Syntheses and Electric Conductivities of Poly(methyl vinyl ketone-co-maleic anhydride)s Reacted with Phosphorus Oxychloride

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SYNOPSIS

Electric conductivity of poly(methyl vinyl ketone-co-maleic anhydride) (poly(MVK-co-MAH)) reacted with phosphorus oxychloride was investigated. It was found that conductivities were strongly dependent on the $POCl_3$ treatment time and concentration for poly(MVK-co-MAH), but were not appreciably affected by the mol fraction of [MAH] and copolymerization temperature when the precursor copolymer was obtained. The conductivities of the poly(MVK-co-MAH)s treated with $POCl_3$ were of the order of 10^{-6} to 10^{-9} S cm^{-1}. The conductivity of the poly(MVK-co-MAH) increased with the treatment time and concentrations of $POCl_3$. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyacetylene is the most investigated of the conductive polymers because of its high electrical conductivity and easiness in synthesis.[1-4] However, its unstability in air and insolubility in organic solvents led researchers to the investigation of several other conducting polymers.[5-7] Among these conducting polymers are substituted polyacetylene, polyarylenes, or poly(arylene vinylene)s.[8-12] Most conducting polymers exhibit usually very low conductivities, at most, being the order of 10^{-10} to 10^{-12} S cm^{-1} in undoped states. They show a dramatic increase in electric conductivities of up to 16 orders of magnitude when doped with some kinds of halogen gases like AsF_5, I_2, BCl_3, or HCN.

Recently, several conductive polymers prepared via precursor routes have attracted much interest. Ogawa et al.[13,14] reported the reaction of poly(alkyl vinyl ketone)s with active chlorides such as phosphoryl chloride to obtain conductive polyacylacetylenes. These polymers showed considerable high conductivities of up to 10^{-4} S cm^{-1} in undoped states,

simply by reacting poly(alkyl vinyl ketone)s as precursor polymers with active chlorides. The conjugated diene structure of the polymers can be easily obtained during the reaction with active chlorides, even though the poly(alkyl vinyl ketone)s themselves do not contain a conjugated double-bond structure. In this vein, our efforts have been directed toward preparing a series of polyacylacetylenes, especially copolymeric polyacylacetylenes, in our laboratory for years.[15,16]

In this paper, copolymers of methyl vinyl ketone and maleic anhydride were prepared and the precursor copolymers were reacted with phosphorus oxychloride to obtain electrically conductive polymers. Maleic anhydride (MAH) was selected because the monomer was easily commercially available and, moreover, contained a strong electron-withdrawing anhydride group, which might give a self-dopant function to a final conductive polymer. It may be also expected that the introduction of MAH improves the stability of the resulting phosphorus oxychloride-treated conductive polymer in air because of its role of blocking oxygen. It may be assumed that the oxygen-rich atmosphere in the anhydride group around the conjugated double bond can block an O_2 attack because of the steric hindrance of the anhydride group and also because of

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the repulsion of the oxygen atoms themselves against O_2 in the air.

The effects of various experimental conditions featuring copolymer compositions, copolymerization temperature, and $POCl_3$ treatment conditions on the electric conductivities of polyacylacetylenes were investigated. The electric conductivity was measured by four-point probe DC method.

EXPERIMENTAL

Materials

Methyl vinyl ketone (MVK; Merck) was dehydrated with calcium chloride and fractionally distilled. Maleic anhydride (MAH; Junsei) and 2,2'-azobis-isobutyronitrile (AIBN; Wako) were recrystallized from chloroform and absolute ethanol, respectively. Phosphorus oxychloride ($POCl_3$; Nakarai) was used without further purification. Tetrahydrofuran (THF; Baker) of HPLC grade was used as received. Other chemicals were purified prior to use by standard methods.

Synthesis of Poly(MVK-co-MAH)

A given amount of MVK and MAH was dissolved in 120 mL of ethyl acetate in a polymerization tube

Table I   Copolymerization Conditions of MVK and MAH, Conversion Percentage, and Copolymer Composition

Copolymerization Conditions of MVK and MAH	Conversion (%)	Mol Fraction of MAH in Copolymer
Mol fraction of [MAH] in feed[a]		
0.20	52	0.30
0.35	48	0.39
0.50	43	0.42
0.65	39	0.45
0.80	31	0.48
Polymerization temp (°C)[b]		
50	37	0.40
60	43	0.42
70	50	0.48

[a] Copolymerization conditions: 48 h, 60°C.
[b] Copolymerization conditions: 48 h, mol fraction of MAH = 0.5.

Table II   POCl₃ Treatment Conditions

Condition	Description
Treatment time (h)[a]	12, 24, 36, 48, 60, 72
POCl₃ concentration (M)[b]	0.05, 0.10, 0.15, 0.20

[a] Copolymerization conditions: 48 h, 60°C, mol fraction of MAH = 0.5; poly(MVK-co-MAH) was treated with $0.05 M$ of $POCl_3$ at 0°C.
[b] Copolymerization conditions: 48 h, 60°C, mol fraction of MAH = 0.5; poly(MVK-co-MAH) was treated with $POCl_3$ at 0°C for 36 h.

and then 0.03 g ($1.5 \times 10^{-4} M$) of AIBN was added. The tube was sealed after charging with nitrogen and polymerizations were carried out under the experimental conditions shown in Table I. After 48 h, the contents were poured into methanol with stirring; the precipitate was filtered and dried *in vacuo* to constant weight. The conversion data for each polymerization are also listed in Table I.

Reaction of Poly(MVK-co-MAH) with POCl₃

The precursor, poly(MVK-co-MAH), was treated with $POCl_3$ by the same method as described previously[16]: One gram of poly(MVK-co-MAH), prepared under different copolymerization conditions, was dissolved in 100 mL of THF and 8.2 g of $POCl_3$ was added and the mixture was kept in an ice bath for 36 h. In this way, the effect of copolymerization conditions on the conductivities of $POCl_3$-treated poly(MVK-co-MAH)s was investigated. Then, one kind of the poly(MVK-co-MAH)s, synthesized with 0.50 mol fraction of [MAH] at 60°C for 48 h, was treated with $POCl_3$ under various treatment conditions in order to investigate the effect of $POCl_3$ treatment conditions on the conductivity of the $POCl_3$-treated poly(MVK-co-MAH) (Table II). After the reactions, the systems were concentrated under vacuum and the reacted polymers were precipitated in petroleum ether, washed with a tenfold excess methanol for a time period long enough to remove the unreacted $POCl_3$ remaining in the final product, and dried in vacuum.

Characterization

The structure of the resulting polymer was identified by an infrared (IR) spectrum (Perkin-Elmer 1330). The copolymer compositions in poly(MVK-co-MAH) were determined by elemental analysis (Perkin-Elmer 240C elemental analyzer). The copolymer compositions in poly(MVK-co-MAH) are

listed in Table I. One can see that the copolymer compositions, ranging from 0.3 to 0.48, are not appreciably changed with different monomer feed ratios. The result implies that the copolymers have presumably alternating sequence distributions regardless of the monomer feed ratios.

The formation of double bonds after reacting with $POCl_3$ was identified by IR and UV (UVIKON 860) spectra. The presence of unreacted $POCl_3$ traces was checked by ^{31}P-NMR spectrophotometry (Bruker AM300). For the ^{31}P-NMR analysis, 1 g of $POCl_3$-treated poly(MVK-*co*-MAH) was dissolved in 5 mL of THF. A mixture of 80% of H_3PO_4 and 20% of D_2O (by v/v) was used as a reference. Averaged were 3320 scans (SF: 121.49 MHz; PW: 350 pulse). The molecular weight of poly(MVK-*co*-MAH) was determined by gel permeation chromatography (GPC) (Waters 244). The measurements were conducted in THF and the apparatus was calibrated with PS standards.

Electric Conductivities

For the measurement of conductivity, circular pellets (diameter in 2.3 cm and thickness in 0.1–0.3 mm) from the powdery samples were prepared by a pressure of 90 kg/cm^2. Gold electrodes were attached on both surfaces of the pellets together with a guard electrode by vacuum evaporation. The conductivity measurements were carried out by four-point probe DC method in a vacuum of 10^{-3} Torr.

RESULTS AND DISCUSSION

Solubility and Characterization

All the $POCl_3$-treated poly(MVK-*co*-MAH)s were soluble in dimethyl sulfoxide (DMSO) and THF but only partially soluble in chlorobenzene and N,N'-dimethylformamide (DMF). Table III shows typical solubility data of the poly(MVK-*co*-MAH) treated with $POCl_3$ for 60 h. The copolymer referred to in Table IV was synthesized with a 0.50 mol fraction

of [MAH] at 60°C for 48 h. In our previous works,[15,16] similar solubility behavior was also observed for the $POCl_3$-treated copolymer of MVK and acrylamide, whereas poly(methyl vinyl ketone) (PMVK) treated with $POCl_3$ was only partially soluble in DMSO. These results support our postulation that the solubility of the electrically conductive $POCl_3$-treated PMVK can be improved by copolymerizing MVK with a second monomer having polor groups such as MAH or acrylamide.

The IR and UV absorption data were obtained from poly(MVK-*co*-MAH) with or without $POCl_3$ treatment. Figure 1 shows IR spectra of (a) poly(MVK-*co*-MAH) and (b) poly(MVK-*co*-MAH) treated with $POCl_3$ for 36 h. The IR spectrum of the precursor copolymer without $POCl_3$ treatment shows characteristic absorption peaks at 2980 cm^{-1} (C—H); 1850 cm^{-1} and 1750 cm^{-1} (C=O in anhydride); and 1710 cm^{-1} (C=O in MVK). On the other hand, when the copolymer was reacted with $POCl_3$, a new peak at 1620 cm^{-1} appeared, indicating that carbon–carbon single bonds were transformed into conjugated double bonds. The formation of double bonds was also identified by a UV spectrum. Figure 2 shows UV spectra of (a) poly(MVK-*co*-MAH) and (b) poly(MVK-*co*-MAH) treated with $POCl_3$ for 36 h in THF. The characteristic peak of poly(MVK-*co*-MAH) was observed at 290 nm in both cases, but a new peak was also observed in the longer wavelength region around 420 nm in the case of the $POCl_3$-treated copolymer, whereas no peak was observed around the wavelength for poly(MVK-*co*-MAH) without treatment of $POCl_3$. The new peak around 420 nm is associated with the phi–phi* transition of a conjugated double bond.

The formation of conjugated double bonds during the reaction of MVK and phosphorus trichloride or phosphoryl chloride was discussed in detail by Ogawa et al.[13] 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. Further detailed studies should be made to reveal accurately

Table III   Solubility of POCl₃-Treated Poly(MVK-*co*-MAH)

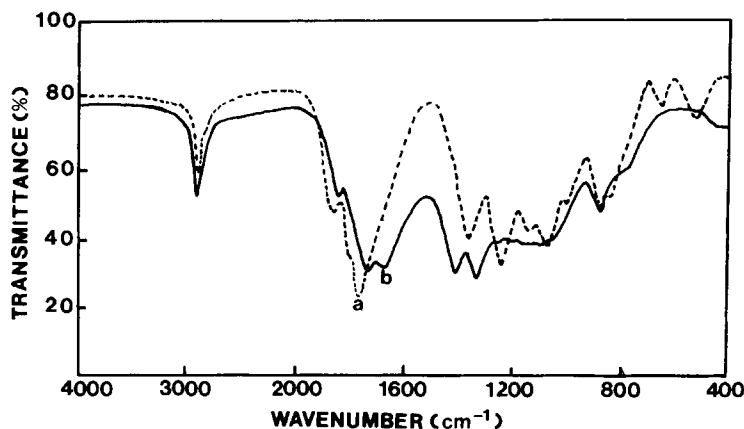|			Solvent			
Benzene	Chlorobenzene	THF	CCl₄	DMF	Methanol	DMSO
+/−	+/−	+	−	+/−	−	+

+, soluble; +/−, partially soluble; −, insoluble.

Figure 1   IR spectra of KBr pellet of (a) poly(MVK-co-MAH) and (b) POCl₃-treated poly(MVK-co-MAH) for 36 h.

what chemical reactions of poly(MVK-co-MAH) with POCl$_3$ take place.

Conductivity

The conductivities of polymers containing conjugated structures are very sensitive to contamination. In fact, it was observed that the conductivities of POCl$_3$-treated PMVK pellets were higher by two to three orders of magnitude in air than in a vacuum.[14,15] Thus, great precaution should be taken to measure the conductivity in a vacuum.

Figure 3 shows the effect of the mol fraction of [MAH] on the conductivity of the POCl$_3$-treated poly(MVK-co-MAH). In this case, the copolymerization was carried out at 60°C for 48 h. The reaction of the precursor copolymer with POCl$_3$ was done at 0°C for 36 h. It is seen that the conductivities increase with increasing mol fraction of [MAH], even though the orders of magnitude (i.e., 10^{-7} S cm^{-1}) are not much different for each mol fraction within the experimental range. It should be remarked, however, that the conductivity values of the copolymers after being treated with POCl$_3$ are higher than that of POCl$_3$-treated PMVK with the same treatment conditions, being of the order of 10^{-9} S cm^{-1},

Figure 2   UV spectra of (a) poly(MVK-co-MAH) and (b) POCl₃-treated poly(MVK-co-MAH) for 36 h in THF.
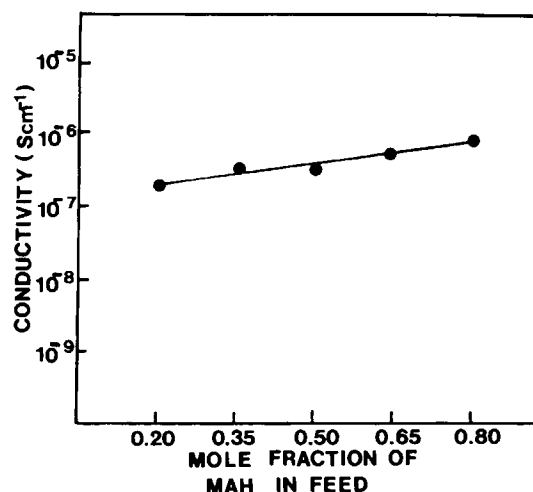

Figure 3   Effect of mol fraction of [MAH] in copolymerization of MVK and MAH on the conductivity of the POCl₃-treated poly(MVK-co-MAH). The copolymerization was carried out at 60°C for 48 h. The poly(MVK-co-MAH) was treated with POCl₃ at 0°C for 36 h.

which had been reported in our previous work.[15] The conductivities of the copolymers treated with POCl$_3$ as well as homopolymer treated in the same way are affected by not only their conjugation length but also by their chemical structure. The result may be ascribed to the pseudodopant role of the anhydride group of MAH in the copolymers, which can withdraw the phi-electron in the double bond of the main chain, even though the copolymers treated with POCl$_3$ may have a shorter conjugation length than that of the homopolymer treated in the same way.

The effect of reaction temperature in obtaining poly(MVK-*co*-MAH) on the conductivity of the precursor copolymer treated with POCl$_3$ is shown in Figure 4. In this case, the copolymerization was carried out for 48 h with 0.50 mol fraction of [MAH]. The reaction of the precursor copolymer with POCl$_3$ was carried out under the same conditions mentioned above. It was found that the conductivity was highest when the precursor copolymer was synthesized at 60°C.

Careful inspection of Figures 3 and 4 indicate that the effect of copolymerization conditions was not substantially significant on the conductivity of the precursor poly(MVK-*co*-MAH) since the orders of magnitude in conductivities are almost the same regardless of the mol fraction of [MAH] and the copolymerization temperature. However, the effect of treatment conditions of POCl$_3$ on the conductivity of poly(MVK-*co*-MAH) is expected to be significant. The conductivities and the stabilities of poly-
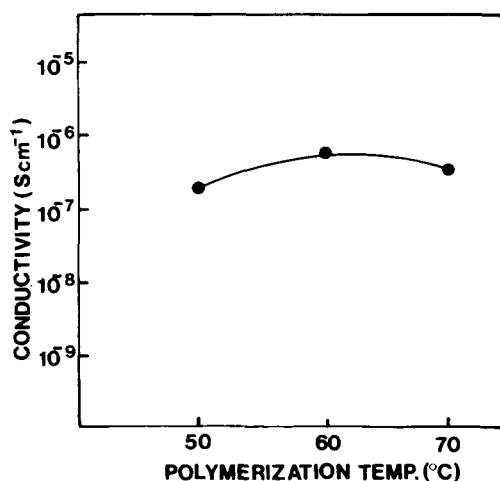
Figure 5   Effect of POCl$_3$ treatment time on the conductivity of the POCl$_3$-treated poly(MVK-*co*-MAH). The copolymerization was carried out with 0.50 mol fraction of [MAH] at 60°C for 48 h. Poly(MVK-*co*-MAH) was treated with 0.05M of POCl$_3$ at 0°C.

acetylene or its derivatives are dependent on the number of double bonds, the regularity of the repeating unit, and the nature of substituents. We used only one kind of poly(MVK-*co*-MAH) with a given molecular weight in order to reduce any combined effects of the factors mentioned above in interpreting our results. In this study, the poly(MVK-*co*-MAH) of a weight-average molecular weight of 56,000 was used for the reaction with POCl$_3$ and for the measurement of electric conductivity. The copolymeri-

Figure 4   Effect of polymerization temperature in copolymerization on the conductivity of the POCl$_3$-treated poly(MVK-*co*-MAH). The copolymerization was carried out with 0.50 mol fraction of [MAH] for 48 h. The poly(MVK-*co*-MAH) was treated with POCl$_3$ at 0°C for 36 h.
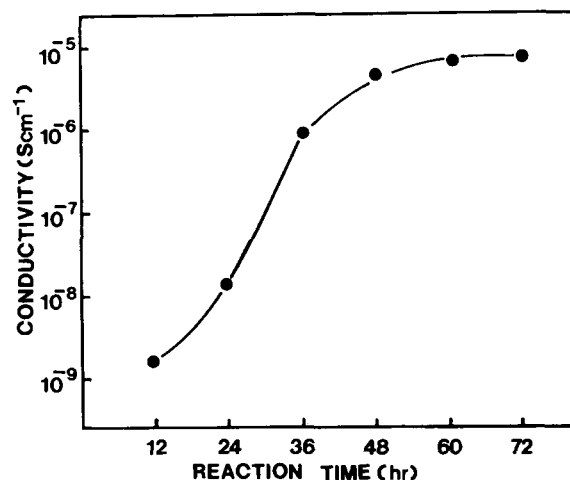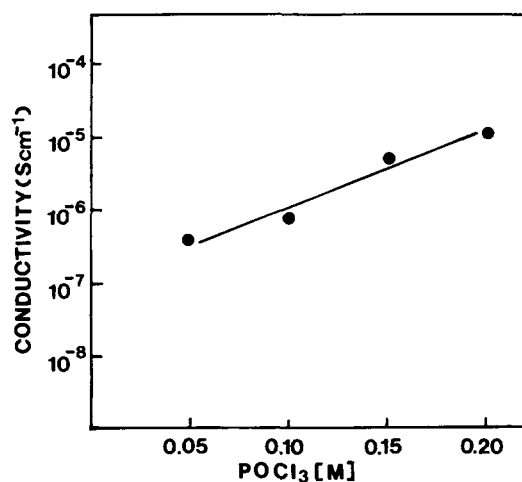
Figure 6   Effect of POCl$_3$ concentration on the conductivity of the POCl$_3$-treated poly(MVK-*co*-MAH). The copolymerization was carried out with 0.50 mol fraction of [MAH] at 60°C for 48 h. Poly(MVK-*co*-MAH) was treated with POCl$_3$ at 0°C for 36 h.
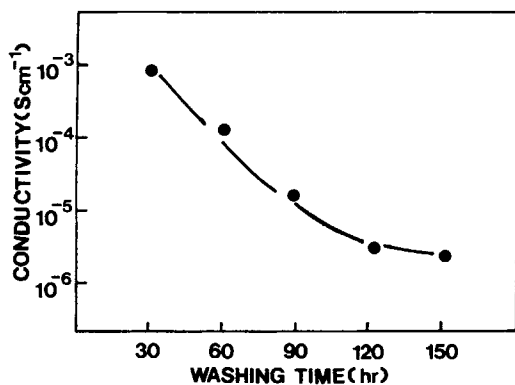
Figure 7   Effect of washing time on the conductivity of the POCl₃-treated poly(MVK-co-MAH). The copolymerization was carried out with 0.50 mol fraction of [MAH] at 60°C for 48 h. Poly(MVK-co-MAH) was treated with POCl₃ at 0°C for 36 h.

zation was carried out at 60°C for 48 h with a fixed mol fraction of [MAH] (0.50).

Figure 5 shows the effect of reaction time with POCl₃ on the conductivity of the poly(MVK-co-MAH). It is seen that the conductivity increases remarkably up to 48 h and then levels off with further increasing reaction time. This may be attributed to the formation of more double bonds in the polymer backbone with increasing reaction time up to 48 h. However, this result implies that further formation of double bonds may not have occurred even if the reaction between the copolymer and POCl₃ proceeds for longer times than 48 h. The conductiv-

ity reaches to 8.7×10^{-6} S cm⁻¹ when the treatment time is above 48 h.

Figure 6 shows the effect of POCl₃ concentration on the conductivity of the poly(MVK-co-MAH). Poly(MVK-co-MAH) was treated with POCl₃ at 0°C for 36 h. The copolymer was the same as that referred to in Figure 5. It is seen that the conductivity increases with increasing POCl₃ concentration due to the formation of more double bonds in the polymer backbone with increasing POCl₃ concentration. The conductivity was 9.0×10^{-6} S cm⁻¹ when the POCl₃ concentration was $0.20 M$.

It may be anticipated that the conductivity would be sensitive to the unreacted POCl₃ remaining in the final product, if any. Previous analysis by the titration method had already exhibited that there were no chlorine residues in the final product if the product was washed with excess methanol for a longer time period than 60 min.[17] To confirm how much the unreacted POCl₃ residues, especially the phosphorous residues, affect the conductivity of the POCl₃-treated copolymer, an experiment was performed to test the effect of the washing time of the product. The product remaining after reacting poly(MVK-co-MAH) with POCl₃ was washed with a 10-fold excess of methanol for various periods. In this case, poly(MVK-co-MAH) was treated with POCl₃ at 0°C for 36 h.

Figure 7 shows the effect of washing time of the product with methanol on the conductivity. It was observed that the conductivity decreased with washing time up to 120 min, but thereafter was not changed appreciably. Thus, we can conclude that
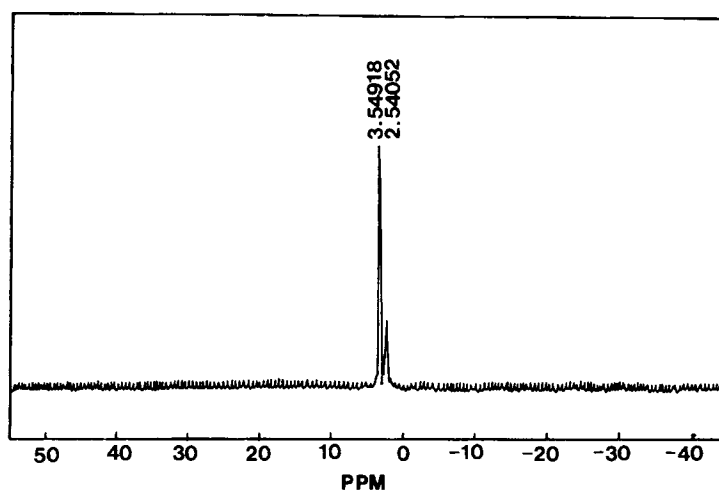

Figure 8   ³¹P-NMR spectrum of the POCl₃-treated poly(MVK-co-MAH)s after washing for 120 min. The copolymerization was carried out with 0.50 mol fraction of [MAH] at 60°C for 48 h. Poly(MVK-co-MAH) was treated with POCl₃ at 0°C for 36 h.

the traces of unreacted $POCl_3$ retained in the final product on the conductivity is negligible if one washes the product for 120 min or longer.

The amount of the $POCl_3$ residues after washing in the product was measured quantitatively by using ^{31}P-NMR spectroscopy. Figure 8 shows a ^{31}P-NMR spectrum of the product after washing with methanol for 120 min. The amount of remaining $POCl_3$ was extremely small, ca. 0.000031 g after washing for 120 min. (Note that the amount of initial $POCl_3$ before reaction was 8.2 g.)

CONCLUSIONS

In this article, we reported conductivities of poly(MVK-*co*-MAH)s after reacting with phosphorus oxychloride. The conductivity increased with increasing mol fraction of [MAH] and it showed a maximum when the precursor copolymer was synthesized at 60°C. However, the effects of copolymerization conditions such as mol fraction of [MAH] and polymerization temperature were not significant. It was found that the effect of treatment conditions of $POCl_3$ on the conductivity of the poly(MVK-*co*-MAH) was shown to be significant. The conductivity increased remarkably up to 48 h and then leveled off with further increasing reaction time of the precursor copolymer with $POCl_3$. The conductivity was higher when the precursor copolymers were treated with higher $POCl_3$ concentration. The ^{31}P-NMR spectroscopic analysis showed that the $POCl_3$ residues in the $POCl_3$-treated poly(MVK-*co*-MAH) were negligible when the final product was washed with excess methanol for 120 min or longer. In conclusion, the conductivities of the poly(MVK-*co*-MAH)s treated with $POCl_3$ were of the order of 10^{-6} to 10^{-9} S cm^{-1}.

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