Syntheses and Electric Conductivities of Poly(Methyl Vinyl Ketone-*co*-Acryl Amide)s Reacted with Phosphorus Oxychloride

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SYNOPSIS

Studies have been made on the conductivities of poly(methyl vinyl ketone-*co*-acryl amide) [poly(MVK-*co*-AAm)]s after having reacted with phosphorus oxychloride. It was found that the conductivities were dependent on the mol ratio of [AAm] to [MVK], copolymerization temperature, and time. The effect of treatment conditions of $POCl_3$ on the conductivities of the poly(MVK-*co*-AAm)s was shown to be significant. It was observed that the conductivities of the poly(MVK-*co*-AAm)s, treated with $POCl_3$, are of the order of $10^{-6} - 10^{-9}$ Scm^{-1}. The maximum conductivity of the $POCl_3$-treated poly(MVK-*co*-AAm) was obtained as 8.7×10^{-6} Scm^{-1} when the mol ratio of AAm to MVK was 0.5. The conductivity of the poly(MVK-*co*-AAm) was increased with the treatment time and concentrations of $POCl_3$. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Electrically conductive polymers have attracted much interest from both the theoretical and practical standpoints. Among these polymers, polyacetylene has been extensively studied because of its high electrical conductivity and ease of synthesis.[1-4] Polyacetylene is, however, unstable in air, is insoluble in the usual organic solvents, and it decomposes before melting.[5-7]

Therefore, studies of the syntheses and properties of substituted polyacetylene, polyarylenes, or poly(arylene vinylene)s have been performed.[8-16]

Ogawa et al.[17,18] reported on the reaction of poly(alkyl vinyl ketone)s with active chlorides, such as phosphoryl chloride, to obtain poly(acylactylene)s and the electric conductivities of the polymer films. Even though several works have been published on the polymerization and copolymerization of methyl vinyl ketone (MVK) and its derivatives,[19-21] no work has appeared on the application of the polymers containing MVK as precursors to develop novel semiconductors, except for the work of Ogawa et al. It might be expected that the conductivities and the stabilities of polyacetylene or its derivatives are dependent on the number of double bonds [e.g., the degree of polymerization of the starting material, poly(alkyl vinyl ketone)], the regularity of the repeating unit, and the kind of substituents.

In our previous work,[22] it was reported that poly(methyl vinyl ketone) (PMVK), even though it was treated with phosphorous oxychloride ($POCl_3$), showed low conductivity, being on the order of 10^{-9} Scm^{-1}. An attempt was made, thus, to improve the conductivity of PMVK by introducing acrylamide into the polymer backbone by radical copolymerization. Acrylamide (AAm) was selected because the monomer contained a strong electron withdrawing C=O group and may give a self-dopant function to PMVK. It might be also expected that the introduction of AAm could improve the solubility of $POCl_3$-treated PMVK because of its polar properties. The copolymer, poly(MVK-*co*-AAm), was reacted with $POCl_3$ under various experimental conditions.

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The electric conductivity was measured by the 4-point probe DC method.

EXPERIMENTAL

Materials

Methyl vinyl ketone (MVK; Merck) was dehydrated with calcium chloride and was fractionally distilled. Acrylamide (AAm; Wako) and 2,2′-azobisisobutyronitrile (AIBN; Wako) were recrystallized from methanol and dehydrated ethanol, respectively. Phosphorous 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 the standard methods.

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

A given amount of MVK and AAm were dissolved in 100 mL of ethanol in a polymerization tube and then 0.01 g of AIBN was added. The tube was sealed, after charging with nitrogen, and the polymerization was carried out under the experimental conditions shown in Table I. After a chosen period, the contents were poured into methanol with stirring; the precipitate was filtered and dried *in vacuo* to constant weight. The resulting polymer was identified by IR spectrum (Perkin–Elmer 1330). The conversion data for each polymerization are listed in Table II.

Analyses of Copolymer Compositions

The copolymer compositions in poly(MVK-*co*-AAm) were determined by quantitative infrared (IR) spectroscopy (Perkin–Elmer 1330) and were confirmed by elemental analysis (Perkin–Elmer 240C Elemental Analyzer). The copolymer compositions in poly(MVK-*co*-AAm) are listed in Table II.

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

Poly(MVK-*co*-AAm) was treated with $POCl_3$, according to the work of Ogawa et al.,[18] with slight modifications in two different experimental methods. One method was to react poly(MVK-*co*-AAm) with $POCl_3$ of fixed concentration for a given treatment time; 1 g of poly(MVK-*co*-AAm) was dissolved in 100 mL of formic acid, 8.225 g of $POCl_3$ was added, and the mixture was kept in an ice bath for 24 h. In this process, the effect of copolymerization conditions on the conductivities of $POCl_3$-treated poly(MVK-*co*-AAm)s was investigated. The other method was to react one kind of copolymer with $POCl_3$ by the same method described above, except with various $POCl_3$ concentrations and reaction times, to investigate the effect of $POCl_3$ treatment conditions on the conductivity of the $POCl_3$-treated poly(MVK-*co*-AAm). In this process, the poly(MVK-*co*-AAm) used for reacting with $POCl_3$ was synthesized with 1/1 mol ratio of [AAm]/[MVK] at 60°C for 48 h. Table III lists the treatment conditions of $POCl_3$ for the copolymer. After reactions in both experiments, the systems were concentrated *in vacuo* and the reacted polymers were precipitated in petroleum ether, were washed rapidly with methanol, and were dried *in vacuo*.

Table I Copolymerization Conditions of MVK and MAH

Conditions	
Mol ratio of [MAH]/[MVK]	0.5, 1.0, 1.5, 2.0, 2.5, 3.0
Polymerization Time (h)	24, 48, 72, 96
Polymerization Temp. (°C)	50, 60, 70

Table II Conversion Percentage and Copolymer Composition

		Conversion (%)	Copolymer Composition Mol Ratio of [AAm]/[MVK]
Monomer feed mol ratio[a]; [AAm]/[MVK]	0.5	50	0.41
	1.0	51	0.76
	1.5	57	2.05
	2.0	62	2.33
	2.5	65	3.51
	3.0	67	4.49
Polymerization Temp. (°C)[b]	50	27	0.77
	60	51	0.76
	70	37	0.75
Polymerization Time (h)[c]	24	38	0.80
	48	51	0.76
	72	59	0.81
	96	65	0.83

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

[b] Copolymerization conditions: 48 h, [AAm]/[MVK] = 1.0.

[c] Copolymerization conditions: 60°C, [AAm]/[MVK] = 1.0.

Measurements

Molecular Weight

The mol wt of poly(MVK-*co*-AAm) with 1/1 mol ratio of [AAm]/[MVK] was determined by gel per-

Table III $POCl_3$ Treatment Conditions

Condition	Description
Treatment Time (h)	12, 24, 36, 48, 60, 72
$POCl_3$ Concentration (mol/L)	0.05, 0.10, 0.15, 0.20

meation chromatography (GPC) (Waters–Water-244). The measurements were conducted in THF and the apparatus was calibrated with PS standards.

Electric Conductivity

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 a 4-point probe DC method in a vacuum of 10^{-3} Torr.

RESULTS AND DISCUSSION

Solubility

All of the $POCl_3$-treated poly(MVK-*co*-AAm)s were soluble in dimethyl sulfoxide (DMSO) and partially soluble in THF and DMF. Table IV shows typical solubility data of the poly(MVK-*co*-AAm) treated with $POCl_3$ for 60 h. The copolymer referred to in Table IV was synthesized with 1/1 mol ratio of [AAm]/[MVK] at 60°C for 48 h. The result is noteworthy since polyacetylene, which has been widely investigated as a pioneering conductive polymer, is not soluble in any of the solvents used in the study.

Conductivity

Figure 1 shows IR spectra of poly(MVK-*co*-AAm) (a) and poly(MVK-*co*-AAm) treated with $POCl_3$ for 60 h (b). The IR spectrum of the copolymer, without $POCl_3$ treatment, shows characteristic absorption peaks at 3500 cm^{-1} ($-NH_2$), 2980 cm^{-1} ($C-H$), and 1650 cm^{-1} ($C=O$). On the other hand, when the copolymer was reacted with $POCl_3$, a new peak at 1615 cm^{-1} appeared, meaning that the carbonyl group was transformed into a conjugated diene group. The double bond was also identified by the UV spectrum (Fig. 2). Figure 2 shows UV spectra of poly(MVK-*co*-AAm) (a) and poly(MVK-*co*-AAm) treated with $POCl_3$ for 60 h (b) in DMSO. The characteristic peak of poly(methyl vinyl ketone) was observed at 290 nm in both cases, but a new peak was observed in the longer wavelength region around 340 nm in the case of the $POCl_3$-treated copolymer, whereas no peak is observed around the wavelength for poly(MVK-*co*-AAm) without treatment of $POCl_3$. The new peak at 340 nm is associated with the phi–phi* transition of conjugated double bond.

The conductivities of polymers containing conjugated structures are sensitive to contamination. In fact, it was observed that the conductivities of $POCl_3$-treated PMVK pellets were two to three orders of magnitude higher in air than *in vacuo.*[18,22] Thus, a precaution should be taken to measure the conductivity *in vacuo.*

Figure 3 shows the effect of mol ratio of [AAm]/[MVK] on the conductivity of the $POCl_3$-treated poly(MVK-*co*-AAm). In this case, the copolymerization was carried out at 60°C for 48 h. The reaction of the poly(MVK-*co*-AAm) with phosphorous oxychloride was carried out at 0°C for 24 h. It is seen that the conductivity decreased with [AAm] content in the copolymer. The maximum conductivity was obtained as 8.7×10^{-6} Scm^{-1} when the mol ratio of [AAm] to [MVK] was 0.5. It should be mentioned that the conductivity values of the copolymers, after treatment with $POCl_3$, are higher than that of $POCl_3$-treated PMVK with the same treatment conditions, being on the order of 10^{-9} Scm^{-1}.

The effect of reaction temperature in obtaining poly(MVK-*co*-AAm) on the conductivity of the copolymer treated with $POCl_3$ is shown in Figure 4. In this case, the copolymerization was carried out

Table IV Solubility of a Typical $POCl_3$-Treated Poly(MVK-*co*-AAm)

Solvent						
Benzene	Chlorobenzene	THF	CCl_4	DMF	Methanol	DMSO
−	−	+/−	−	+/−	−	+

(+) Soluble, (+/−) Partially soluble, (−) Insoluble.

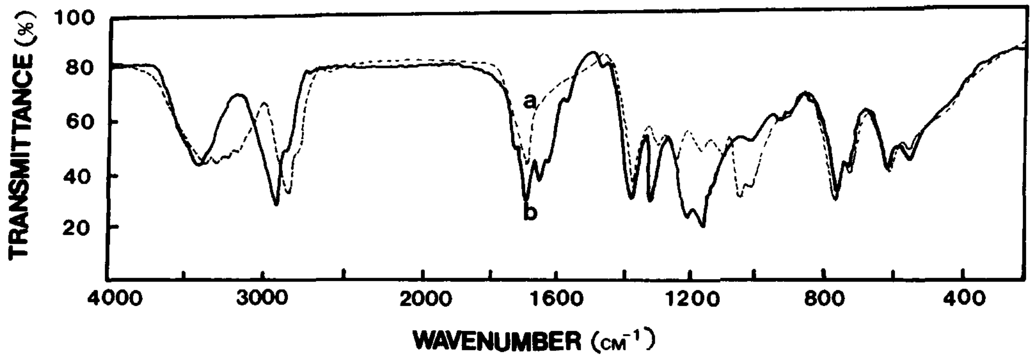

Figure 1 IR spectra of KBr pellet of (a) poly(MVK-*co*-AAm) and (b) $POCl_3$-treated poly(MVK-*co*-AAm) for 24 h.

for 48 h with 1 : 1 mol ratio of [AAm] to [MVK]. The reaction of the precursor copolymer with phosphorous oxychloride was carried out under the same conditions as mentioned above. It was found that the conductivity was highest when the precursor copolymer was synthesized at 60°C. The result may be ascribed to the mol wt of the precursor copolymer. It may be assumed that the precursor copolymer, with higher mol wt, tends to form more conjugated double bonds when reacting with $POCl_3$ and thus exhibits higher conductivity. The result is different from that of Ogawa et al.[18] Ogawa et al. explained that the PMVK with higher mol wt shows slower reaction with $POCl_3$ and shows lower conductivities when compared at a given time because of the slower penetration of $POCl_3$. The exact reason for this difference is not clear at present.

Figure 5 shows the effect of copolymerization time of MVK and AAm on the conductivity of the copolymer treated with $POCl_3$. In this case, the polymerization was carried out at 60°C with a fixed mol ratio of [AAm]/[MVK] (1 : 1). The reaction of the copolymer with phosphorous oxychloride was carried out under the same conditions as above. The conductivity of $POCl_3$-treated poly(MVK-*co*-AAm) shows a maximum at 48 h and decreases with further increasing copolymerization time. The conductivity is on the order of $10^{-7} - 10^{-9}$ Scm^{-1}.

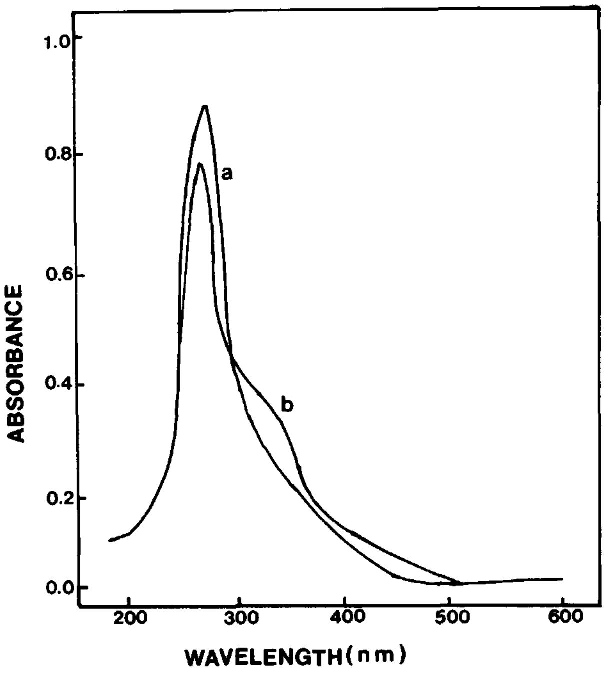

Figure 2 UV spectra of (a) poly(MVK-*co*-AAm) and (b) $POCl_3$-treated poly(MVK-*co*-AAm) for 24 h in DMSO.

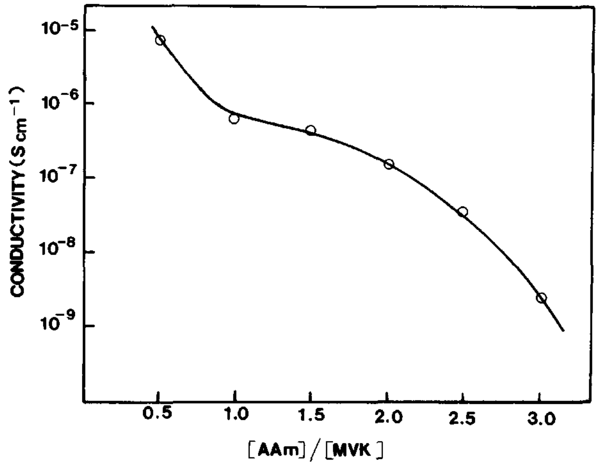

Figure 3 Effect of mol ratio of [AAm] to [MVK] in copolymerization on the conductivity of the $POCl_3$-treated poly(MVK-*co*-AAm). The copolymerization was carried out at 60°C for 48 h. The poly(MVK-*co*-AAm) was treated with $POCl_3$ at 0°C for 24 h.

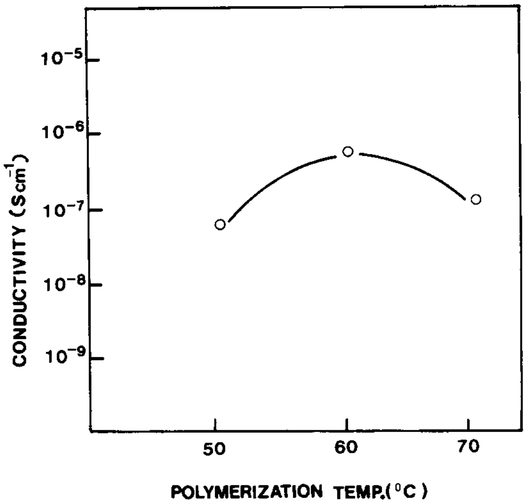

Figure 4 Effect of polymerization temperature in copolymerization on the conductivity of the $POCl_3$-treated poly(MVK-*co*-AAm). The copolymerization was carried out with 1 : 1 mol ratio of [AAm] to [MVK] for 48 h. The poly(MVK-*co*-AAm) was treated with $POCl_3$ at 0°C for 24 h.

The results of Figures 4 and 5 imply that the effects of the copolymerization time and temperature on the conductivity are closely related to the mol wt differences of the precursor copolymers. Unfortunately, however, the mol wt data of most of the precursors, prepared under different experimental conditions, could not be obtained since they were hardly dissolved in THF, which was used commonly as an effluent to measure polystyrene-equivalent mol wts, except when the mole ratio of [AAm]/[MVK] was below 1.0. It should be mentioned that further quantitative analyses should be made to explain clearly the effect of mol wt, as well as copolymer composition, on the conductivity and the data on the mol wt should shed light on the phenomena shown in Figs. 4 and 5.

The effect of treatment conditions of $POCl_3$ on the conductivity of poly(MVK-*co*-AAm) is expected to be significant. It was mentioned that the conductivities and the stabilities of polyacetylene 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*-AAm) with a given mol wt in order to reduce any combined effects of the factors mentioned above in interpreting our results. In this study, the poly(MVK-*co*-AAm) of weight-average mol wt of 62,000 was used for the reaction with $POCl_3$ and for the measurement of electric conductivity. The copolymerization was carried out at 60°C for 48 h with a fixed mol ratio of [AAm]/[MVK] (1 : 1).

Figure 6 shows the effect of reaction time with $POCl_3$ on the conductivity of the poly(MVK-*co*-AAm). It is seen that the conductivity increases remarkably up to 48 h and levels off with further increase in reaction time. This may be attributed to the formation of more double bonds in the polymer backbone with increasing reaction time. The conductivity is on the order of 10^{-6} Scm^{-1} when the treatment time is above 48 h.

Figure 7 shows the effect of $POCl_3$ concentration on the conductivity of the poly(MVK-*co*-AAm). Poly(MVK-*co*-AAm) was treated with phosphorous oxychloride at 0°C for 24 h. The copolymer was the same as that referred to in Figure 6. It is seen that the conductivity increases with increasing $POCl_3$ concentration, due to the formation of more double bonds in polymer backbone with increasing reaction time. The conductivity is on the order of 10^{-6} Scm^{-1} when the $POCl_3$ concentration is above 0.10 M.

It may be anticipated that the conductivity would be sensitive to the unreacted $POCl_3$ remaining in the final product, if any. To confirm how much the unreacted $POCl_3$ residues affect the conductivity of the $POCl_3$-treated copolymer, an experiment was performed to test the effect of washing times of the product. The product, after reacting poly(MVK-*co*-AAm) with $POCl_3$, was washed with a 10-fold excess of methanol for various periods. In this case, poly(MVK-*co*-AAm) was treated with $POCl_3$ at 0°C for 24 h. If there are negligible $POCl_3$ residues in the product, then no appreciable change in the con-

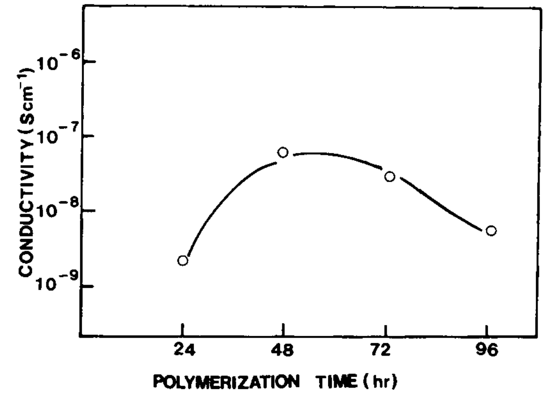

Figure 5 Effect of polymerization time in copolymerization on the conductivity of the $POCl_3$-treated poly(MVK-*co*-AAm). The copolymerization was carried out with 1 : 1 mol ratio of [AAm] to [MVK] at 60°C. The poly(MVK-*co*-AAm) was treated with $POCl_3$ at 0°C for 24 h.

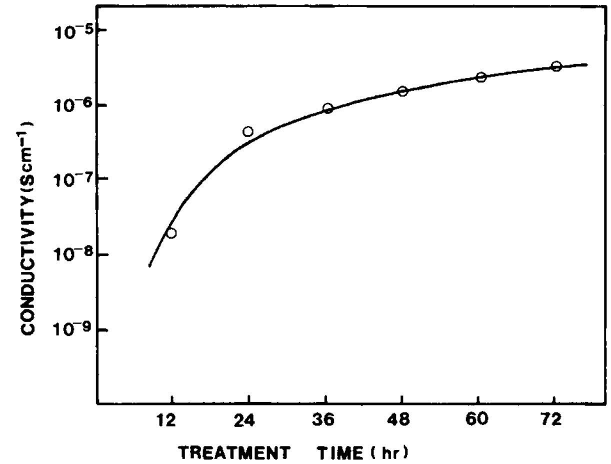

Figure 6 Effect of $POCl_3$ treatment time on the conductivity of the $POCl_3$-treated poly(MVK-*co*-AAm). The copolymerization was carried out with 1 : 1 mol ratio of [AAm] to [MVK] at 60°C for 48 h. Poly(MVK-*co*-AAm) was treated with 0.05 M of $POCl_3$ at 0°C.

Table V Effect of Washing Time on the Conductivity of Reaction Product of Poly(MVK-*co*-AAm) with $POCl_3$

Washing Time (min)	Conductivity (Scm^{-1})
30	8.7×10^{-5}
60	5.0×10^{-5}
90	3.6×10^{-6}
120	7.1×10^{-7}
150	7.4×10^{-7}

ductivity would be expected. Table V 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 the traces of unreacted $POCl_3$ are washed out and the effect of $POCl_3$ retained in the final product on the conductivity is negligible, if one washes the product for 120 min or longer.

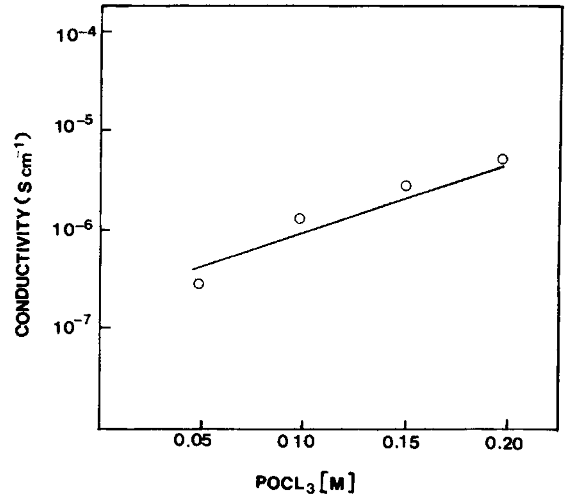

Figure 7 Effect of $POCl_3$ concentration on the conductivity of the $POCl_3$-treated poly(MVK-*co*-AAm). The copolymerization was carried out with 1 : 1 mol ratio of [AAm] to [MVK] at 60°C for 48 h. Poly(MVK-*co*-AAm) was treated with $POCl_3$ at 0°C for 24 h.

The amount of the $POCl_3$ residues in the product after washing for 120 min was analyzed by ^{31}P–NMR spectroscopy.[22] In fact, the amount of remaining $POCl_3$ was extremely small, *ca.* 0.00003 g. (Note that the amount of initial $POCl_3$ before reaction was 8.225 g.)

CONCLUSIONS

In this article, we reported conductivities of poly(MVK-*co*-AAm)s after reacting with phosphorus oxychloride. It was found that the conductivity decreased with [AAm] content in poly(MVK-*co*-AAm). The conductivity was highest, 8.7×10^{-6} Scm^{-1} for the $POCl_3$-treated poly(MVK-*co*-AAm), when the copolymer was synthesized with the mol ratio of [MAH] to [MVK] of 0.5 at 60°C. It is seen that the conductivity of the $POCl_3$-treated poly(MVK-*co*-MAH) reached a maximum when the copolymer was synthesized for 48 h and decreased with further increasing reaction time. The conductivity of the copolymer after treatment with $POCl_3$ is on the order of $10^{-6} - 10^{-9}$ Scm^{-1}. The effect of treatment conditions of $POCl_3$ on the conductivity of the poly(MVK-*co*-AAm) was shown to be significant. It was shown that the conductivity increased remarkably up to 48 h and leveled off with further increasing reaction time with $POCl_3$. The conductivity was increased with $POCl_3$ concentration.

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