Synthesis and Electronical Property of Antimony-Substituted Polysilanes and Iron-Substituted Polysilanes

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Abstract: Novel polysilanes, antimony-substituted polysilanes (APS) and iron-substituted polysilanes (IPS), were synthesized and characterized in this paper. To prepare these new metal-containing polymers, high reactive polymers, polymethylsilane (PMS) and polychloromethylsilane (PCMS) were used as mother polymers. The APS was synthesized directly by the reaction of PMS with $SbCl_3$, while IPS was obtained from the reaction of PCMS with $Na_2Fe(CO)_4$ in the solvent of *n*-hexane. The polymers were characterized by elemental analysis, FT-IR, ^{1}H-NMR, ^{29}Si CP/MAS NMR, GPC, and UV. The number average molecular weights of these two polymers are between 1400 and 1600. These polymers show good semiconductive properties, whose intrinsic conductivities are in the range of $10^{-8} \sim 10^{-7}$ S/cm, and can be increased to 10^{-5} S/cm after being doped with iodine.

Keywords: Antimony-substituted polysilanes, Iron-substituted polysilanes, electrical property.

1. INTRODUCTION

Polysilane is a class of polymer made of linear Si-Si backbone with two substituents at each Si atom. The σ-electrons in the main chain of polysilanes are strongly delocalized due to the availability of the $3d$ vacant orbital of Si atoms [1-3]. Polysilanes have been of interest due to their unique properties and potential applications as functional materials such as semi-conductors, photoconductors, nonlinear optical materials, etc [4, 5]. The properties of polysilanes depend on the varieties and structures of the side groups [6-8]. Usually the side groups of the polymer are organic, and if inorganic groups are introduced into the main chain of -Si-Si-, its properties will be changed and its potential applications will be widened. The theoretical calculations show that the electronic energy gap will be decreased effectively [9, 10], and the semiconducting performance will be improved, when the inorganic groups are introduced into the side chain of polysilanes.

The conventional method for synthesis of the polysilanes is the Wurtz method by reducing and coupling of dichloro- or trichloro-silanes, using an alkali metal as reductive agent in high-boiling solvents [11, 12]. Due to the severe conditions, the polymer side chains are normally limited to be aryl and alkyl groups. It is difficult to prepare dichloro- and trichloro-silanes with inorganic groups. So the inorganic group-substituted polysilanes, especially the metal-containing polysilanes, cannot be synthesized by this method. Bonding inorganic elements to some small molecular organosilicon compounds have been reported in many papers, such as $(Me_3Si)_3Sb$ [13], $Me_3AlSb(SiMe_3)_3$ [14], $(\eta^5\text{-}Cp)(CO)_2FeSiMe_3$ [15], *etc*. It is proved that the

silicon can be bonded to many metal elements and this structure can also exist stably in the polysilanes.

Our group has reported that the metal-containing polysilanes can be synthesized by polymer reaction method [16-18]. In this paper, antimony-substituted polysilanes (APS) and iron-substituted polysilanes (IPS) were prepared. High reactive polymers, polymethylsilane (PMS; $[\text{-SiH(CH}_3\text{)-]}_n$) and polychloromethylsilane (PCMS; $[\text{-SiCl(CH}_3\text{)-]}_n$) were used as mother polymers. It is a feasible method for the preparation of polysilanes containing the inorganic side group, which are inaccessible by the Wurtz coupling method. These polymers show good semiconductive properties.

2. EXPERIMENTAL

2.1. General Considerations

All the reactions and processes were carried out in argon atmosphere, by means of standard Schlenk manipulations or inside a glove box. Solvents were dried and distilled before use.

2.2. Synthesis of Polymers

2.2.1. Synthesis of Mother Polymers: PMS and PCMS

PMS was prepared from dichloromethylsilane (52.5ml, 510mmol; 99%, Aldrich) and sodium (23g, 1000mmol; 97%, Lingfeng, China) in toluene (350ml) [19]. The synthesized polymer solution was pressured into a round-bottom flask through a cannula equipped with a filter tip. The oily pale yellow PMS was obtained with a yield of about 71% after evaporated.

PCMS was synthesized from chlorination of PMS (4.4g, 100mmol; as synthesized) using CCl_4 (50ml; 99.9%, Aldrich) as the chlorinating agent [20]. After 48hr, 90% of the Si-H bonds had been chlorinated under these conditions. The yellow powder of the polymer PCMS was obtained after evaporated under vacuum.

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2.2.2. Synthesis of APS

A three-necked round-bottom flask, equipped with a Telfon-coated magnetic stir bar, over-dried, and flushed with argon, was fitted with a pressure-equalizing addition funnel, a reflux condenser and an argon inlet and outlet. Then the PMS as-synthesized and the pyridine dissolved in 100 ml of THF were put into the flask, the $SbCl_3$ (99%, Shanghai Regent, China) dissolved in the THF was put into the funnel, and $SbCl_3$ solution was added dropwise when the magnetic bar was vigorous stirring. Stirring for 16 h at room temperature, the mixture was filtered under argon to remove the Py·HCl. The resulting clear deep yellow solution was concentrated under vacuum, until it reached approximately 20ml, and the APS was precipitated, from the mixture of methanol and isopropanol (the ratio of the volume is 1:1), as a deep yellow powder. APS was dried under vacuum at 50℃ for 4hr. $\overline{Mn}$ =1600. The yield of the polymer was 75.2%.

2.2.3. Synthesis of IPS

$Na_2Fe(CO)_4$ was prepared from 2.45g (12.5mmol) of $Fe(CO)_5$ (99.5%, Aldrich) and 0.60g (26.1mmol) of sodium [21].

The equipment for the synthesis of IPS is the same as that of APS above. 1.96g (25.0mmol) of PCMS (as synthesized) was dissolved in 20ml of n-hexane, then the solution was added dropwise into the flask. The mixture was stirred at room temperature for 15hr, during which the color changed from light brown to deep maroon. It was filtered under argon to remove the NaCl. The polymer can be obtained from the distilled filtrate.

For the polymer bears some Si-Cl groups, it can be hydrogenation with $LiAlH_4$: $LiAlH_4$ (0.95 g, 25 mmol, Aldrich) was dissolved in 20 ml of dried diethyl ether and the solution of the synthesized above in 10ml of hexane was added. After stirring for 2 h at room temperature the solution was hydrolyzed carefully with dilute HCl/ice. The ether layer was separated and dried over Na_2SO_4, and the solvent was removed in vacuum, yielding IPS as deep brown powders. $\overline{Mn}$ =1440. The yield was 45.3%.

2.3. Preparation of Semiconducting Polymer Film

The polymer, PMS, APS, or IPS (0.2 g), was dissolved in 10 ml THF at R.T. This was cast in clean glass petridish by complete solvent evaporation in the 50°C, and dried under vacuum to give polymer films (30 μm thick).

The I_2 doping was carried out by contacting the polymer film with gaseous I_2 under vacuum in a sealed glass tube. The polymer was exposed to the dopant for an appropriate period until the electrical resistance came to equilibrium. All handling was carried out in a dry box to remove the influence of oxygen and moisture.

2.4. Characterization

The structure of the polymer was analyzed using IR (Nicolet-360), Raman Spectroscopy (SPEX 1403), ^{1}H-NMR (Bruker AC-80) and ^{29}Si CP/MAS NMR (Bruker DSX-300). Gel permeation chromatography (GPC, Water-244) was performed in THF solution at a flow rate of 0.5 ml/min and the molecular weights obtained were determined by reference to polystyrene standard. UV absorption spectra (Hitachi-3500) were measured with band-pass of 1 nm, the solvent used is hexamethylene, and the sample concentration is 0.01g/L. Electrical conductivity was measured at room temperature by the two-probe technique using a Keithley model 236 source measure unit. The resistance of the doped film was monitored at regular time intervals, keeping the film strictly at 25°C.

3. RESULTS AND DISCUSSION

3.1. Molecular Structures of APS and IPS

PMS was prepared from dichloromethylsilane in toluene yielding a partially branched polymer, $Me_3Si[(MeHSi)_{0.73}(MeSi)_{0.27}]_nSiMe_3$, as a viscous oil with low molecular weight ($\overline{Mw}$ = 1742, $\overline{Mn}$ = 820). When PMS was reacted with $SbCl_3$ in THF at room temperature, HCl was evaporated and the system was exothermic. The liquid mixture gradually turned to deep yellow gel after 16 hrs and APS was obtained after distilled. PCMS obtained from the chlorination of PMS in CCl_4, $Me_3Si[(MeHSi)_{0.05}(MeClSi)_{0.68}(MeSi)_{0.27}]_n SiMe_3$, can react with $Na_2Fe(CO)_4$ and lead to IPS when the precipitated NaCl and the solvent were removed.

The FT-IR spectra are shown in Fig. (**1**). The absorption peaks of Si-H (2100cm^{-1}, 930cm^{-1}) are strong in PMS (**1a**), weak in APS (**1c**) and IPS (**1d**), and nearly disappear in PCMS (**1b**). It is reasonable for the weakness of PCMS because most Si-H bond changed into Si-Cl bond during chlorination. While for APS, it is the most likely that HCl was eliminated as a condensation of Si-H and Sb-Cl bonds, leading to the crosslinking of PMS through Si-Sb or Si-CH$_2$-Sb bonds, as shown in Schemes (**1**) and (**2**). The similar Si-H consuming by reacting with other metallic halides has been reported [22-24]. Similarly for the PCMS-derived IPS, as shown in Scheme (**3**) and (**4**), a stable structure of Si-Fe(CO)$_4$-Si might be formed with a consumption of Si-Cl bonds. The typical absorption peaks of carbonyls in the 2050 to 1950cm^{-1} region affirmed that the carbonyls were incorporated into the polymer. The changes of molecular weights and elemental compositions of these polymers are shown in Table **1**. After polymer reactions, Sb and Fe are introduced into the polymer, and the amount of Sb is 15.1 wt%, Fe is 7.5wt% (APS-1 and IPS-1). At the same time the molecular weight of the two polymers are increased. In APS, the branching-crosslinking structure was formed through the Si-Sb or Si-CH$_2$-Sb structures. Due to the formation of stable structure Si-Fe(CO)$_4$-Si in IPS, Fe becomes the center of crosslinking of the polymer. These crosslinking structures lead to the increasing of the molecular weight distributions of the new polymers. When the amount of Sb and Fe increased, the polymer become poor dissoluble and even turn to be insoluble and infusible because of the more complex crosslinking structures.

^{29}Si CP/MAS NMR spectra are shown in Fig. (**2**). PMS displays a peak at around -70 ppm (Fig. **2a**), corresponding to MeH**Si**-Si$_2$ as the linear part of PMS molecular structure; another peak at around -75 ppm can be assigned to Si-(Me**Si**)Si$_2$ as the branched part; The small peak at -35 ppm can be assigned to terminal Si-**Si**H(CH$_3$)Cl or Si-**Si**H(CH$_3$)OH. When PMS reacts with $SbCl_3$ and forms a new polymer APS (Fig. **2b**), the peak at -70 ppm

$$\text{SbCl}_3 \;+\; \equiv\!\text{Si}\!-\!\text{H} \;\longrightarrow\; \equiv\!\text{Si}\!-\!\text{SbCl}_2 \;+\; \text{HCl (g)} \qquad\qquad \text{(Scheme 1)}$$

$$\equiv\!\text{Si}\!-\!\text{CH}_3 \;+\; \text{SbCl}_3 \;\longrightarrow\; \equiv\!\text{Si}\!-\!\text{CH}_2\!-\!\text{SbCl}_2 \;+\; \text{HCl (g)} \qquad \text{(Scheme 2)}$$

(Scheme 3)

(Scheme 4)
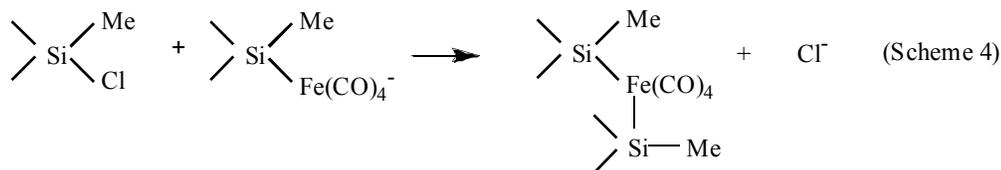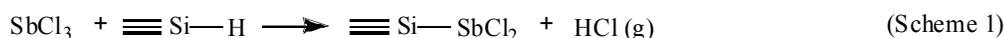
disappeared and the peak at -75 ppm gets broader and stronger. It proves that Si-H bonds were consumed and more branched structure forms. Other peaks from -30 to 4 ppm come into being, among which 0 ppm corresponds to SiC_4 and -17 ppm to **Si**-CH$_2$-Si [25]. It is very likely that **Si**-Sb bond or Si-CH$_2$-Sb bonds was formed from the weak signals from 4 to 12ppm [26]. It is similar in Fig. (**2c**), corresponding to the polymer IPS. The peak centered at 18 ppm can be assigned to **Si**-Fe, and the result is consistent with Pannell's work [27].

Fig. (**3**) shows the UV absorption spectra of PMS, APS and IPS dissolved in THF. The absorption maximum wavelengths (λ_{max}) are observed at 280nm, 330nm, and 325nm respectively. It proves that the polymers can retain Si-Si delocalization structures. The red shift in APS and IPS is likely to be caused by the effect of the side group of Sb or Fe. And another strong absorption at 285nm had shown in Fig. (**3b**) belongs to the carbonyls of the polymer IPS.

Their ^{1}H-NMR spectra are show in Fig. (**4**). PMS displays several peaks at 0.15, 0.24, and 0.62 ppm in the characteristic region of Si-C**H**$_3$ groups, a broad peak at around 3.7 ppm assigns to the vibration of Si-**H**, and a short peak at 5.1 ppm assigns to Si-O**H** (Fig. **4a**). A chemical composition, $[(\text{MeHSi})_{0.05}(\text{MeClSi})_{0.68}(\text{MeSi})_{0.27}]_n$, can be derived for PMS from the area integral analysis. Other short peaks appear at around 1.1 ppm and 4.1 ppm in Fig. (**4b**) can

be assigned to Si-C**H**$_2$-Si and Si-**H**. It can be presumed that the short peak at 4.1ppm is caused by Si-H adjacent to Si-Sb.
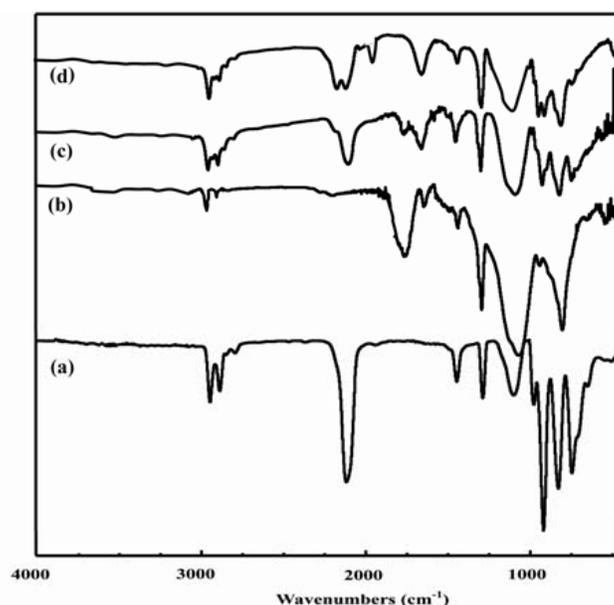
Fig. (1). FT-IR spectra of (**c**) APS and (**d**) IPS in comparison with the spectra of (**b**) PCMS and (**a**) PMS.

Table 1.   Molecular Weights and Element Analysis of APS and IPS in Comparison with PMS.

Sample	Solubility	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mw}/\overline{Mn}$	Element Analysis/wt%				
					Si	Sb	Fe	Cl	O
APS-1	dissoluble	1600	6260	3.91	47.3	15.1	/	3.3	5.3
APS-2	poor dissoluble	1700	6970	4.10	45.8	16.5	/	2.8	4.6
APS-3	insoluble and infusible	/	/	/	44.6	17.0	/	2.0	3.5
IPS-1	dissoluble	1440	5054	3.51	54.5	/	7.5	3.3	14.5
IPS-2	poor dissoluble	1520	5396	3.55	53.2	/	8.1	3.2	11.9
IPS-3	insoluble and infusible	/	/	/	52.4	/	8.6	3.5	13.7
PMS	dissoluble	820	1742	2.12	58.8	/	/	/	4.2
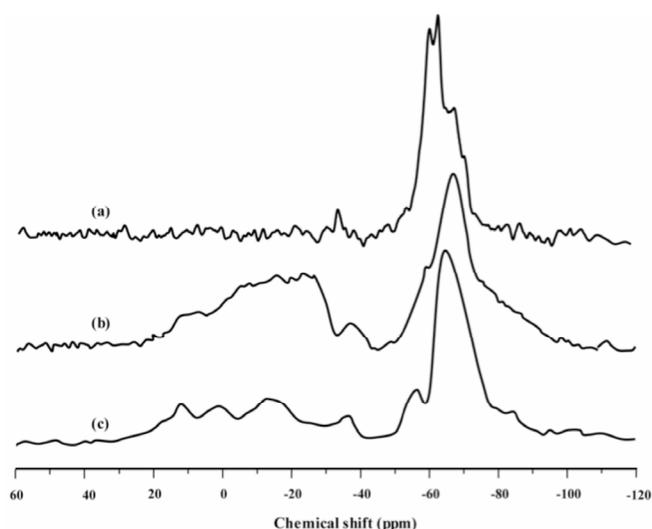
Fig. (2). ^{29}Si CP/MAS NMR spectra of (**b**) APS and (**c**) IPS in comparison with the spectrum of (**a**) PMS.

There are three main structure units in the polymer structure of APS according to the analysis above: Si-CH$_2$-Si, Si-SiH(CH$_3$)Cl, and Si-SiH(CH$_3$)OH.

3.2. Semi-Conductivities of APS and IPS

PMS is an insulator both before and after doped with iodine, but APS and IPS show semi-conductive properties. As shown in Table **2**, the electric conductivities of the APS and IPS are in the order of 10^{-8}~10^{-7}S/cm, and the electrical conductivities can be improved to 10^{-5}S/cm when doped with iodine. The amount of Sb and Fe of the polymers influence on the conductivity is not very clear, the resistance of the doped film still at the level of 10^{-5}S/cm. This can be explained by the "self-doping" mechanism [28, 29], *i.e.*, the inorganic side chains have strong electron donating or accepting properties.

As shown in Fig. (**5**), when iodine is incorporated into the polymers after exposure to gaseous I$_2$, their conductivities increased with the doping time. The maximum values of conductivities are corresponding to 22 h for APS and 18h for IPS. The conductivities decrease slowly when the doping time is prolonged. It is likely that part Si-Si chains were decomposed when exposure to excessive oxidant (I$_2$).

4. CONCLUSIONS

We succeeded in introducing the metallic elements of antimony (Sb) and iron (Fe) quantitatively at the side chains of polysilanes. In APS, Si-Sb or Si-CH$_2$-Sb bonds were found to be formed its tri-functional structure. The IPS have the stable Si-Fe(CO)$_4$-Si structure, Fe is the center of crosslinking of the polymer.

These new polysilanes show semi-conductive properties, whose intrinsic conductivities are in the range of 10^{-8}~10^{-7}S/cm and can be increased above 10^{-5}S/cm after doped with iodine. These inorganic group-substituted polysilanes show some unique semi-conductor properties and good solubility in common solvents; they are potential functional materials in many fields. Furthermore, we plan to apply this procedure to synthesize a series of new polysilanes containing other metal elements.
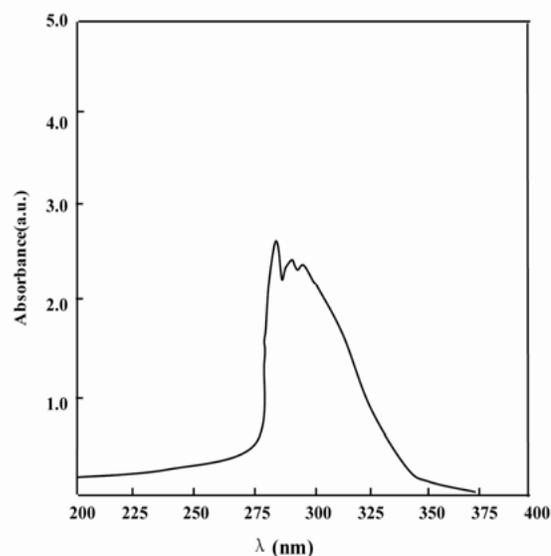
(a)
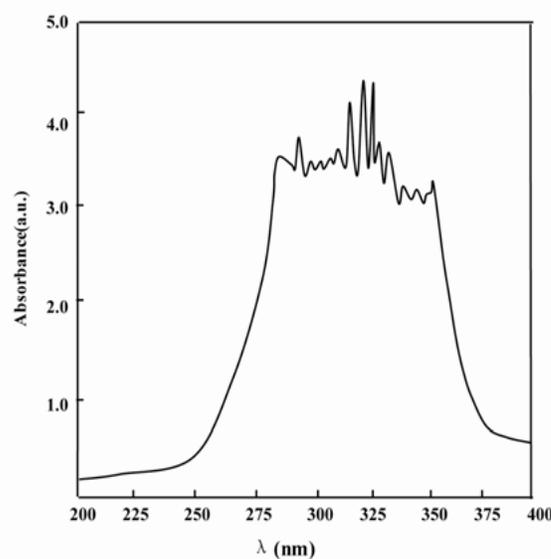
(b)
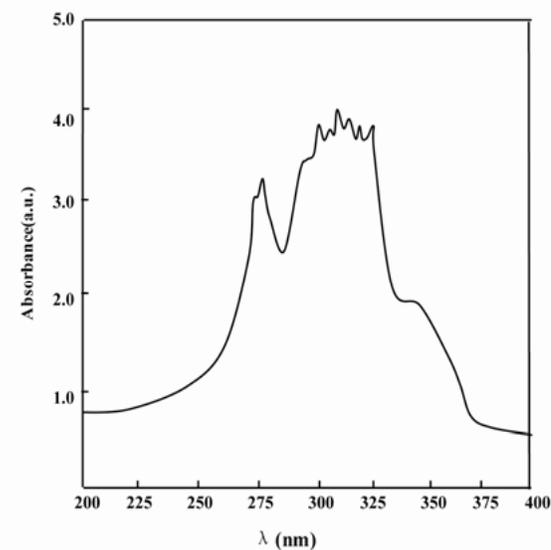
(c)

Fig. (3). UV spectra of (**a**) PMS, (**b**) APS, and (**c**) IPS.
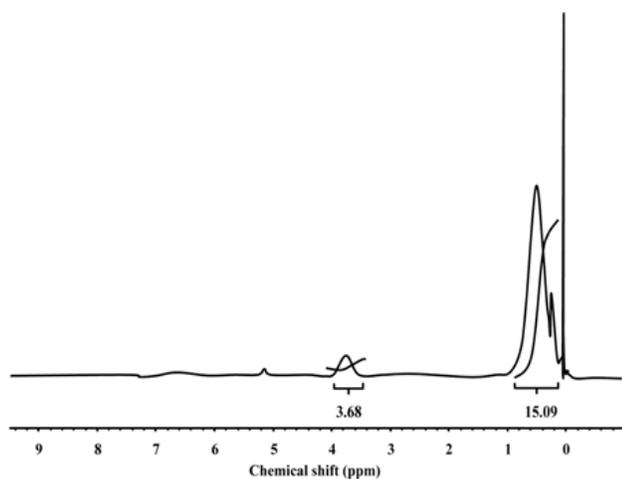
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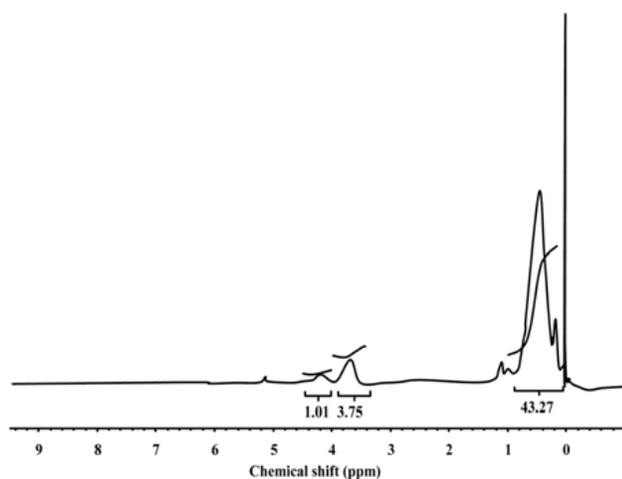
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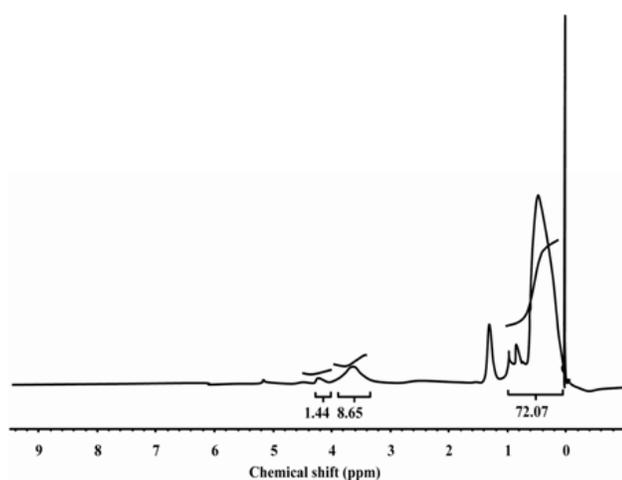
(c)

Fig. (4). ^{1}H-NMR spectra of (**a**) PMS, (**b**) APS and (**c**) IPS.
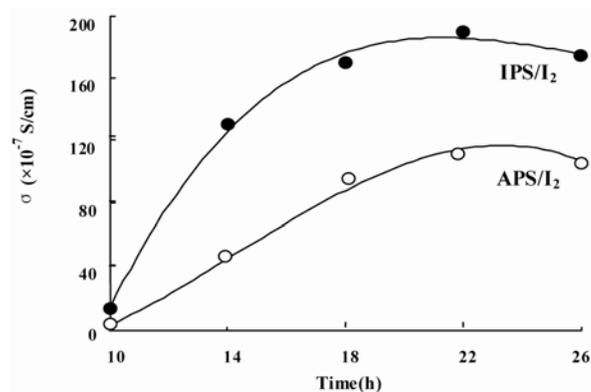
Fig. (5). Influence of doping time on conductivities of APS/I_2 and IPS/I_2.

Table 2.   Conductivities of APS and IPS Before and After Doping with Iodine

Film	Doping Time (h)	p(kPa)	σ (S/cm)	Appearance
APS	/	/	1.5×10^{-7}	Brown solid
IPS	/	/	2.2×10^{-7}	Brown solid
APS-1/I_2	7	2.0	1.1×10^{-5}	Black brown solid
APS-2/I_2	7	2.0	2.5×10^{-5}	Black brown solid
IPS-1/I_2	7	2.0	1.9×10^{-5}	Dark brown solid
IPS-2/I_2	7	2.0	3.6×10^{-5}	Dark brown solid

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CONFLICT OF INTEREST

Declared none.

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