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Characterization of Undoped and Doped Isomeric o,m,p-Polyphenylenes by X-ray, FTIR and Electrical Conductivity Measurements

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Isomeric o,m,p-polyphenylenes were prepared by oxidation-cationic polymerization of biphenyl with various proportions of the polymerization components biphenyl- AlCl_3 - Cu-Cl_2 . The insoluble fraction in chlorobenzene was separated. The insoluble polyphenylenes were then doped with anhydrous FeCl_3 , AlCl_3 , and SnCl_4 in solutions of acetonitrile (ACN), nitrobenzene (N), and acetone (A). X-ray diffraction, Fourier Transform Infrared Spectroscopy (FTIR), and electrical conductivity measurements were carried out to characterize the undoped and doped materials. Some of the o,m,p-polyphenylenes had semiconductive properties after doping depending on the proportion of biphenyl- AlCl_3 - CuCl_2 and the doping system (dopant and solvent).

KEY WORDS Polyphenylenes, electrical conductive polymers, doping

INTRODUCTION

Polyphenylenes are aromatic polymers that can be prepared mainly from benzene or other aromatic nuclei, such as biphenyl and terphenyl using usually oxidative cationic polymerization (e.g., Kovacic procedure using benzene-aluminum chloride-cupric chloride) or other methods (e.g., modified Grignard reactions.) [1] The para-coupling of benzene leads to polyparaphenylene, which is infusible and insoluble. The reaction of biphenyl, however, leads to meta-, ortho- and para-coupling, so that the obtained isomeric polyphenylenes are fusible and soluble and therefore easier to be processed [2, 3].

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Polyphenylenes as well as other polymers with polyconjugated structure are insulators in the ground state [4]; however, such polymers can be converted to highly conductive materials by doping with either electron acceptors or donors [5]. Undoped and doped polymer systems are only partially crystallized and in some cases completely amorphous. This often makes characterization and, consequently, description of the chemistry and physics very difficult [6].

The main purpose of this study is to characterize the o,m,p-polyphenylenes prepared by oxidation-cationic polymerization and doped with different doping systems, by X-ray, FTIR, and electrical conductivity measurements. The different doping systems, as well as the different chemical and crystal structure of polyphenylenes, influence the alternating electrical conductivity σ' [7].

EXPERIMENTAL

o,m,p-Polyphenylenes were prepared by oxidation-cationic polymerization [2] of biphenyl (B) using various molecular proportions of CuCl_2 (O) as oxidizer and AlCl_3 (C) as catalyst. After the purification by extraction with hexane, and then with chlorobenzene, the insoluble fraction was isolated. Each of the polyphenylenes prepared were doped with 10% solutions of FeCl_3 , AlCl_3 , and SnCl_4 in nitrobenzene (N), acetonitrile (ACN), and acetone (A) for 24 h at 20°C.

The alternating electrical conductivity σ' of dried polyphenylenes (24 h at 60°C) was measured by using an impedance analyzer (Hewlett-Packard) controlled by computer. FTIR spectroscopy was carried out using KBr discs. X-ray diffraction measurements were performed using $\text{CuK}\alpha$ radiation and a photographic technique and followed by photometric procedure of the film calibrated with CaF_2 .

RESULTS AND DISCUSSION

Table I describes briefly all the polymerization and doping conditions as well as the abbreviations used. The alternating electrical conductivity σ' of 2AD and 5AD doped with FeCl_3 -ACN is shown in Figure 1. 2AD appears to have a higher value of σ' than 5AD measured just after doping. However, one year later the value of σ' of 2AD decreases dramatically and becomes even lower than that of 5AD at the same time, which remains almost constant. Both 2AD and 5AD doped with FeCl_3 -ACN system, are semiconductors just after doping as well as one year after doping, as seen in Figure 2, taking into consideration that the curve below 45° indicates conducting current [3].

In the case of the doped 6A, the doping systems of FeCl_3 -N, FeCl_3 -ACN and AlCl_3 -A give higher values of σ' at the total range of frequencies (Figure 3). Furthermore, all the doping systems which were used, led to semiconductive materials (Figure 4). Although the value of the alternating electrical conductivity σ' in the case of FeCl_3 -N, FeCl_3 -ACN and SnCl_4 -ACN doping systems decreased 10 months after the doping (Figure 5), these materials continue to be semiconductive (Figure 6). Comparing Figures 1 and 3 it can be noticed that the value of σ' of 2AD and 5AD is clearly higher than that of doped 6A (Figure 3). Generally, higher

TABLE I

Description of polymerization and doping conditions of materials prepared and explanation of the abbreviations used

No.	Materials	Polymerization conditions	Doping	Post
		B:O:C/S,U,E*	dopant-solution***	treatment
1	2A	1:2:1.5/S	—	—
2	2AD	1:2:1.5/S	FeCl ₃ -ACN	—
3	2AD*	1:2:1.5/S	FeCl ₃ -ACN	1 year after D**
4	4A	1:2:0.75/S	—	—
5	4AD1	1:2:0.75/S	FeCl ₃ -N	—
6	4AD2	1:2:0.75/S	FeCl ₃ -ACN	—
7	4AD3	1:2:0.75/S	SnCl ₄ -ACN	—
8	4AD4	1:2:0.75/S	FeCl ₃ -N	Heated at 180°C for 2h
9	5A	1:1:1.5/U	—	—
10	5AD	1:1:1.5/U	FeCl ₃ -ACN	—
11	5AD*	1:1:1.5/U	FeCl ₃ -ACN	1 year after D
12	6A	1:3:0.75/E	—	—
13	6AD1	1:3:0.75/E	FeCl ₃ -ACN	—
14	6AD2	1:3:0.75/E	FeCl ₃ -N	—
15	6AD3	1:3:0.75/E	FeCl ₃ -A	—
16	6AD4	1:3:0.75/E	AlCl ₃ -N	—
17	6AD5	1:3:0.75/E	AlCl ₃ -A	—
18	6AD6	1:3:0.75/E	SnCl ₄ -N	—
19	6AD7	1:3:0.75/E	SnCl ₄ -ACN	—
20	6AD8	1:3:0.75/E	SnCl ₄ -A	—
21	6AD*1	1:3:0.75/E	FeCl ₃ -ACN	10 months after D
22	6AD*2	1:3:0.75/E	FeCl ₃ -N	10 months after D
23	6AD*7	1:3:0.75/E	SnCl ₄ -ACN	10 months after D
24	6AD*8	1:3:0.75/E	SnCl ₄ -A	10 months after D

* B: Biphenyl; O: CuCl₂; C: AlCl₃; S: Stoichiometric proportion of B:O; U: Under-stoichiometry; E: Excess of stoichiometry.

** D: doping.

*** ACN: acetonitrile; N: nitrobenzene; A: acetone.

values of σ' have been noticed in stoichiometrical (2AD) or under-stoichiometrical (5AD) proportions of biphenyl:CuCl₂ [8]. Polyphenylenes prepared with an excess of CuCl₂ (e.g., doped 6A), however, are semiconductors with lower conductivity σ' , probably because of the presence of chlorine instead of hydrogen atoms in the aromatic ring, which eliminates the formation of radical cations in the polymer chain by the dopant [8]. From Figures 3 and 5, it can be said that although the σ' value for the FeCl₃-ACN doping system seems to be the highest one, it decreases 10 months later and becomes even less than the σ' value of FeCl₃-N system measured at the same time. It is obvious that these systems can be considerably affected by time. The decrease of conductivity σ' with time depends on the stability of the dopant-polymer interaction. During doping, the dopant influences polyphenylene resulting in, for example, PPP⁺AlCl₄⁻ which undergo degradation with time due to a redox process resulting in PPP⁰ + AlCl₃ + Cl⁻ [13].

Figure 7 shows FTIR spectra of 4A and 4A doped with different doping systems. There were no remarkable changes in the chemical structure of the undoped and doped stage of the materials. Only small changes, which are discussed below, have been detected. The following evaluation of the various bands was carried out according to the literature [2, 9, 10]. The intense band around 1400 cm⁻¹ is characteristic of the aromatic ring. The band at 813 cm⁻¹ can be attributed to

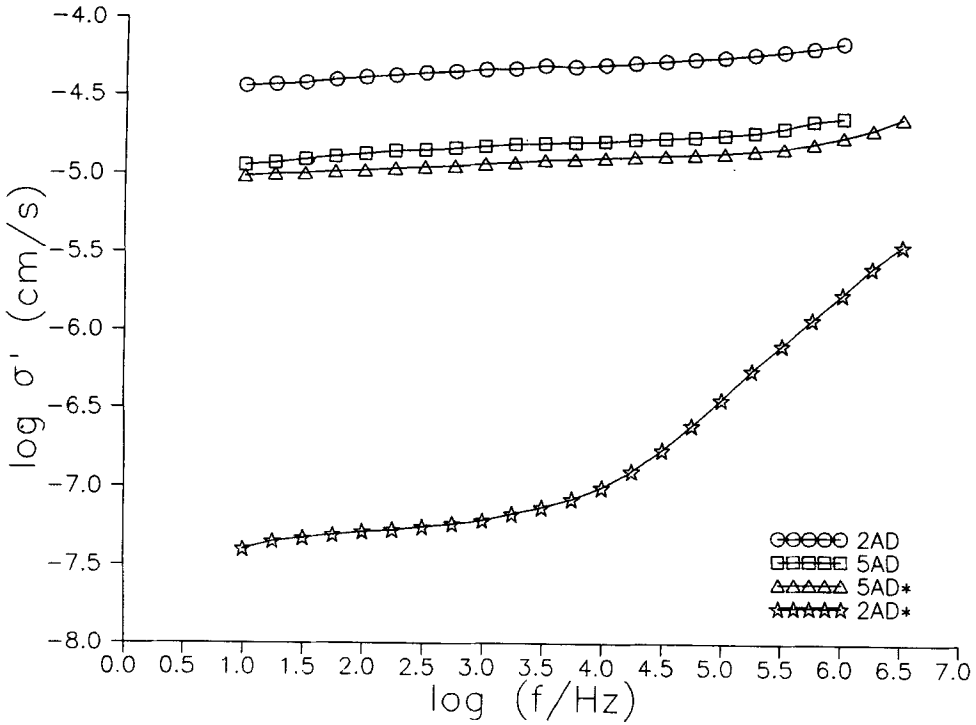


FIGURE 1 Variation of the alternating electrical conductivity σ' of 2AD, 5AD, 2AD*, and 5AD* with frequency.

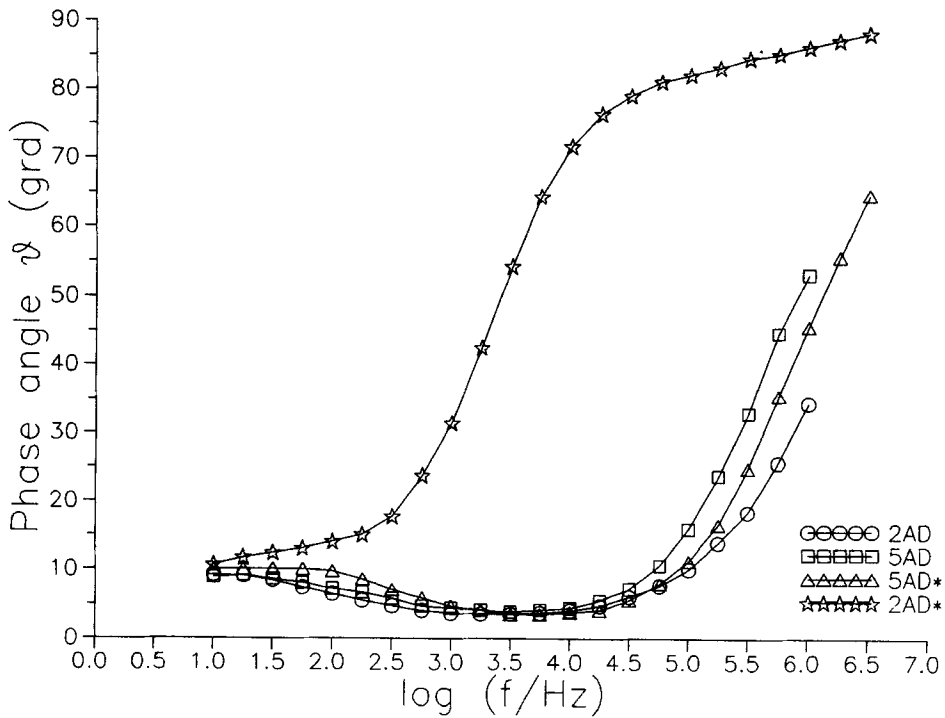


FIGURE 2 Variation of the phase angle θ of 2AD, 5AD, 2AD*, and 5AD* with frequency.

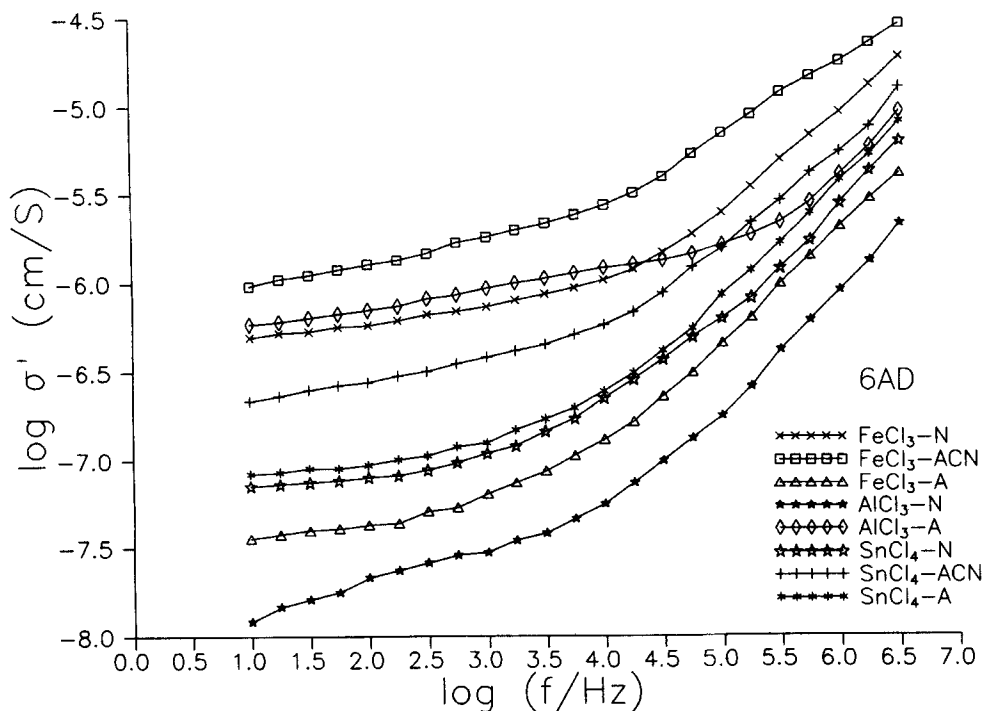


FIGURE 3 Variation of the alternating electrical conductivity σ' of 6AD doped with different doping systems, with frequency.

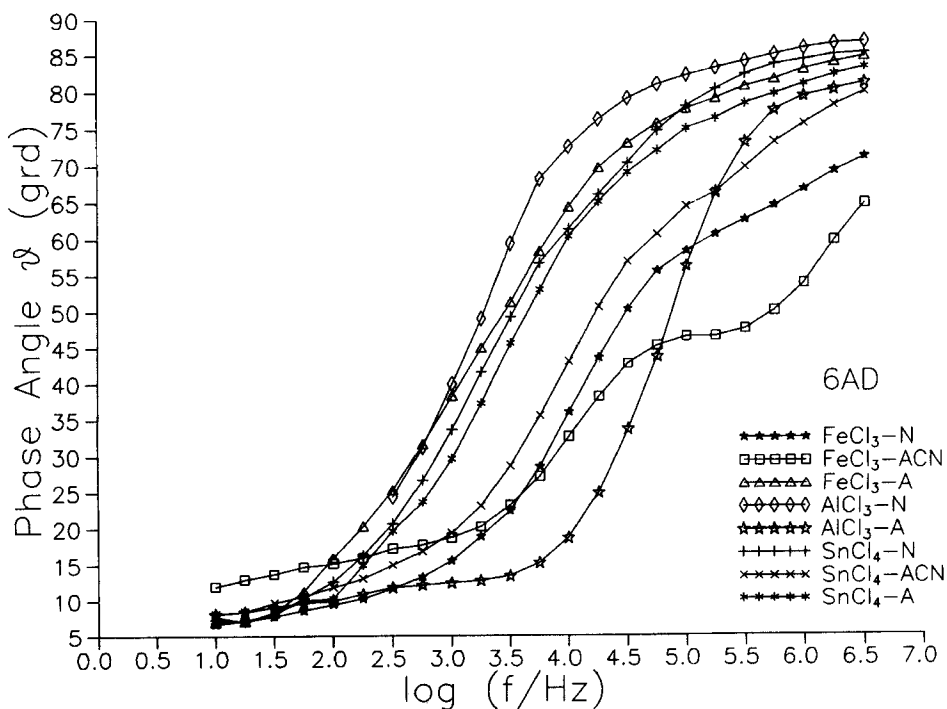


FIGURE 4 Variation of the phase angle θ of 6AD doped with different doping systems, with frequency.

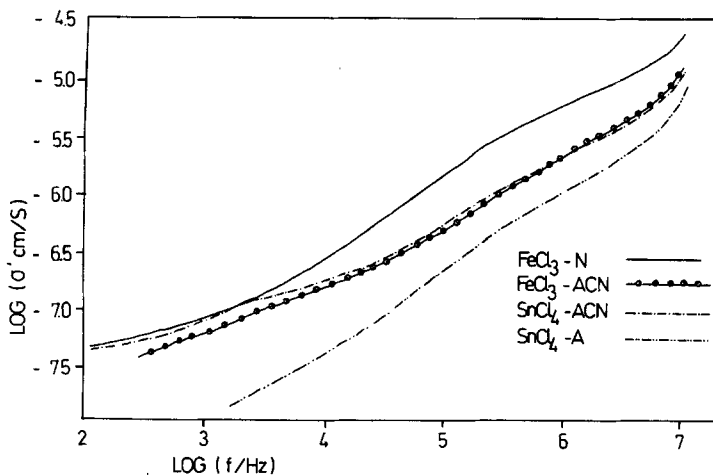


FIGURE 5 Variation of the alternating electrical conductivity σ' (measured 10 months after doping) of 6AD doped with different dopant systems, with frequency.

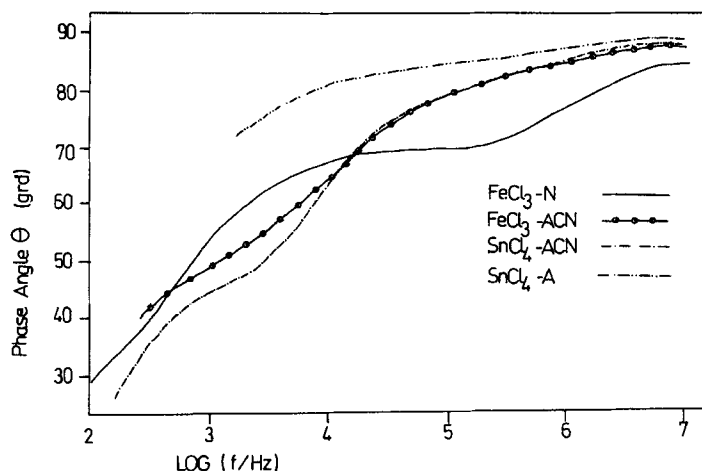


FIGURE 6 Variation of the phase angle θ (measured 10 months after doping) of 6AD doped with different doping systems, with frequency.

para-substitution, whereas the bands at 760 cm^{-1} and 692 cm^{-1} are characteristic of the aromatic rings at the end of the polymer, that is, (mono) endgroups and they can be associated with meta-substitution in the case of the presence of the bands around 880 cm^{-1} . These bands seem to disappear in the cases of 4AD1 and 4AD4 both doped with $\text{FeCl}_3\text{-N}$ doping system. Small changes between undoped and doped polyphenylenes are observed at 1560 cm^{-1} which is attributed to the quinoid structure and also at 1380 cm^{-1} and 1180 cm^{-1} owing to C-H group [11]. Generally, transmission IR spectra of polyphenylenes doped with electron donors or acceptors are unattainable, because of the darker color of the doped polymer, however photoacoustic FTIR methods provide more detailed information [5, 12].

Differences in the structure between undoped and doped materials in the case of 4A, however, are observed in the x-ray diffraction curves (number of reflectives,

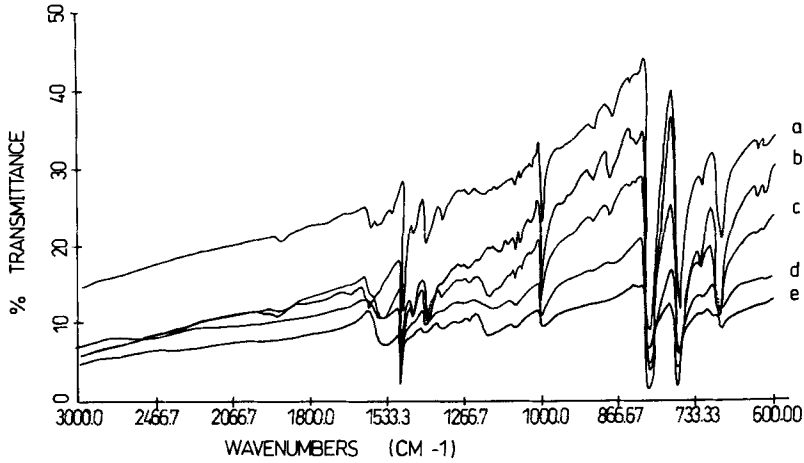


FIGURE 7 FTIR-Spectra of 4A and 4AD doped with different doping systems: a: 4AD3; b: 4A; c: 4AD2; d: 4AD4; e: 4AD1.

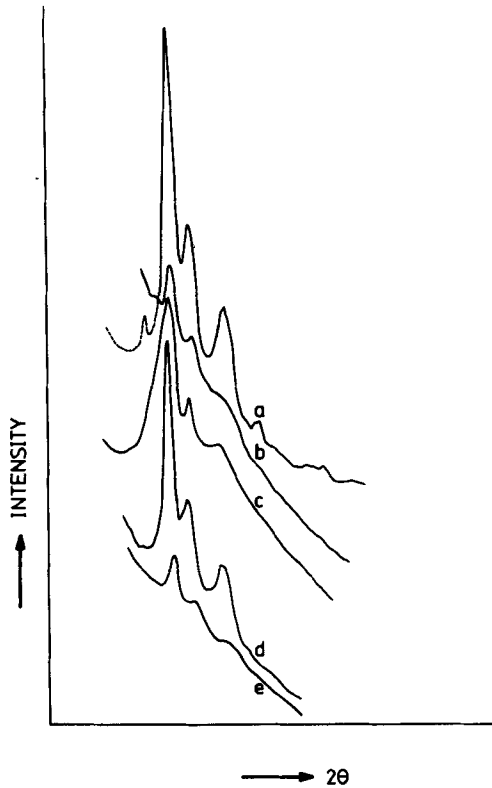


FIGURE 8 X-ray diffraction measurements of 4A and 4AD doped with different doping systems: a: 4A; b: 4AD1; c: 4AD2; d: 4AD3; e: 4AD4.

TABLE II

Crystallographic data of undoped and doped 4A (4A, 4AD1, 4AD2, 4AD3 and 4AD4)

Material	Interference	
	Angle, 2θ ($^\circ$)	Intensity*
4A	16.2	w
	19.4	vs
	22.5	m
	27.3	m
	31.4	vw
	38.5	vw
4AD1	19.9	m
	22.8	vw
	27.1	vw
4AD2	19.5	vs
	22.8	w
	28.0	vw
4AD3	19.6	vs
	21.8	w
	26.3	m
4AD4	19.9	m
	22.8	vw
	27.3	vw

* Symbols: vw—very weak; w—weak; m—medium; s—strong; vs—very strong.

their intensities and shapes) and are presented in Figure 8 and Table II. The intensity of reflections represents a measure of the crystallinity, and the width of the reflection depends on the crystallite size and the local fluctuation of the crystal lattice. Crystals with higher order give diffractograms with sharp reflections, while very small crystals or crystals of low concentration cannot be detected by x-ray analysis. The halos below the reflections represent the amorphous region, while the well-defined reflections are caused by the crystalline region of the polymer [14, 15]. It is obvious that the undoped material, compared with the doped one, shows a larger number of reflections with different intensities. Also, in recent studies [8], x-ray diffractograms exhibited changes of the crystalline structure after doping, especially in the case of under-stoichiometric (e.g., 5A) and stoichiometric (e.g., 2A, 4A) proportion. Consequently, the introduction of the doping system into the polyphenylenes influences not only the amorphous but also the crystalline region.

CONCLUSIONS

The polyphenylenes, which represent the stoichiometry (2A, 4A) and the under-stoichiometry (5A), doped with $\text{FeCl}_3\text{-ACN}$ exhibit higher values of σ' compared with those which have excess stoichiometry (6A) and are doped with different doping systems. Generally, σ' decreases as the time after doping increases. The value of σ' remains almost constant one year after doping in the case of the under-stoichiometric polyphenylenes. Almost all the doped materials are semiconductors and remain so even one year after their doping. X-ray diffraction studies exhibit significant changes of the crystalline structure after doping, whereas FTIR studies show only small changes between the undoped and doped stage.

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