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CONDUCTIVE POLYMER VIA PRECURSOR ROUTES. 4. SYNTHESES AND ELECTRIC CONDUCTIVITIES OF POLY(ACRYLAMIDE-*co*-MALEIC ANHYDRIDE)S REACTED WITH PHOSPHORUS OXYCHLORIDE

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Key Words: Poly(acrylamide-*co*-maleic anhydride); Phosphorus oxychloride; Electric conductivity; 4-Point probe d.c. method; Precursor route

ABSTRACT

The electric conductivity of poly(acrylamide-*co*-maleic anhydride) (poly(AAm-*co*-MAH)) after reaction with phosphorus oxychloride was investigated. It was found that conductivities were dependent on the $POCl_3$ treatment time and the concentration of poly(AAm-*co*-MAH) as well as on such copolymerization conditions as mole ratio of AAm, copolymerization time, and temperature. The conductivities of poly(AAm-*co*-MAH)s treated with $POCl_3$ were of the order of 10^{-6} to 10^{-8} $S\cdot cm^{-1}$. When carbon black was mixed with $POCl_3$-treated poly(AAm-*co*-MAH), the conductivities increased with amount of carbon black up to 7 wt% and thereafter gradually approached 2.0×10^{-2} $S\cdot cm^{-1}$.

INTRODUCTION

Recently we found that the conductive poly(acylacetylene)s can be obtained by simply reacting a precursor polymer containing methyl vinyl ketone with phosphorus oxychloride, and these polymers showed conductivities of up to the order of 10^{-4} $S \cdot cm^{-1}$ in their undoped states [1-3]. Our previous results also indicated that the conjugated diene structure of the polymers could be easily obtained by reaction with $POCl_3$, even though the poly(alkyl vinyl ketone)s themselves do not contain conjugated double bond structures. In those studies the poly(acylacetylene)s, starting from copolymeric precursors, showed better solubility as well as higher conductivities than those from homopolymeric precursors because of the function of the polar groups introduced such as the carbonyl group.

Our interest in conductive polymers via precursor routes [4-6] led us to carry out further studies on copolymeric precursors having carbonyl groups. The present paper is concerned with the conductivities of copolymers of acrylamide and maleic anhydride as precursor copolymers on being treated with phosphorus oxychloride. Both maleic anhydride (MAH) and acrylamide (AAm) were selected because the monomers were easily available commercially and contained the carbonyl groups, which might be expected to give the self-dopant function to the final conductive polymers. The effects of various experimental conditions such as copolymer compositions, copolymerization temperature, and $POCl_3$ treatment conditions on the electric conductivities of poly(acylacetylene)s were investigated. Many reports have recently been published on the improvement of the electric conductivity of polymer composites [7-9]. The effect of carbon-black mixing is also discussed.

EXPERIMENTAL

Materials

Acrylamide (AAm, Wako) was recrystallized from methanol. Maleic anhydride (MAH, Junsei) and 2,2′-azobisisobutyronitrile (AIBN, Wako) were recrystallized from chloroform and absolute ethanol, respectively. Phosphorus oxychloride ($POCl_3$, Nakarai) was used without further purification. Other chemicals were purified prior to use by standard procedures. Carbon black (Ketjhen black EC 300J) was obtained from the Ketjhen Black International Co. The carbon black has the following physical characteristics: average particle diameter, 35 μm; N_2 surface area, 254 m^2/g, DBP (dibutyl phthalate) absorption of 200 $cm^3/100$ g; and electric conductivity of 10.0 ± 3.0 $S \cdot cm^{-1}$.

Synthesis of Poly(AAm-*co*-MAH)

Copolymerization of AAm with MAH was carried out with AIBN in acetonitrile under various experimental conditions, as shown in Table 1. Taking poly-

TABLE 1. Copolymerization Conditions of AAm and MAH

Conditions	
Mole ratio of [AAm] in feed	0.50, 1.0, 1.5, 2.0, 2.5, 3.0
Polymerization time (h)	24, 48, 60, 72, 96
Polymerization temperatutre (°C)	50, 60, 70

(AAm-*co*-MAH) with a 1/1 mole ratio in the feed as an typical example, a solution of 2.13 g (0.03 mol) AAm, 2.94 g (0.03 mol) MAH, and 0.01 g (6.1 × 10^{-5} mol) of AIBN in 20 mL acetonitrile was introduced in a polymerization tube. The tube was sealed after being degassed twice by purging with purified N_2 gas and placed in a regulated thermostat at 60 ± 0.05°C for specified time periods. The polymer solution obtained was precipitated in excess ethyl ether with stirring; the precipitate was filtered and dried in vacuo to constant weight. The elemental analysis results showed that this copolymer had a composition of 63/37 [AAm]/[MAH] (C, 43.1%; N, 10.9%; H, 5.8%). The conversion data for each polymerization are listed in Table 2.

Reaction of Poly(AAm-*co*-MAH) with $POCl_3$

The precursor, poly(AAm-*co*-MAH), was treated with $POCl_3$, in a manner identical to that described previously [1-3]. To a stirred solution of 1 g poly(AAm-*co*-MAH), prepared under different copolymerization conditions, in 100 mL DMF was slowly added 8.225 g $POCl_3$, and the reaction was carried out at 0°C for 24 hours. In this way the effect of copolymerization conditions on the conductivities of $POCl_3$-treated poly(AAm-*co*-MAH)s was investigated. One kind of the poly(AAm-*co*-MAH)s, synthesized with a 1.0 mole ratio of [MAH] at 60°C for 48 hours, was reacted with $POCl_3$ under various experimental conditions in order to investigate the effect of $POCl_3$ treatment conditions on the conductivity of $POCl_3$-treated poly(AAm-*co*-MAH) (Table 3). After reaction, the product was precipitated

TABLE 2. Conversion Percentages of Precursor Polymers and Their Electric Conductivities after Having Reacted with $POCl_3$

Copolymerization conditions		Conversion, %	Conductivities,[d] $S\cdot cm^{-1}$
Mole ratio of [AAm] in feed[a]	0.5	35	1.00 (± 0.03) × 10^{-6}
	1.0	59	9.60 (± 0.33) × 10^{-7}
	1.5	62	7.20 (± 0.17) × 10^{-7}
	2.0	69	4.30 (± 0.12) × 10^{-7}
	2.5	74	2.00 (± 0.14) × 10^{-7}
	3.0	77	9.90 (± 0.29) × 10^{-8}
Polymerization temperature (°C)[b]	50	42	1.20 (± 0.05) × 10^{-6}
	60	59	9.60 (± 0.34) × 10^{-7}
	70	63	7.20 (± 0.54) × 10^{-7}
Polymerization time (h)[c]	24	44	4.82 (± 0.46) × 10^{-7}
	48	59	9.60 (± 0.34) × 10^{-7}
	72	65	3.28 (± 0.17) × 10^{-6}
	96	69	1.30 (± 0.11) × 10^{-6}

[a] Copolymerization conditions: 48 hours, 60°C.

[b] Copolymerization conditions: 48 hours, mole ratio = 1.0.

[c] Copolymerization conditions: mole ratio = 1.0, 60°C.

[d] The precursor copolymers were reacted with $POCl_3$ at 0°C for 24 hours.

TABLE 3. Effect of $POCl_3$ Treatment Conditions on Electric Conductivities of Poly(AAm-*co*-MAH) after Having Reacted with $POCl_3$

Conditions	Description	Conductivities, $S \cdot cm^{-1}$
Treatment time (h)[a]	24	$9.60\ (\pm\ 0.34) \times 10^{-7}$
	48	$2.30\ (\pm\ 0.19) \times 10^{-6}$
	72	$4.00\ (\pm\ 0.10) \times 10^{-6}$
	96	$5.20\ (\pm\ 0.09) \times 10^{-6}$
$POCl_3$ concentration (M)[b]	0.05	$9.60\ (\pm\ 0.37) \times 10^{-7}$
	0.10	$3.57\ (\pm\ 0.33) \times 10^{-6}$
	0.15	$5.23\ (\pm\ 0.41) \times 10^{-6}$
	0.20	$7.83\ (\pm\ 0.64) \times 10^{-6}$

[a] Copolymerization conditions: 48 hours, 60°C, mole ratio of AAm = 1.0; poly(AAm-co-MAH) was treated with 0.05 M of $POCl_3$ in DMF at 0°C.

[b] Copolymerization conditions: 48 hours, 60°C, mole ratio of AAm = 1.0; poly(AAm-co-MAH) was treated with $POCl_3$ in DMF at 0°C for 24 hours.

in a tenfold excess of toluene with stirring for 120 minutes and then dried in vacuo.

Carbon Black Mixing

One gram of $POCl_3$-treated poly(AAm-*co*-MAH) was mixed with various amounts of carbon black, ranging from 0 to 15 wt%, in a mortar. The copolymer was obtained after treatment at 60°C for 48 hours with a 1.0 mole ratio of [AAm]. The reaction of the precursor copolymer with $POCl_3$ was carried out at 0°C for 24 hours.

Measurements

Infrared (IR) spectra were recorded on a Perkin-Elmer 1330 series IR spectrophotometer using KBr pellets. The UV absorption spectra were obtained in dimethylsulfoxide (DMSO) on an UVIKON 860 ultraviolet spectrophotometer. ^{1}H-NMR spectra were obtained in DMSO-d_6 on a Jeol 60 NMR spectrophotometer. Elemental analysis was conducted with an Elemental Analyzer (Perkin-Elmer 240C). The molecular weight was determined using *N,N*-dimethylformamide as an effluent by gel permeation chromatography (GPC) (Waters-Water 244). The apparatus was calibrated with polystyrene standards. Intrinsic viscosity was measured at 20 ± 0.01 °C with a Cannon-Fenske viscometer in H_2O.

Conductivity Measurements

For the measurement of conductivity, circular pellets (diameter 2.3 cm and thickness 0.1-0.3 mm) from the powdery samples were prepared at a pressure of 90 kg/cm^2. Gold electrodes were attached to both surfaces of the pellets by vacuum evaporation together with a guard electrode. The conductivity measurements were carried out by the 4-point probe d.c. method in vacuo of 10^{-3} torr [1]. Ten measurements were averaged.

RESULTS AND DISCUSSION

Solubility and Characterization

Table 4 shows typical solubility data of the poly(AAm-*co*-MAH) treated with $POCl_3$ for 24 hours. All of the $POCl_3$-treated poly(AAm-*co*-MAH)s were readily soluble in DMSO and *N*,*N*-dimethylformamide and slightly soluble in acetone and methanol. The copolymer referred to in Table 4 was synthesized with a 1.0 mole ratio of AAm at 60°C for 48 hours. The result is noteworthy since polyacetylene, which has been widely investigated as a pioneering conductive polymer [10–16], is insoluble in any of the solvents used in the study. The good solubility may come from the polar properties of carbonyl groups both in AAm and MAH. In our previous work [4], a similar solubility behavior was also observed for $POCl_3$-treated copolymer of methyl vinyl ketone (MVK) and acrylamide.

Figure 1 shows IR spectra of poly(AAm-*co*-MAH) before (a) and after (b) $POCl_3$ treatment for 24 hours. The IR spectrum of the precursor copolymer before $POCl_3$ treatment shows characteristic absorption peaks at 3400 cm^{-1} (NH_2 in amide), 2980 cm^{-1} (C—H), 1780 and 1710 cm^{-1} (C=O in anhydride), and 1650 cm^{-1} (C=O in AAm). On the other hand, the IR spectrum of the copolymer after $POCl_3$ treatment shows a new peak at 1620 cm^{-1}, indicating that the C—C group in the precursor polymer was transformed into a conjugated diene group. The ^{1}H-NMR spectrum of the precursor copolymer showed peaks at 2.1, 3.5, and a broad peak at 7.8 ppm, which are attributed to methylenic, methynic, and N—H protons, respectively, whereas the ^{1}H-NMR spectrum of the copolymer after $POCl_3$ treatment showed a peak at 6.4 ppm due to the conjugated diene as well as a broad peak at 8.0 ppm due to the N—H protons. Additional evidence for this extended conjugation is provided by the UV absorption at longer wavelength for poly(AAm-*co*-MAH) after $POCl_3$ treatment. Figure 2 shows UV spectra of poly(AAm-*co*-MAH) (a) and poly(AAm-*co*-MAH) treated with $POCl_3$ for 24 hours (b). The poly(AAm-*co*-MAH) shows an absorption maximum around 260 nm but does not show any UV absorption peak above 300 nm. An absorption maximum for the $POCl_3$-treated copolymer was observed around 385 nm. The large shifts of absorption to longer wavelengths is indicative of the formation of conjugated double bonds along the polymer backbone.

TABLE 4. Solubility of $POCl_3$-Treated Poly(AAm-*co*-MAH)[a]

Solvent						
THF	Benzene	DMF	MeOH	DMSO	H_2O	Acetone
○	×	●	○	●	×	○

[a] ●, Very soluble; ○, soluble; ×, insoluble.

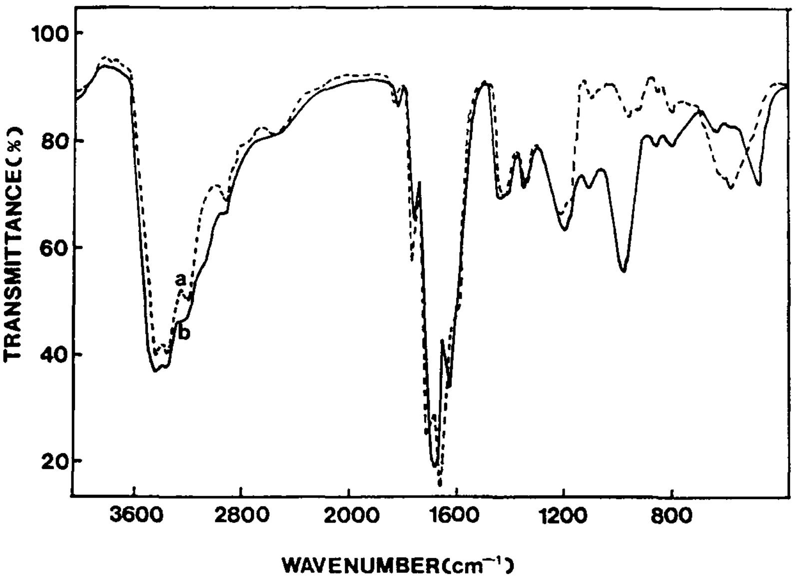

FIG. 1. IR spectra of KBr pellets of (a) poly(AAm-*co*-MAH) and (b) $POCl_3$-treated poly(AAm-*co*-MAH). Time: 24 hours.

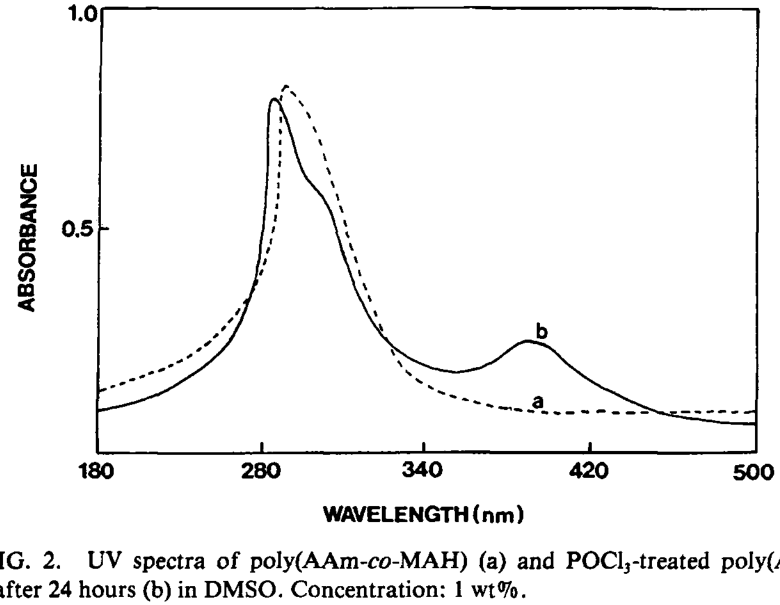

FIG. 2. UV spectra of poly(AAm-*co*-MAH) (a) and $POCl_3$-treated poly(AAm-*co*-MAH) after 24 hours (b) in DMSO. Concentration: 1 wt%.

The formation of conjugated double bonds during the reaction of methyl vinyl ketone and phosphorus trichloride or phosphoryl chloride was discussed in detail by Ogawa et al. [5]. They studied the identification of conjugated double bonds of PMVK or poly(ethyl vinyl ketone) treated with phosphorus trichloride or phosphoryl chloride by IR spectroscopy and suggested several reaction mechanisms. A similar mechanism is expected for the formation of double bonds in the $POCl_3$ treatment of poly(AAm-*co*-MAH). Further detailed studies should be made to reveal accurately what chemical reactions of poly(AAm-*co*-MAH) with $POCl_3$ take place.

Electric Conductivity

Table 2 summarizes the effects of such copolymerization conditions as mole ratio of [AAm], copolymerization time, and temperature on the conductivities of the $POCl_3$-treated poly(AAm-*co*-MAH). Figure 3 shows a typical plot of the conductivity of the $POCl_3$-treated poly(AAm-*co*-MAH) against the mole ratio of [AAm]. In this case the copolymerization was carried out at 60°C for 48 hours. The reaction of the precursor copolymer with phosphorus oxychloride was made at 0°C for 24 hours. It is seen that the conductivities decrease with an increasing mole ratio of [AAm]. The conductivity ranged from 10^{-6} to 10^{-8} $S \cdot cm^{-1}$. The order of magnitude is given in Table 2. Similar results were observed for poly(AAm-*co*-MVK) after reaction with $POCl_3$ [4]. The results mean that AAm is not a good candidate for a precursor polymer that will lead to a conductive polymer after $POCl_3$ treatment when compared with methyl vinyl ketone or maleic anhydride.

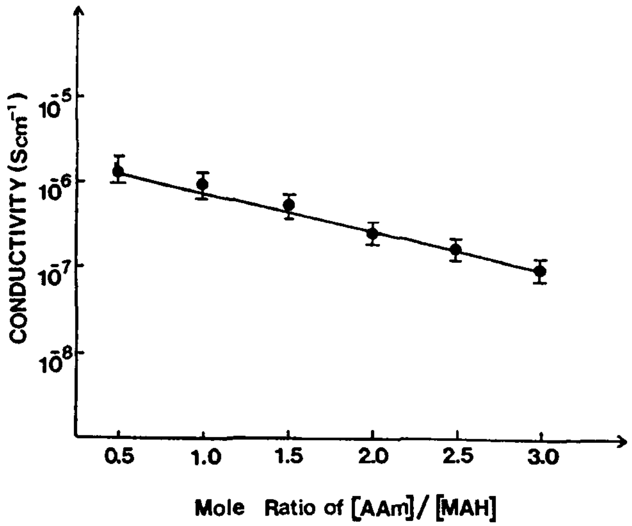

FIG. 3. Effect of the mole ratio of [AAm] in the copolymerization of AAm and MAH on the conductivity of $POCl_3$-treated poly(AAm-*co*-MAH). The copolymerization was carried out at 60°C for 48 hours. The poly(AAm-*co*-MAH) was treated with $POCl_3$ at 0°C for 24 hours.

AAm was expected to enhance the conductivity of the copolymer containing the component as well as its solubility because of its polar NH_2 group.

The effect of reaction temperature in obtaining poly(AAm-*co*-MAH) on the conductivity of the precursor copolymer treated with $POCl_3$ is also shown in Table 2. In this case the copolymerization was carried out for 48 hours with a 1.0 mole ratio of [AAm]. The reaction of the precursor copolymer with phosphorus oxychloride was carried out under the same conditions as mentioned above. As the copolymerization temperature increased, the conductivity was lower.

Table 2 also shows the effect of reaction time with $POCl_3$ on the conductivity of poly(AAm-*co*-MAH). In order to investigate the effect of $POCl_3$ treatment, one kind of copolymer with a given molecular weight was used. In this case the copolymerization was carried out at 60°C for 48 hours with a fixed mole ratio of [AAm] (1.0). The weight-average molecular weight of the copolymer was 22,000 (M_w/M_n = 1.16). (Intrinsic viscosity: 0.952 in H_2O at 20 ± 0.01°C.) The conductivity increases up to 72 hours and then levels off with any further increase in reaction time. The conductivity reached 1.3×10^{-6} S·cm^{-1} when the treatment time was 96 hours.

The effects of $POCl_3$ treatment conditions on the conductivity of poly(AAm-*co*-MAH) are summarized in Table 3. To investigate the effect of $POCl_3$ concentration on the conductivity of poly(AAm-*co*-MAH), it was treated with phosphorus oxychloride at 0°C for 24 hours. The copolymer used here was synthesized at 60°C for 48 hours with a fixed mole ratio of [AAm] (1.0). The conductivity increased with $POCl_3$ concentration up to a certain value and thereafter leveled off. The conductivity was 7.93×10^{-6} S·cm^{-1} when the $POCl_3$ concentration was 0.20 M. The effect of $POCl_3$ treatment time is also shown in Table 3. Similar results were obtained as in the case of the effect of $POCl_3$ concentration. The increase of conductivity with increasing $POCl_3$ treatment time and concentrations may be due to the formation of more double bonds in the polymer backbone.

Effect of Carbon Black Dispersion

Electric conductivities of polymers have been reported to be improved by dispersing conductive materials such as graphite or carbon fiber as fillers [7–9]. Recently, Agari et al. [17] measured the electric conductivities of polyethylene composites filled with graphite by different mixing methods and estimated the ease of forming conductive chains of graphite particles from their electric conductivity. They concluded that the conductivities of the composites were significantly affected by the ease of forming conductive chains; that is, the dispersion state in the polymer composites.

The conductivities of the $POCl_3$-treated poly(AAm-*co*-MAH)s were found to be on the order of 10^{-6}–10^{-8} S·cm^{-1}. An attempt was therefore made to improve the electric conductivity of the copolymer after it was reacted with $POCl_3$ by mixing carbon black with the copolymer. Figure 4 shows the conductivity changes when $POCl_3$-treated poly(AAm-*co*-MAH) is mixed with different weight fractions of carbon black. In this case the copolymerization was carried out at 60°C for 48 hours with a 1.0 mole ratio of [AAm]. The reaction of the precursor copolymer with $POCl_3$ was carried out at 0°C for 24 hours. It was found that the conductivities increased with the amount of carbon black up to 7 wt% of loading, but they

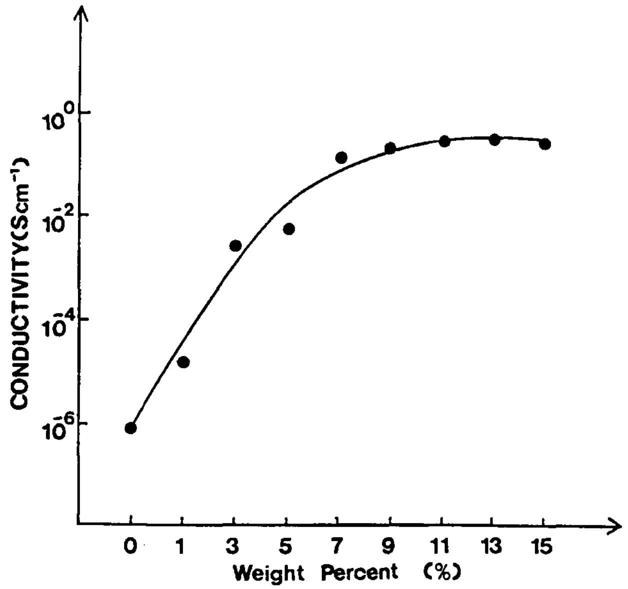

FIG. 4. Effect of weight percent of carbon black on conductivity. The copolymerization was carried out with a 1.0 mole ratio of [AAm] at 60°C for 48 hours. Poly(AAm-*co*-MAH) was treated with $POCl_3$ at 0°C for 24 hours.

gradually approached a certain value. When the polymer is mixed with carbon black, the conductivity reaches up to 2.0×10^{-2} $S \cdot cm^{-1}$. The result implies that the dispersed carbon black particles surround the powdery copolymer structure and can easily form conductive chains when at least 7 wt% of carbon blacks are mixed with the $POCl_3$-treated copolymer [17].

CONCLUSIONS

In this article we reported the conductivities of poly(AAm-*co*-MAH)s after reaction with phosphorus oxychloride. The conductivity decreased with an increasing mole ratio of [AAm] and the copolymerization temperature. It showed a maximum when the precursor copolymer was synthesized for 72 hours at 60°C. The conductivity increased up to 72 hours and leveled off with any further increasing reaction time of the precursor copolymer with $POCl_3$. The conductivity was higher when the precursor copolymers were treated with a higher $POCl_3$ concentration. When carbon black was loaded to the polymer, the conductivity increased with the amount of carbon black up to 7 wt% and gradually approached a value of 2.0×10^{-2} $S \cdot cm^{-1}$. This means that conductive chains can be easily formed only when more than 7 wt% of carbon blacks is mixed with the $POCl_3$-treated copolymer.

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