIR spectra. Specifically, the ratio of *para*- to *meta*- linkages (R) in the macromolecule can be determined from the ratio of the intensity of the band at 806 cm^{-1} (I_p) to the sum of the intensities of the bands at 765 cm^{-1} (I_{m_1}) and 695 cm^{-1} (I_{m_2}):^{4,23,29,31,34,35}

$$R = \frac{I_p}{I_{m_1} + I_{m_2}} \quad (1)$$

The values of the ratio R of the undoped polyphenylenes produced are presented in Table III. H-PPP has the highest value of R , confirming that it contains exclusively *para*- linkages. Comparing the insoluble in chlorobenzene polyphenylenes with the corresponding soluble ones (e.g., H-PP-I with H-PP-S), the former have higher values of R , approxi-

mately by a factor of 1.5 in relation to the latter, confirming that the insoluble polyphenylenes contain more *para*- linkages than the soluble ones. Moreover, the value of R of both insoluble and soluble polyphenylenes, increases linearly by decreasing the feed molar proportion of biphenyl. Specifically, the value of the ratio R increases according to the order: H-PPP > C₂-I > C₁-I > H-PP-I for the insoluble polyphenylenes and: C₂-S > C₁-S > H-PP-S for soluble polyphenylenes.

Figures 3 and 4 show the X-ray diffractograms of the undoped insoluble polyphenylenes (H-PPP, H-PP-I, C₁-I, and C₂-I) and of the undoped soluble polyphenylenes (H-PP-S, C₁-S, and C₂-S), respectively. All the polyphenylenes, except H-PP-S, show crystallinity and they have three main reflections, i.e., in the regions $19.1\text{--}20.4$, $21.0\text{--}22.8$, and $26.3\text{--}28.0^\circ$. The latter reflection for the insoluble copolymers (C₁-I and C₂-I) appears as a double peak, approximately at 27.0 and 27.6° . H-PP-I has three less intense reflections, i.e., at 16 , 32 , and 39° , where the first of them is also present in the soluble copolymers (C₁-S and C₂-S). It is worth noticing the significant crystallinity of the soluble copolymers, contrary to the lack of crystallinity of the soluble homopolymer H-PP-S.

From the diffractograms, the degree of crystallinity x_c (%), of polyphenylenes, their crystal system and their unit cell were estimated and the results are presented in Table IV. The degree of crystallinity of polyphenylenes is determined based on Refs. ⁴⁰ and ⁴¹ Although the doped copolymers have crystallinity, the doped homopolymers do not have. On the basis of the literature,^{42–45} the polyphenylenes belong to the orthorhombic or to the monoclinic crystal system. The reflections of the diffractograms of the polyphenylenes were indexed,^{42,43,46} to define the appropriate crystal system for every polyphenylene and their unit cell dimensions. The crystal system of H-PPP, C₁-I, C₂-I, C₁-I-D, and C₂-I-D is the orthorhombic, whereas that of H-PP-I, C₁-S, C₂-S, C₁-S-D

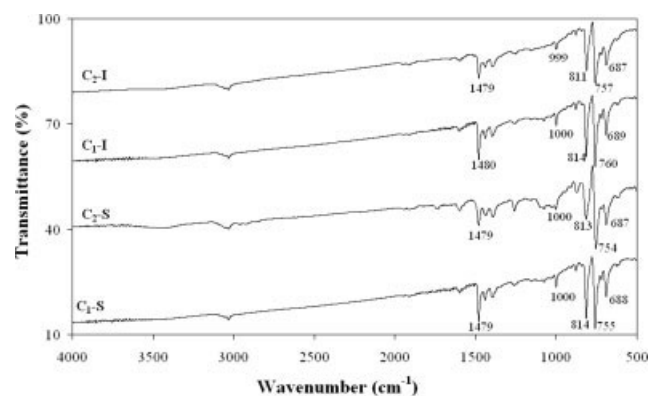


Figure 2 FTIR spectra of undoped copolymers C₁-I, C₁-S, C₂-I, and C₂-S (for the codes see Table I).

TABLE II
Description of FTIR Bands of Undoped Polyphenylenes

Characteristic bonds	Wavenumber according to literature (cm ⁻¹)	Polyphenylenes							
		Homopolymers				Copolymers			
		H-PPP	H-PP-I	H-PP-S	C ₁ -I	C ₁ -S	C ₂ -I	C ₂ -S	
C-H : aromatic stretching vibrations	3030	3024	3029	3024	3047; 3027	3044; 3025	3050; 3027	3050; 3026	
>CH ₂ : aliphatic (cyclic and linear) parts	2980-2950	2949	n	2959	2951	2950	-	2954	
C=C : stretching vibrations of aromatic ring	2890-2850	n	n	n	-	-	-	2842	
C-C : bending vibrations in aromatic ring	1600	n	1592	1596	1594	1594	1594	1594	
CH ₂ : aliphatic (cyclic and linear) parts	1480	1479	1478	1474	1480	1479	1479	1479	
C-H : "in plane" bending vibrations, characteristic of para- substitution	1400	1397	1393	1380	1389	1388	1388	1388	
C-H : "out of plane" bending vibrations, characteristic of separated H in aromatic ring	1440	-	1439	1433	1438	1436	1438	1434	
C-H : "out of plane" bending vibrations of two neighbouring H in aromatic ring, characteristic of para- substitution	1094-1000	1092; 999	1076; 999	1075; 1018	1073; 1000	1074; 1000	1072; 999	1073; 1000	
C-H : bending vibrations of four or five neighbouring H in aromatic ring	876	873	868	868	876	875	876	868	
ortho-substitution	806	806	807	800	814	814	811	813	
CH ₂ : aliphatic (cyclic and linear) parts	765	762	757	758	760	755	757	754	
"ring puckering" in aromatic ring; observed in mono, 1,3-, 1,3,5- and 1,2,3- substituted phenylene	740	-	742	749	n	n	-	-	
	722	-	-	n	721	720	720	717	
	695	n	690	693	689	688	687	687	

n, negligible.

TABLE III
Ratio of para- to- meta- Linkages, R , of the Undoped Polyphenylenes

Polyphenylenes	$R = \frac{I_p}{I_{m_1} + I_{m_2}}$
H-PPP	4.75
H-PP-I	0.78
H-PP-S	0.52
C ₁ -I	0.83
C ₁ -S	0.56
C ₂ -I	0.87
C ₂ -S	0.58

I_p : intensity of the absorption band of para-linkages at 806 cm^{-1} .

I_{m_1} : intensity of the absorption band of meta-linkages at 765 cm^{-1} .

I_{m_2} : intensity of the absorption band of meta-linkages at 695 cm^{-1} .

and C₂-S-D is the monoclinic. The crystal system of doped copolymers is the same as that of the corresponding undoped copolymers; however their unit cell dimensions are slightly increased.

Figures 5 and 6 show the TGA curves of the undoped and the doped polyphenylenes, respectively. The weight loss of the undoped homopolymers H-PPP, H-PP-I, and H-PP-S is lower than that of the undoped copolymers (Fig. 5), the latter exhibiting an abrupt loss (up to 80% of their initial weight) in the region 400–600°C. The doped polyphenylenes (Fig. 6) show a similar behavior. The weight loss of the polyphenylenes is analyzed in three regions: the first up to 400°C, the second up to 800°C and the final up to 1000°C, as it is shown in Table V that includes also the total weight loss. Comparing every pair of undoped and doped homopolymer (Table V), it is observed that the weight loss of the doped is higher than that of the corresponding undoped. However, the opposite situation occurs for the copolymers, i.e., the doped copolymers have less weight loss than the corresponding undoped. This behavior will be explained below. Even though the total weight loss of the copolymers (both doped and undoped) is quite large, in the first temperature region, up to 400°C, they exhibit lower weight loss compared with the homopolymers, indicating that they are more stable in this region.

Figure 7(a–d) show the SEM micrographs of H-PPP and C₁-I, respectively, at different magnifications, which are representative for all the polyphenylenes. C₁-I has a highly ordered structure with crystalline regions, whereas H-PPP has a less ordered structure with smaller crystalline regions.

The electrical conductivity in constant current of the doped polyphenylenes at room temperature was determined and the results are summarized in Table VI. The conductivity of all the undoped polyphenylenes is in the order of 10^{-12} S/cm , i.e., they are

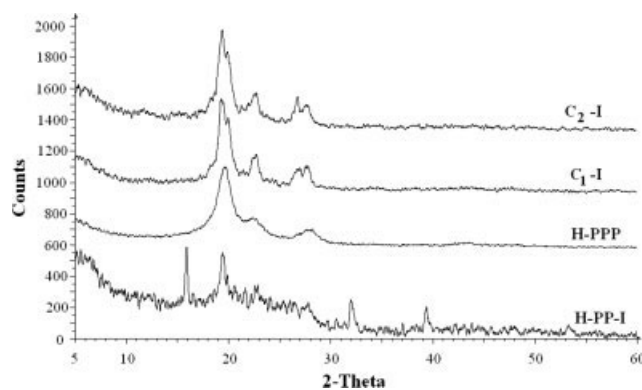


Figure 3 X-ray diffractograms of undoped, insoluble in chlorobezene polyphenylenes (for the codes see Table I).

insulators. H-PPP-D exhibits the highest conductivity (in the order of 10^{-3} S/cm). The conductivity of H-PP-I-D is in the order of 10^{-6} S/cm and that of H-PP-S-D is much lower (in the order of 10^{-9} S/cm). The copolymers, both insoluble and soluble, have conductivity in the order of 10^{-4} to 10^{-5} S/cm , i.e., they are closer to that of H-PPP-D instead of H-PP-I-D.

Figure 8 shows the electrical conductivity in constant current of the doped polyphenylenes at room temperature versus time after doping. The curves of the copolymers are between that of H-PPP-D (having the highest values) and H-PP-I-D. The electrical conductivity of H-PP-S-D decreases rapidly, reaching the state of insulator, which is a strong disadvantage for technological applications. The other polyphenylenes remain semiconductors even after 14 months. The copolymers are more stable than the homopolymers, since their electrical conductivity decreases with slower rate.

All the undoped polyphenylenes, except for the totally amorphous H-PP-S, have a degree of crystallinity between 34.4 and 66.7% and their crystal system is the orthorhombic or the monoclinic (Table IV). For poly(*p*-phenylene) an orthorhombic^{31,42,43,45,47–50} or a monoclinic structure^{31,43,47,50} has

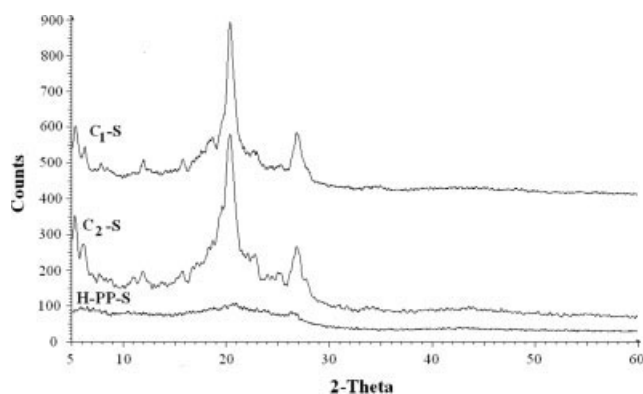


Figure 4 X-ray diffractograms of undoped, soluble in chlorobezene polyphenylenes (for the codes see Table I).

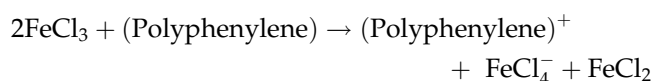
TABLE IV
Crystallographic Data of the Undoped and Doped Polyphenylenes

Polyphenylenes	Degree of crystallinity, χ_c (%)	Crystal system*	a (Å)	b (Å)	c (Å)	α (deg.)	β (deg.)	γ (deg.)	V (Å ³)
H-PPP	47.5	O	7.793	5.553	4.193	90	90	90	184.7
H-PPP-D	0.9	—	—	—	—	—	—	—	—
H-PP-I	34.4	M	8.277	5.301	4.309	90	109	90	178.7
H-PP-I-D	0.0	—	—	—	—	—	—	—	—
H-PP-S	0.0	—	—	—	—	—	—	—	—
H-PP-S-D	0.0	—	—	—	—	—	—	—	—
C ₁ -I	66.1	O	7.829	5.767	4.415	90	90	90	199.3
C ₁ -I-D	45.1	O	7.863	5.708	4.526	90	90	90	203.2
C ₁ -S	57.1	M	7.921	5.270	4.717	90	109	90	186.2
C ₁ -S-D	35.7	M	8.310	5.276	4.717	90	109	90	195.6
C ₂ -I	66.7	O	7.900	5.565	4.415	90	90	90	194.0
C ₂ -I-D	41.1	O	7.820	5.602	4.437	90	90	90	194.4
C ₂ -S	44.6	M	7.924	5.369	4.644	90	109	90	186.7
zC ₂ -S-D	25.9	M	8.273	5.276	4.644	90	109	90	191.7

* O: orthorhombic, M: Monoclinic.

been proposed with two monomeric units per unit cell for both crystal systems. The unit cell dimensions of the orthorhombic system have been reported as: $a = 7.81$ Å, $b = 5.53$ Å and $c = 4.20$ Å^{45,47,50} and that of the monoclinic system as: $a = 7.79$ Å, $b = 5.62$ Å, $c = 4.26$ Å and $\beta = 79^\circ$.^{31,47,50} Furthermore, the unit cell of the orthorhombic system of poly(*p*-phenylene) has been reported as: $a = 7.78$ Å, $b = 5.52$ Å and $c = 8.54$ Å,^{46,48,51} where the data are more scattered for the c parameter due to possible monoclinic distortions that depend on the conjugation length, degree of polymerization and disorder.^{48,52} The dimensions of the unit cell of H-PPP are similar to the above-mentioned and its crystal system is the orthorhombic. The crystal system of H-PP-I is the monoclinic that is in agreement with the literature for insoluble *ortho*-, *meta*-, *para*-polyphenylenes, where the dimensions of the unit cell depends on the proportion of the raw materials, i.e., biphenyl/oxidizer and biphenyl/catalyst.³¹

Concerning the undoped copolymers, the crystal system of the insoluble in chlorobenzene polyphenylenes, C₁-I and C₂-I, is the orthorhombic, whereas that of the soluble ones, C₁-S and C₂-S, is the monoclinic, having slightly lower unit volume compared with the insoluble polyphenylenes. The doped homopolymers have no crystallinity, however the doped copolymers exhibit crystallinity and they have the same crystal system like that of the corresponding undoped. The volume of the unit cell of the doped copolymers increases slightly compared with the corresponding undoped copolymers. The dopant FeCl₃ causes oxidation of the polyphenylenes according to the reaction^{53,54}:



As already mentioned, two main differences between the copolymers and homopolymers are

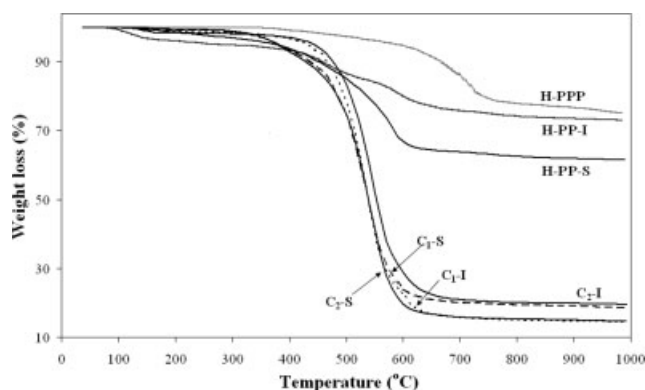


Figure 5 TGA curves of undoped polyphenylenes in inert atmosphere (for the codes see Table I).

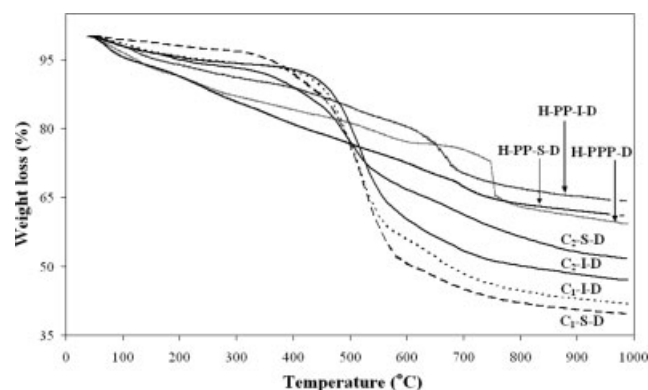


Figure 6 TGA curves of doped polyphenylenes in inert atmosphere (for the codes see Table I).

TABLE V
Weight loss (%) for Different Temperature Ranges According to TGA for the Undoped and Doped Polyphenylenes

Polyphenylenes	Weight loss (%) for temperature ranges			Total weight loss (%)
	25–400°C	400°C–800°C	800°C–1000°C	
H-PPP	0.77	21.42	2.63	24.82
H-PPP-D	16.05	21.07	3.63	40.75
H-PP-I	6.67	19.18	1.09	26.94
H-PP-I-D	11.27	21.83	2.73	35.83
H-PP-S	5.83	31.63	1.02	38.48
H-PP-S-D	18.87	17.36	2.82	39.10
C ₁ -I	3.09	81.93	0.57	85.59
C ₁ -I-D	7.59	47.67	2.86	58.12
C ₁ -S	5.83	74.74	0.91	81.48
C ₁ -S-D	8.52	49.40	2.46	60.38
C ₂ -I	2.97	76.97	0.50	80.44
C ₂ -I-D	7.30	42.55	3.16	53.01
C ₂ -S	6.41	78.31	0.72	85.44
C ₂ -S-D	11.37	31.95	4.95	48.27

observed, i.e., the degree of crystallinity of the undoped copolymers is generally higher than that of the undoped homopolymers and only the doped

copolymers have crystallinity. More pronounced are the differences between the copolymers and the homopolymers from the point of view of the ther-

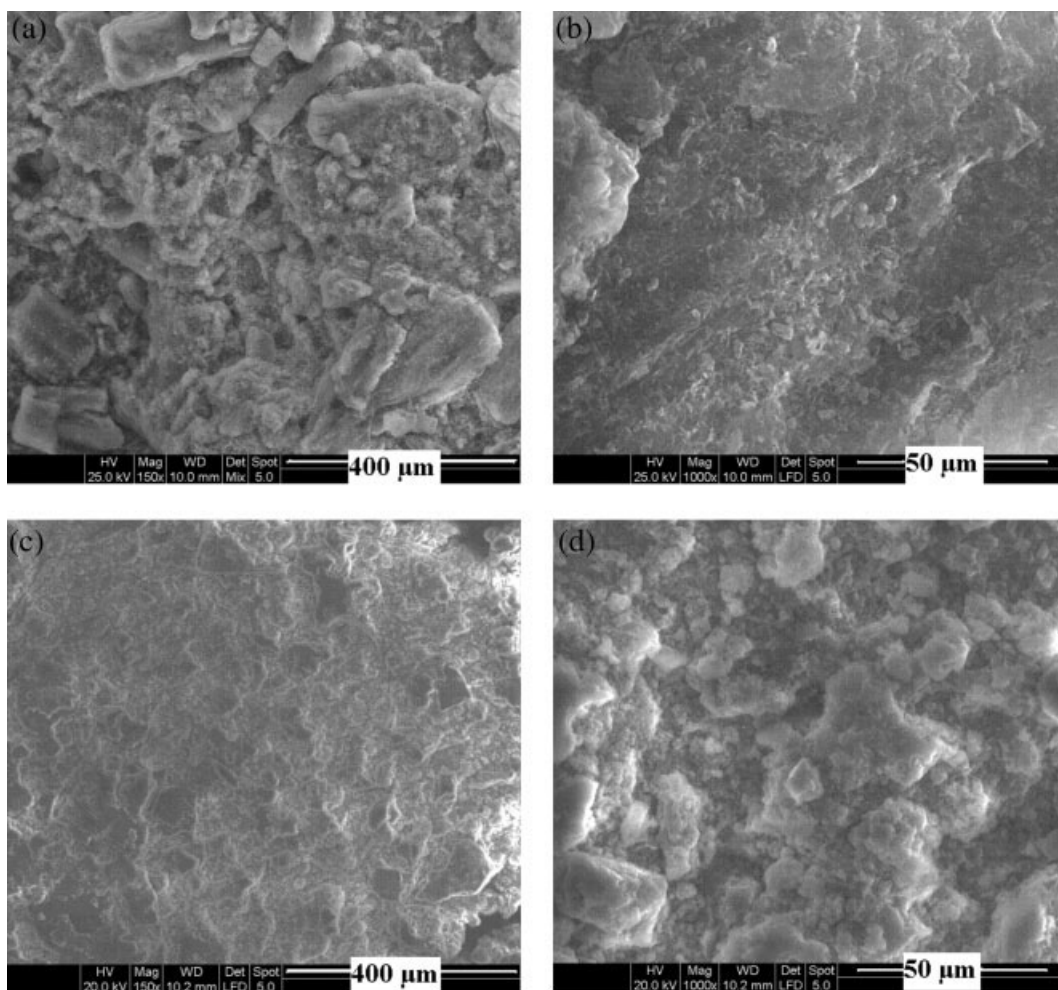


Figure 7 SEM micrographs of undoped polyphenylenes (a), H-PPP (b) and C₁-I (for the codes see Table I) (c,d).

TABLE VI
Electrical Conductivity in Constant Current of Doped Polyphenylenes at Room Temperature, Immediately after Their Doping

Polyphenylenes	Electrical conductivity, σ , (S/cm)
H-PPP-D	8.0×10^{-3}
H-PP-I-D	7.6×10^{-6}
H-PP-S-D	1.2×10^{-9}
C ₁ -I-D	3.9×10^{-5}
C ₁ -S-D	2.1×10^{-5}
C ₂ -I-D	5.7×10^{-4}
C ₂ -S-D	3.1×10^{-5}

mogravimetry. Indeed, the curves of the weight loss versus temperature of the undoped copolymers are completely different from those of the undoped homopolymers (Fig. 5) and especially above 400°C. The same differences are observed between the doped copolymers and doped homopolymers (Fig. 6). To interpret these results, the ortho-, meta-, para-linkages in the macromolecules of all polyphenylenes should be considered. On the basis of the parameter R calculated from the FTIR spectra, compared with the undoped homopolymers H-PPP, H-PP-I, and H-PP-S, the former, produced from benzene, contains exclusively para-linkages (Table III) whereas both other, produced from biphenyl, contain mainly meta-linkages and especially the soluble polyphenylene (H-PP-S). The insoluble copolymers have more para-linkages than the soluble ones (Table III), the crystal system of the former is the orthorhombic and that of the latter is the monoclinic.

The weight loss of the undoped homopolymers is higher for H-PP-S, which contain more meta-linkages and the lowest is for H-PPP, which contain exclusively para-linkages. The undoped copolymers are thermally stable up to practically 400°C and then they exhibit an abrupt weight loss up to 600°C. The homopolymer H-PPP has benzene units linked in *para*-positions, whereas H-PP-I and H-PP-S have biphenyl units linked either in *para*- or in *meta*-positions. Therefore, it would be expected for the copolymers to have a similar weight loss behavior because their structure contains benzene and biphenyl units. However, their abrupt weight loss between 400 and 600°C resembles the weight loss of polymers due to defect positions^{41,55} leading to long molecular chain fragments. Below, a molecular structure is proposed, which represents benzene units linked in *para*-positions and biphenyl units linked in *para*- or *meta*-positions, as well as a defect position of a separate benzene unit in *meta*-position between two biphenyl units (Fig. 9). The latter constitutes a defect during the thermal degradation of the copolymers. Taking into consideration that the degree of crystallinity of the copolymers is very high (Table IV), this

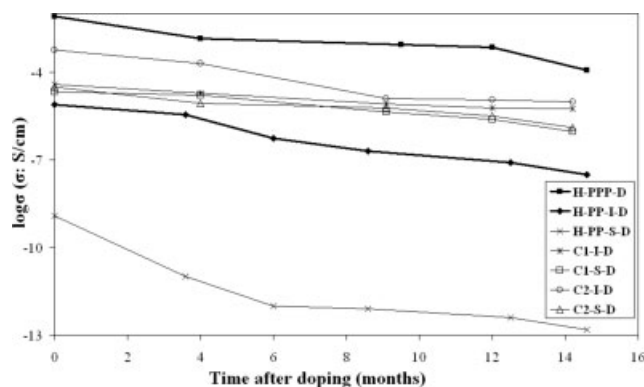


Figure 8 Electrical conductivity in constant current of doped polyphenylenes at room temperature versus time after doping (for the codes see Table I).

defect must not disturb the order of the macromolecule, i.e., the two molecular segments between the defect must be parallel to the chain axis. Concerning the poly(*p*-phenylene),^{42,48,56} the benzene rings of a macromolecule could be planar or twisted. The benzene rings along the chain twist clockwise or anticlockwise round the molecule axis with equal statistical probability so that they could settle in an energetically favorite position deviated from the planar structure. Even though the orientation of the benzene rings changes randomly, the chain still keeps firmly the regularity of the atomic position in the direction of the chain axis and has a planar conformation as an average.^{42,48,56} On the other hand, the insoluble copolymers have higher degree of crystallinity than H-PPP (Table IV), indicating that their conformation is more regular.

The weight loss of the doped homopolymers is higher and begins at lower temperatures (below 400°C) than the corresponding undoped homopolymers. Their differences can be attributed to the dopant. Namely, according to reaction (1), FeCl₃ sublimates already at 315°C.⁵⁷⁻⁵⁹ On the other hand, the TGA curves of doped copolymers are similar to that of the undoped copolymers up to 500°C, however above that temperature the weight loss of the doped copolymers is much lower than that of the undoped (Figs. 5 and 6, Table V). It is obvious that the influence of FeCl₃ on the weight loss of the doped copolymers is not the same as that on the doped homopolymers. It is known from the literature that

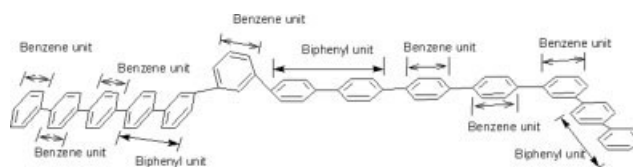


Figure 9 Configuration of a possible structure of the copolymers.

Lewis acid-type transition metal chloride additives, such as FeCl_3 , influence the thermal degradation of many polymers, such as ABS or polyacrylonitrile,⁶⁰ leading to a significant increase of the solid residue at 600°C under nitrogen atmosphere. Moreover, the addition of a catalyst, such as FeCl_3 , to the initial pitch or hydrocarbons increases the coke yield during the pyrolysis,⁶¹ because it favors hydrogen evolution at lower temperature and provokes more polycondensation reactions.

Therefore, for the doped copolymers, it seems that the dopant FeCl_3 has a catalytic effect on their thermal degradation leading to much lower weight loss than the undoped copolymers. This behavior could be attributed to the ability of FeCl_3 to be retained as dopant anion, FeCl_4^- , near the defect position between the parallel segments of a macromolecule (Fig. 9), stabilizing the defect position and acting as catalyst during the thermal degradation of the copolymers. Furthermore, opposite to the doped homopolymers, the doped copolymers have crystallinity, which contributes to the retaining of FeCl_3 into the crystalline region and acting catalytically during the thermal degradation of the copolymers.

The influence of the structure of the different polyphenylenes on their electrical conductivity can be concluded based on the chemical structure which describes a macromolecule alone and the physical structure which describes many macromolecules together.⁶² For the former, the FTIR spectra give useful information related to para-, ortho- or meta- linkages, whereas for the latter the X-ray diffractograms are related to the crystallinity. Furthermore, the thermal degradation of the polyphenylenes based on the TGA gives indirect information for their structure. The electrical conductivity of doped polyphenylenes follows the order:

$$\text{H-PPP-D} > \text{C}_2\text{-I-D} > \text{C}_1\text{-I-D} \approx \text{C}_2\text{-S-D} \approx \text{C}_1\text{-S-D} \\ > \text{H-PP-I-D} > \text{H-PP-S-D}$$

The H-PPP-D has exclusively para- linkages, however it has no crystallinity and the corresponding undoped has lower crystallinity than $\text{C}_2\text{-I}$, $\text{C}_1\text{-I}$, and $\text{C}_1\text{-S}$. On the other hand, $\text{C}_2\text{-I-D}$ has an electrical conductivity one order lower than that of H-PPP-D, higher ratio R (ratio of para- to meta- linkages) than the rest polyphenylenes (apart from H-PPP) and high crystallinity as undoped and doped. The thermal degradation above 400°C of the copolymers, undoped and doped, is higher than that of the homopolymers. The degree of crystallinity of the copolymers, undoped and doped, is higher than that of the homopolymers. The ratio R for $\text{C}_1\text{-I}$ and $\text{C}_2\text{-I}$ is higher than that of H-PP-I and the ratio R for $\text{C}_1\text{-S}$ and $\text{C}_2\text{-S}$ is higher than that of H-PP-S. Therefore, the ratio R is more important factor than the crystallinity for the electrical conductivity of the polypheny-

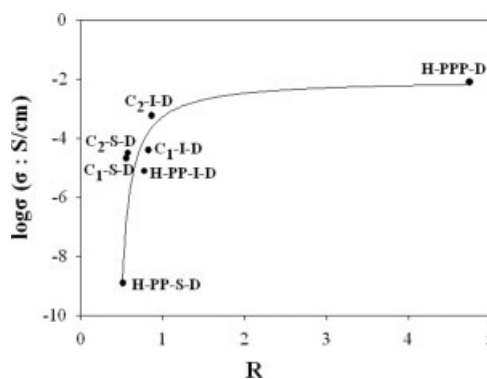


Figure 10 Electrical conductivity in constant current of doped polyphenylenes at room temperature versus the ratio of para- to meta- linkages, R (for the codes see Table I).

lenes. The correlation between the electrical conductivity of doped polyphenylenes with the ratio of para- to meta- linkages, R , is shown in Figure 10, where it seems that the fitting curve is of hyperbolic type.

The copolymers produced by the polymerization of benzene with biphenyl have electrical conductivity in the order of 10^{-5} to 10^{-4} S/cm and they almost preserve it even after 14 months (by decreasing one order of magnitude). Conductivity values for polymers in the order of 10^{-7} to 10^{-6} S/cm are required for electrostatic discharge applications, values in the region of 10^{-5} S/cm are required for touch screen displays, whereas values of 10^{-4} S/cm are required for flat panel devices and possibly for electromagnetic interference shielding.⁶³

CONCLUSIONS

New electrically conductive polyphenylenes have been produced by the copolymerization of benzene with biphenyl, which differ significantly from the corresponding homopolymers produced from benzene or biphenyl. The insoluble and soluble copolymers have higher crystallinity than the homopolymers and their conductivity is between that of the homopolymers. The disadvantage of higher thermal degradation of the copolymers above 400°C has no practical meaning, since the conducting polymers (including polyphenylenes) are used at considerably lower temperatures. The ratio of para- to meta- linkages is very important for the electrical conductivity. The combination of good electrical conductivity with stability for a long time is very promising for many technological applications, especially for the soluble copolymers which have the advantage of easier processability.

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