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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Conductive Polymers via Precursor Routes. 5. Effect of Heat Treatment on the Electric Conductivity of Phosphorus-Oxychloride-Treated Poly(Acrylamide-co-Maleic Anhydride)

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To cite this Article Kim, Dae Young , Kim, Yoon Seok , Ha, Chang Sik and Cho, Won Jei(1995) 'Conductive Polymers via Precursor Routes. 5. Effect of Heat Treatment on the Electric Conductivity of Phosphorus-Oxychloride-Treated Poly(Acrylamide-co-Maleic Anhydride)', *Journal of Macromolecular Science, Part A*, 32: 1, 103 – 114

To link to this Article: DOI: 10.1080/10601329508011067

URL: <http://dx.doi.org/10.1080/10601329508011067>

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CONDUCTIVE POLYMERS VIA PRECURSOR ROUTES. 5. EFFECT OF HEAT TREATMENT ON THE ELECTRIC CONDUCTIVITY OF PHOSPHORUS-OXYCHLORIDE- TREATED POLY(ACRYLAMIDE-*co*-MALEIC ANHYDRIDE)

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

ABSTRACT

A copolymer of acrylamide (AAm) and maleic anhydride (MAH) [poly(AAm-*co*-MAH)] was reacted with phosphorus oxychloride to obtain an electrically conductive polymer. The effects of heat treatment for the poly(AAm-*co*-MAH) before or after having reacted with POCl₃ on their electric conductivities were investigated. The copolymer both before and after POCl₃ treatment was subjected to heat for various periods (8–24 hours) at 180°C or for 8 hours at different temperatures (60–180°C). The solubility of the POCl₃-treated poly(AAm-*co*-MAH) became poorer as heating time and temperature increased for the precursor polymer before POCl₃ treatment, but that was not much changed with different heating conditions for the precursor polymer after POCl₃ treatment. It was concluded that the effect of heat treatment on the conductivities of the POCl₃-treated poly(AAm-*co*-MAH) was more prominent when the precursor polymer was treated with heat after POCl₃ treatment

than before POCl_3 treatment, exhibiting significant structural changes when subjected to heat especially at higher temperature for a given period or for longer periods at a given temperature.

INTRODUCTION

Electrically conductive polymers have attracted much interest from both theoretical and practical standpoints. Among them, polyacetylene has been extensively studied because of its high electrical conductivity and easiness in synthesis [1–4]. Polyacetylene is, however, unstable in air and insoluble in the usual organic solvents, and decomposes before melting [5–7]. Therefore, studies of the syntheses and properties of substituted polyacetylene, polyarylenes, poly(arylene vinylene)s, etc. have been intensively made [8–12].

Our previous paper [13] reported that the conductive poly(acetylene)s could be obtained by simply reacting a copolymer of acrylamide (AAM) and maleic anhydride (MAH) as a precursor polymer with phosphorus oxychloride. It has been shown that the conjugated diene structure of the polymers could be easily obtained during the reaction with POCl_3 , even though the copolymer of AAM and MAH, poly(AAM-co-MAH) itself did not contain a conjugated double bond structure [13–17]. In the previous work the POCl_3 -treated poly(AAM-co-MAH) showed good solubility in common organic solvents because of the polar properties of the carbonyl groups in both AAM and MAH. However, those copolymers showed relatively lower conductivities, being on the order of 10^{-6} to $10^{-8} \text{ S}\cdot\text{cm}^{-1}$ in undoped states.

The present paper is concerned with the effect of heat treatment for poly(AAM-co-MAH) before or after reaction with POCl_3 on the conductivities of the POCl_3 -treated copolymer. It will be shown that POCl_3 -treated poly(AAM-co-MAH) exhibits higher conductivities, being on the order of $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ if the precursor copolymer is treated with heat before having reacted with POCl_3 . The electric conductivity was measured by the 4-point probe d.c. method.

EXPERIMENTAL

Materials

The same materials as those described in the previous paper were used for this work. Details of the materials are described elsewhere [13].

Synthesis of Poly(AAM-co-MAH)

2.13 g (0.03 M) of AAM and 2.94 g (0.03 M) of MAH were dissolved in 20 mL acetonitrile in a polymerization tube and 0.01 g (6.1×10^{-5} mol) AIBN was added to the stirred solution. The tube was sealed after charging with nitrogen, and polymerizations were carried out at 60°C for 48 hours. After reaction, the contents were poured into ethyl ether with stirring; the precipitate was filtered and dried in vacuo to constant weight. The conversion was 59% [13].

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

To a stirred solution of 1 g of the poly(AAm-co-MAH) in 100 mL DMF was slowly added 8.2 g POCl₃, and the reaction was carried out at 0°C for 24 hours. After reaction, the product was precipitated in a tenfold excess of toluene with stirring for 120 minutes and dried under vacuum.

Heat Treatment

The precursor poly(AAm-co-MAH) was subjected to heat treatment in a vacuum oven under various time and temperatures before or after reaction with POCl₃ treatment. In one experiment the polymer was treated with heat for a given period, from 8 to 24 hours, at 180°C. In another experiment the polymer was treated with heat for 8 hours at different temperatures, ranged from 60 to 180°C.

Measurements

Infrared (IR) spectra were obtained using a Perkin-Elmer 1330 spectrophotometer. The electric conductivity was measured by using the standard four-probe technique on pressed pellets mounted on gold electrodes, as described elsewhere [13].

RESULTS AND DISCUSSION

Solubility

All of the POCl₃-treated poly(AAm-co-MAH)s were readily soluble in DMSO and *N,N'*-dimethylformamide but only slightly soluble in acetone and methanol. Such good solubility might come from the polar properties of the carbonyl groups in both maleic anhydride and acrylamide of the copolymer. The solubilities of the POCl₃-treated copolymers, however, became poorer when they were subjected to heat treatment. Tables 1 and 2 show the effects of heat treatment on the solubilities of poly(AAm-co-MAH) before and after reaction with POCl₃, respectively.

It is seen that the solubilities of POCl₃-treated poly(AAm-co-MAH) become slightly poorer when their precursor polymers are annealed at higher temperatures for a given period or for longer periods at a given temperature before being treated with POCl₃. The solubilities of the POCl₃-treated poly(AAm-co-MAH)s become much poorer, however, when they are annealed at higher temperatures for a fixed time or for longer periods at a constant temperature after being reacted with POCl₃. It is pertinent to note that the effect of heating conditions, especially the heating temperature, is very large for POCl₃-treated poly(AAm-co-MAH)s. The structural changes during heat treatment for the precursor copolymer both before and after being reacted with POCl₃ will be discussed later.

Conductivity

Figure 1 shows that the effect of heating temperature for the precursor polymer before being reacted with POCl₃ on the conductivities of the polymer after being reacted with POCl₃. The polymer was treated with heat for 8 hours. The

TABLE 1. Effect of Heat Treatment on the Solubility of POCl₃-Treated Poly(AAm-co-MAH) When the Polymer Was Treated with Heat before Having Reacted with POCl₃

Heating temperature (°C) or heating time (h)	Solvent ^a						
	THF	Benzene	DMF	MeOH	DMSO	H ₂ O	Acetone
No heating	○	×	●	○	●	×	○
60°C ^b	×	×	○	×	○	×	×
100°C ^b	×	×	○	×	○	×	×
140°C ^b	×	×	○	×	○	×	×
180°C ^b	×	×	○	×	○	×	×
8 h ^c	×	×	○	×	○	×	×
16 h ^c	×	×	○	×	○	×	×
24 h ^c	×	×	○	×	○	×	×

^a ● = very soluble, ○ = soluble, × = insoluble.

^b Heating POCl₃-treated polymer for 8 hours at a given temperature.

^c Heating POCl₃-treated polymer at 180°C for a given time.

TABLE 2. Effect of Heat Treatment on the Solubility of POCl₃-Treated Poly(AAm-co-MAH) When the Polymer Was Treated with Heat after Having Reacted with POCl₃

Heating temperature (°C) or heating time (h)	Solvent ^a						
	THF	Benzene	DMF	MeOH	DMSO	H ₂ O	Acetone
No heating	○	×	●	○	●	×	○
60°C ^b	×	×	●	×	○	×	×
100°C ^b	×	×	◐	×	○	×	×
140°C ^b	×	×	◐	×	◐	×	×
180°C ^b	×	×	◐	×	◐	×	×
8 h ^c	×	×	○	×	○	×	×
16 h ^c	×	×	◐	×	○	×	×
24 h ^c	×	×	◐	×	◐	×	×

^a ● = very soluble, ○ = soluble, ◐ = slightly soluble, × = insoluble.

^b Heating POCl₃-treated polymer for 8 hours at a given temperature.

^c Heating POCl₃-treated polymer at 180°C for a given time.

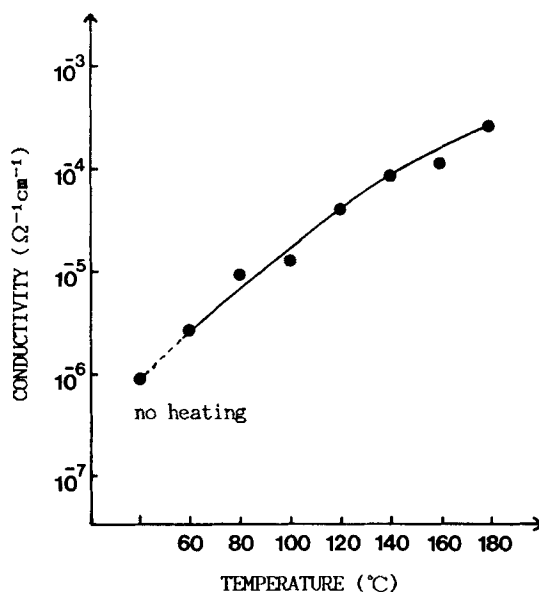


FIG. 1. Effect of heat treatment temperature on the conductivity of POCl_3 -treated poly(AAm-co-MAH) when the polymer was treated with heat before being reacted with POCl_3 .

conductivity increased as the temperature of heat treatment increased. Figure 2 shows the conductivity change of the POCl_3 -treated poly(AAm-co-MAH) as a function of heating time at 180°C for the precursor copolymer before being reacted with POCl_3 . The conductivity showed a maximum at 16 hours but the orders of magnitude were not much different with different heating temperatures.

Of great significance is the effect of heat treatment of the POCl_3 -treated copolymer after being reacted with POCl_3 on the conductivities. The conductivities of the polymer when treated with heat after being reacted with POCl_3 at various temperatures for 8 hours are shown in Fig. 3. The conductivity increased up to 100°C but thereafter decreased with a further rise in heating temperature.

Figure 4 represents the conductivity of the precursor copolymer when it is heated after being reacted with POCl_3 for a given time at 180°C . The effect of heat treatment time on conductivity was very significant, and the conductivity showed a maximum at 8 hours but thereafter decreased drastically with any further increase of heating time.

The results, shown in Figs. 1 through 4, imply that the conductivities of the polymer are affected more severely when it is treated with heat after being reacted with POCl_3 than before being reacted with POCl_3 . It may be assumed that these results are closely related to the structural changes of the polymer due to heat treatment.

Structural Change Due to Heat Treatment

Figure 5 shows the effect of structural change on the IR spectra of the POCl_3 -treated polymer when the precursor polymer has been treated with heat at two

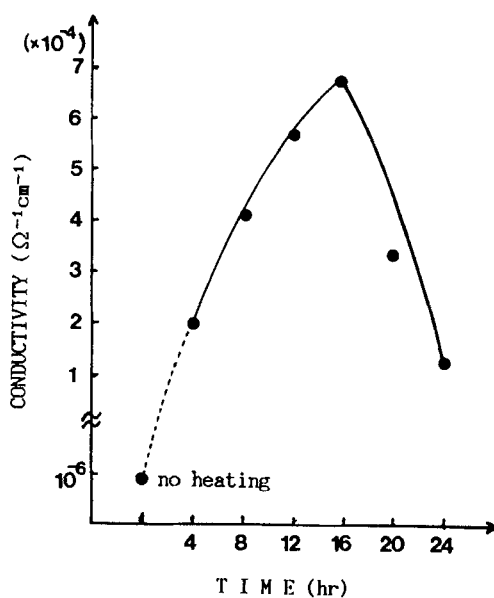


FIG. 2. Effect of heat treatment time on the conductivity of POCl_3 -treated poly(AAm-co-MAH) when the polymer was treated with heat before being reacted with POCl_3 .

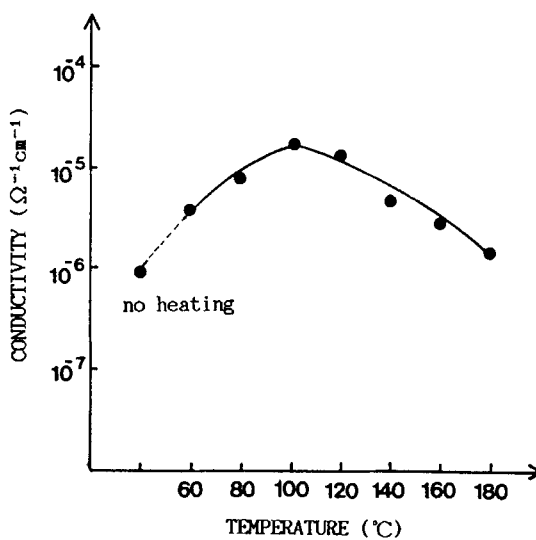


FIG. 3. Effect of heat treatment temperature on the conductivity of POCl_3 -treated poly(AAm-co-MAH) when the polymer was treated with heat after being reacted with POCl_3 .

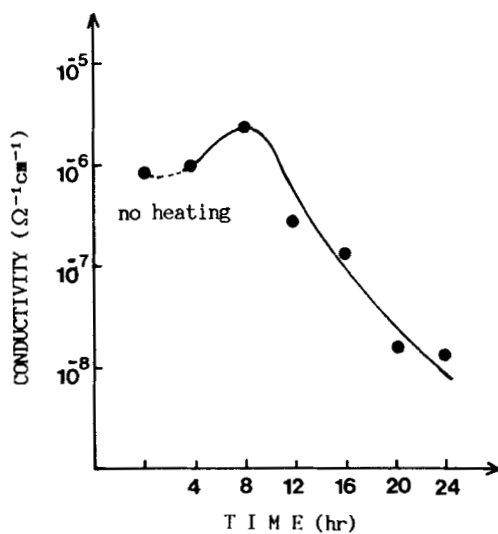


FIG. 4. Effect of heat treatment time on the conductivity of POCl_3 -treated poly(AAm-co-MAH) when the polymer was treated with heat after being reacted with POCl_3 .

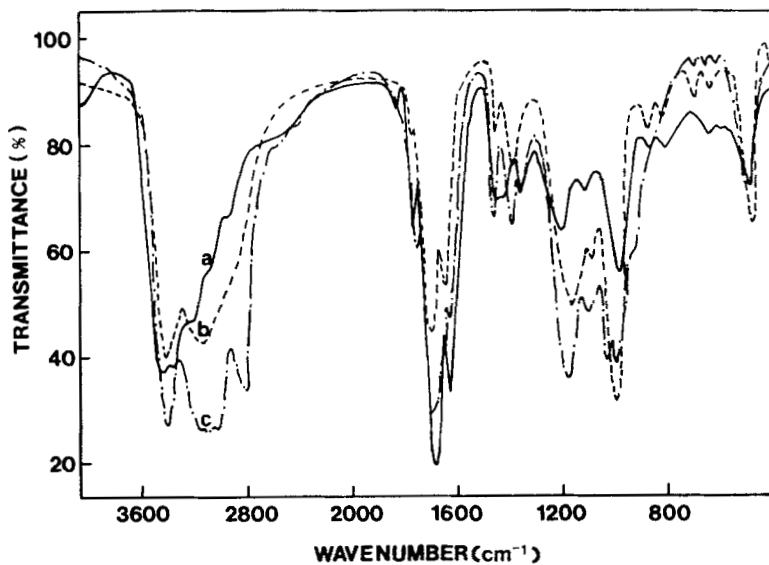
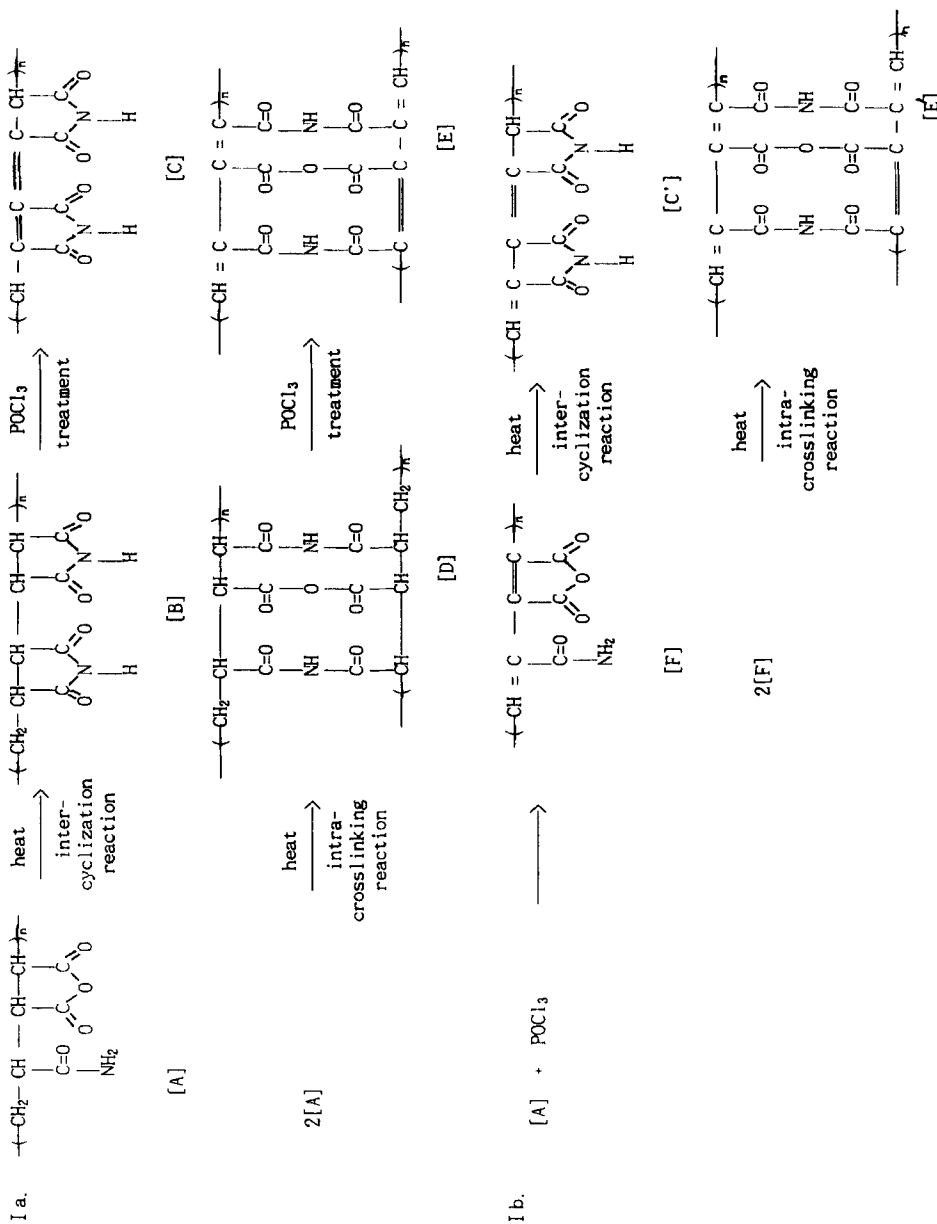


FIG. 5. Effect of heat treatment temperature on the IR spectra of POCl_3 -treated poly(AAm-co-MAH) when the polymer was treated with heat after being reacted with POCl_3 ; (a) no heating; (b) heated at 60°C ; (c) heated at 180°C .

different temperatures, 60 and 180°C, after being reacted with POCl₃. In this figure the IR spectrum of the POCl₃-treated polymer without heat treatment is also shown. One can see that the characteristic peak with a shoulder due to NH₂ at 3000 cm⁻¹ disappears and is replaced by new single peaks due to NH at 3300 cm⁻¹, and that the peaks due to the C=C double bond have almost disappeared when the polymer has been treated with heat at high temperatures. This means that significant structural change occurred when the POCl₃-treated poly(AAm-co-MAH) was treated with heat. The structural change was more clearly observed when the polymer was treated with higher temperatures. There is no doubt that this structural change affects the solubility and the conductivity of the polymer.

The structural change may occur by the following sequence (although more precise research should be conducted): When the polymer is heated above a certain temperature (here 100°C) for a given time (8 hours), the NH₂ groups in the polymer are transformed into NH groups by intercyclization or intracrosslinking reactions of amino and anhydride groups in the polymer. The formation of cyclic or crosslinked polymers improves the coplanarity of conjugated double bonds in the polymer backbone, while the polymers before heat treatment possess dangling side chains, which disturb the planarity of the polymer backbone. It is suggested that the increase in conductivity as well as the decrease in solubility with increasing heat treatment temperature are believed to be partly due to the improved coplanarity of the conjugated double bonds. Scheme 1 summarizes the postulated structural changes of the precursor polymers before (a) and after (b) POCl₃ treatment when they are subjected to heat treatment. It may be assumed that the final structure is given in the same form for both precursor polymers (see the structures C and C' or E and E'). Evans [18] explained that a number of factors which affect the conductivity of a conducting polymer can be explained in terms of steric interactions which affect the conjugation of the π -system, i.e., by disrupting the planarity of the polymer backbone and affecting the degree of orbital overlap. Diaz et al. [19], for example, found that alkyl substituents at the *N*-position cause lower conductivity values for *N*-alkyl-substituted polypyrrole relative to polypyrrole due to the steric effects disturbing the planarity of the polymer backbone and destabilizing the changed form of the material. When the polymer is heated beyond a critical temperature, however, the conducting polymer is subjected to thermal degradation and the C=C double bond is scissored to a slight degree. The conductivity decreases with any further increase in the temperature of heat treatment. The TGA curve of POCl₃-treated poly(AAm-co-MAH) in Fig. 6 proves our speculations. It can be seen that the polymer is thermally degraded from around 100°C, implying that CO₂ is eliminated from the polymer by thermal degradation. The trend is similar when the polymer is treated with heat for longer periods at a higher temperature (180°C).

Figure 7 shows the IR spectra of the precursor polymer when it has been treated with heat at two different temperatures, 60 and 180°C, before being reacted with POCl₃. When the precursor polymer was heated at a higher temperature before POCl₃ treatment, the characteristic dual bond absorption (a) of NH₂ at 3400 cm⁻¹ was lost and replaced with a new band due to NH around 3400 cm⁻¹. The result is also ascribed to structural changes of the precursor polymer due to heat treatment. However, the structural change was relatively smaller than what was observed when the precursor polymer was treated with heat after being reacted with POCl₃ at the same conditions of heat treatment.



SCHEME 1. Possible structural change due to heat treatment for the poly(AAm-co-MAH) before (a) and after (b) POCl₃ treatment.

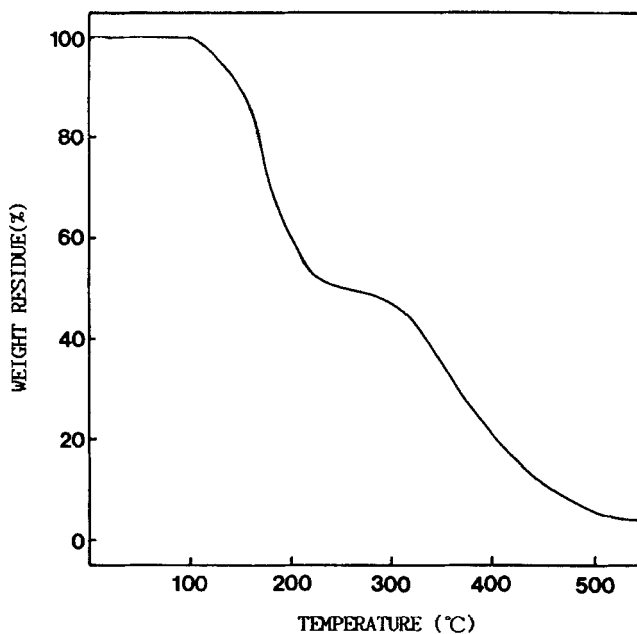


FIG. 6. TGA curve of the POCl₃-treated poly(AAm-co-MAH).

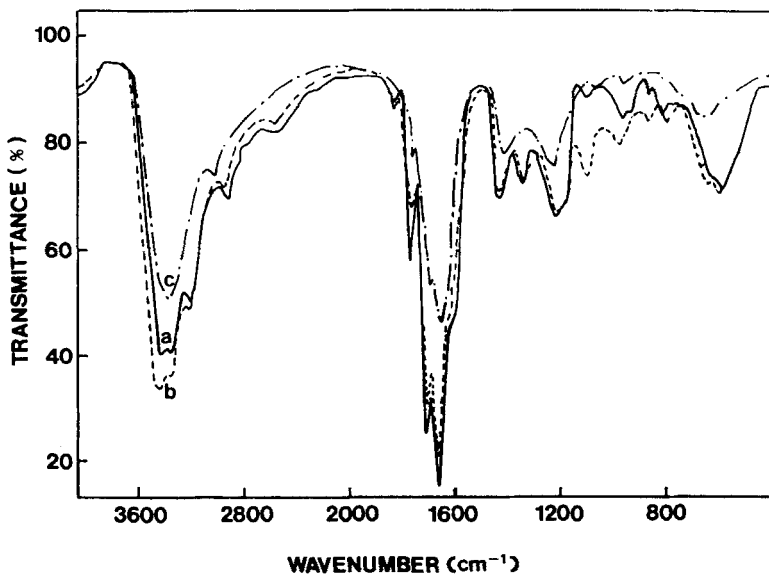


FIG. 7. Effect of heat treatment temperature on the IR spectra of POCl₃-treated poly(AAm-co-MAH) when the polymer was treated with heat before being reacted with POCl₃: (a) no heating; (b) heated at 60°C; (c) heated at 180°C.

CONCLUSIONS

In this work a copolymer of acrylamide (AAM) and maleic anhydride (MAH) [poly(AAM-co-MAH)] was reacted with phosphorus oxychloride to obtain an electrically conductive polymer. The effect of heat treatment on poly(AAM-co-MAH) before or after being reacted with POCl₃ on their electric conductivity was investigated. The copolymer both before and after POCl₃ treatment was subjected to heat for various time periods (8–24 hours) at 180°C or for 8 hours at different temperatures (60–180°C). It was found that the conductivities of POCl₃-treated poly(AAM-co-MAH)s increased with rising heat treatment temperatures when the precursor copolymer was subjected to heat treatment before POCl₃ treatment. They went through a maximum at 100°C when the copolymer was subjected to heat treatment after POCl₃ treatment. The effect of heat treatment time on the conductivities of POCl₃-treated poly(AAM-co-MAH)s was not significant for the precursor copolymer, but the effect was observed to be significant when the copolymer was subjected to heat treatment after POCl₃ treatment. The conductivities showed a maximum at 8 hours but thereafter decreased drastically with any further increase in heating time. The solubilities of the POCl₃-treated poly(AAM-co-MAH)s became poorer as the heating time and temperature increased for the precursor polymer before POCl₃ treatment but did not change much with different heating conditions for the polymer after POCl₃ treatment. It was concluded that the effect of heat treatment on the conductivities of the POCl₃-treated poly(AAM-co-MAH)s was more prominent when the precursor polymer was treated with heat after being reacted with POCl₃, exhibiting significant structural change when subjected to heat, especially higher temperatures for a given period or for longer periods at constant temperature.

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Received January 14, 1994

Revision received March 28, 1994