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CHARACTERIZATIONS AND ELECTRIC CONDUCTIVITIES OF PHOSPHOROUS OXYCHLORIDE-TREATED POLYMERS CONTAINING METHYL VINYL KETONE

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ABSTRACT

Studies have been made on the characterizations and conductivities of poly(methyl vinyl ketone) (PMVK) and its copolymer with methyl methacrylate (poly(MVK-co-MMA)) after being reacted with phosphorus oxychloride ($POCl_3$). The $POCl_3$-treated polymers containing methyl vinyl ketone (MVK) were characterized by IR and UV spectroscopies to prove the structure of conjugated double bonds. The conductivities of all the MVK-containing polymers treated with $POCl_3$ were very low, ca.10^{-17} S/cm, in a vacuum regardless of the treatment time. The conductivities of the polymers when doped with iodine are in the range of the order of 10^{-4} to 10^{-6} S/cm. It was found that the conductivity of the $POCl_3$-treated copolymer is slightly lower than that of PMVK.

INTRODUCTION

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

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

Ogawa et al. [17, 18] reported the reaction of poly(alkyl vinyl ketone)s with active chlorides to obtain poly(acyl acetylene)s and the electric conductivities of the polymer films. They revealed that some of the films showed specific conductivities of up to the order of 10^{-2} S cm^{-1} when reacted with phosphorous oxychloride at 0°C. The result is noteworthy because the conductivity value is almost the same order as that of TCNQ complexes with ionene or pyridinium and relatively high enough for a semiconductor [19, 20]. However, it is still controversial whether the high conductivity is attributed to the intrinsic properties of the polymers. In this connection, the works of Ogawa et al. are not enough to explain systematically the conductivity of the poly(alkyl vinyl ketone)s reacted with phosphoryl chloride, and more fundamental experimental data are needed.

In this work, we report the electric conductivities of poly(methyl vinyl ketone) reacted with phosphorous oxychloride and discuss some differences in the results from those of Ogawa et al. It will be mentioned later that poly(methyl vinyl ketone) (PMVK), even though it was treated with $POCl_3$, showed very low conductivity in our work. We also prepared a copolymer of methyl vinyl ketone (MVK) and methyl methacrylate (MMA) and measured its conductivity. MMA was selected because the monomer contains the same CO group as in MVK. The polymers were reacted with $POCl_3$ under various treatment times. The electric conductivity was measured by four-point probe DC method.

For comparison, the conductivities of the $POCl_3$-treated polymers doped with iodine were also presented.

EXPERIMENTAL

Materials

Methyl vinyl ketone (MVK;Merck) was dehydrated with calcium chloride and fractionally distilled. 2,2′-Azobisisobutyronitrile (AIBN;Wako) was recrystallized from dehydrated ethanol. Methyl methacrylate (MMA;Wako) was purified by the standard procedure. Phosphorous oxychloride ($POCl_3$;Nakarai) was used without further purification. Tetrahydrofuran (THF;Baker) of HPLC grade was used as received. Solvents were purified prior to use by the standard methods.

Synthesis of Poly(methyl vinyl ketone) (PMVK)

0.37 *M* of MVK was dissolved in 100 mL of benzene in a polymerization tube and then added with $3.7 \times 10^{-5} M$ of AIBN. The tube was sealed after charging with nitrogen and the reaction was carried out at 50 ± 0.05°C. After 7 h, the contents were poured into methanol with stirring; the precipitate was filtered and dried in vacuo to constant weight. Identification of the resulting polymer was conducted by IR spectrophotometer (Perkin-Elmer 1330).

Synthesis of Poly(MVK-co-MMA)

The copolymer poly(methyl vinyl ketone-co-methyl methacrylate) (Poly(MVK-co-MMA)) was prepared by reacting a mixture of MVK and MMA dissolved in 50 mL of benzene with 0.01 g of AIBN by the same method described for preparation of PMVK.

Reaction of PMVK with $POCl_3$

The PMVK was treated with $POCl_3$ according to the method of Ogawa et al. [18] with slight modifications. One gram of PMVK was dissolved in 100 mL of chloroform, 8.225 g of $POCl_3$ was added to 250 mL of a three-necked flask equipped with stirrer, gas inlet, and outlet, and the mixture was stirred in an ice bath for a specified time (12–72 h). After the reaction, the system was concentrated under vacuum and the reacted polymer was precipitated in petroleum ether, washed rapidly with methanol, and dried in vacuum.

Analysis: Calculated for $(C_4H_4O)_n$: C, 70.58; H, 5.88%, Found: C, 70.37; H, 7.29%.

Reaction of Poly(MVK-co-MMA) with $POCl_3$

Poly(MVK-co-MMA) was treated with $POCl_3$ by the same method as described for PMVK, except that the treatment time was fixed at 60 h.

Doping with Iodine

Powder or pellets of the $POCl_3$-treated PMVK and copolymer samples were exposed to iodine vapor for 1.5–3.0 h at a pressure of 0.1 mmHg. Rectangular pellets were made by pressing 500 kg/cm^2 with a Caver Laboratory Press. The maximum uptake of iodine was determined by weighing the samples at periodic intervals until a constant weight was obtained.

Molecular Weight

The molecular weights of PVMK and poly(MVK-co-MMA) were determined by gel permeation chromatography (GPC) (Waters-Water-244). The measurements were conducted in THF and the apparatus was calibrated with PS standards. Intrinsic viscosity was measured at 20 ± 0.01°C with a Cannon-Fenske viscometer in THF.

Electric Conductivities

For measurement of conductivity, pellets (thickness; 200 μm) from the powdery samples were prepared by a pressure of 500 kg/cm^2. Gold electrodes were attached on both surfaces of the pellets together with 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

Characterizations

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 ketones)] and the regularity of the repeating unit. Thus, we used only one kind of PMVK or poly(MVK-co-MMA) with a given molecular weight in order to reduce any ambiguity or combined effects of the factors mentioned above in interpreting our results. In this study, the PVMK of weight-average molecular weight of 56,000 (intrinsic viscosity; 0.991 in THF at 20°C) was used for the reaction with $POCl_3$ and for the measurement of electric conductivity. Similarly, the molecular weight of the copolymer used was 51,000 (the intrinsic viscosity is 0.980 in THF at 20°C).

Table 1 shows the solubilities of the $POCl_3$-treated PMVKs with various treatment times in several polar solvents, such as chloroform, THF, *N,N'*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The PMVK treated for a short time (e.g., 5 h) with $POCl_3$ was completely soluble in common polar solvents, but the PMVKs treated for a long time (e.g., more than 72 h) were no longer soluble. As expected, the solubility of PMVK in those solvents was decreased with the treatment time. The result may be ascribed to the formation of more conjugated double bonds in the precursor polymer as the treatment time increases.

Figure 1 shows IR spectra of PMVK and PMVK treated with $POCl_3$ for 60 h. The IR spectrum of PMVK showed a characteristic absorption band at 2810 cm^{-1} (C—H) and 1660 cm^{-1} (C=O) (Fig. 1a), and it is seen from this spectrum that an absorption band due to the carbonyl group (b) became weak and a new peak at

TABLE 1. Solubility of Poly(methyl Vinyl Ketone)s Treated with $POCl_3$ for Various Periods of Time

Reaction time (h)	Solvents			
	Chloroform	THF	DMF	DMSO
5	a	a		
12	b	b	b	b
36	b	b	b	b
60	b	b	b	b
Poly(MVK-co-MMA)		b	b	

[a] Completely soluble.
[b] Slightly soluble.

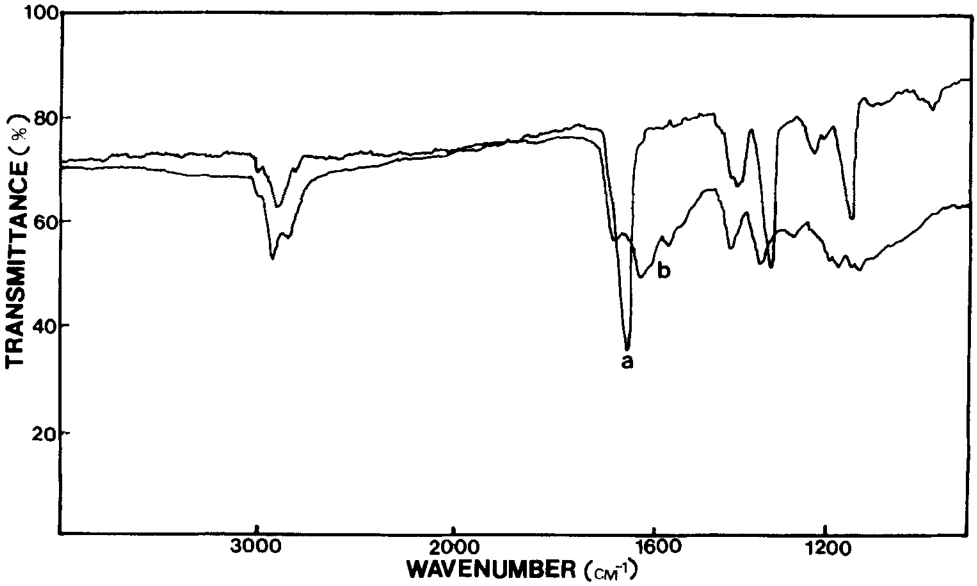


FIG. 1. IR spectra of KBr pellet of (a) PMVK and (b) $POCl_3$-treated PMVK for 60 h.

1616 cm^{-1} (C=C) appeared when PMVK was reacted with $POCl_3$ (Fig. 1b). This absorption is associated with the fact that the carbonyl groups might transform into conjugated groups. Similar results were also reported by Ogawa et al. We obtained UV and visible reflectance spectra to confirm the conjugation structure of the PMVK reacted with $POCl_3$. Figure 2 shows UV spectra of PMVK(a) and PMVK reacted with $POCl_3$ for 24 h in THF(b). The characteristic peak of PMVK 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 PMVK reacted with $POCl_3$. However, no peak was observed in the wavelength longer than 400 nm even for PMVK treated with $POCl_3$.

In Fig. 3, a visible reflectance spectrum of a PMVK pellet treated with $POCl_3$ for 72 h shows absorption of light as far as 600 nm. It may be assumed that the spectrum shown in Fig. 3 suggests that π-conjugation extends along the polymer chains [21].

Fig.4 shows IR spectra of poly(MVK-co-MMA) and $POCl_3$-treated poly(MVK-co-MMA) for 60 h. The IR spectrum of the copolymer without $POCl_3$ treatment showed characteristic absorption peaks at 2810 cm^{-1} (C—H), 1660 cm^{-1} (C=O), and 1201 cm^{-1} (C—O—C). And, when the copolymer was reacted with $POCl_3$, a new peak at 1616 cm^{-1} appeared, suggesting that the carbonyl groups were possibly transformed into conjugated diene groups. The spectral results of Figs. 1-4 confirm that a double-bond structure was successfully formed by the reaction of $POCl_3$ with the polymers containing methyl vinyl ketone.

Conductivity

The conductivity measurements were carried out in a vacuum of 10^{-3} torr by the four-point probe method. The conductivities of all the PMVK pellets treated with $POCl_3$ were very low, ca. 10^{-17} S/cm, regardless of the treatment time (Table

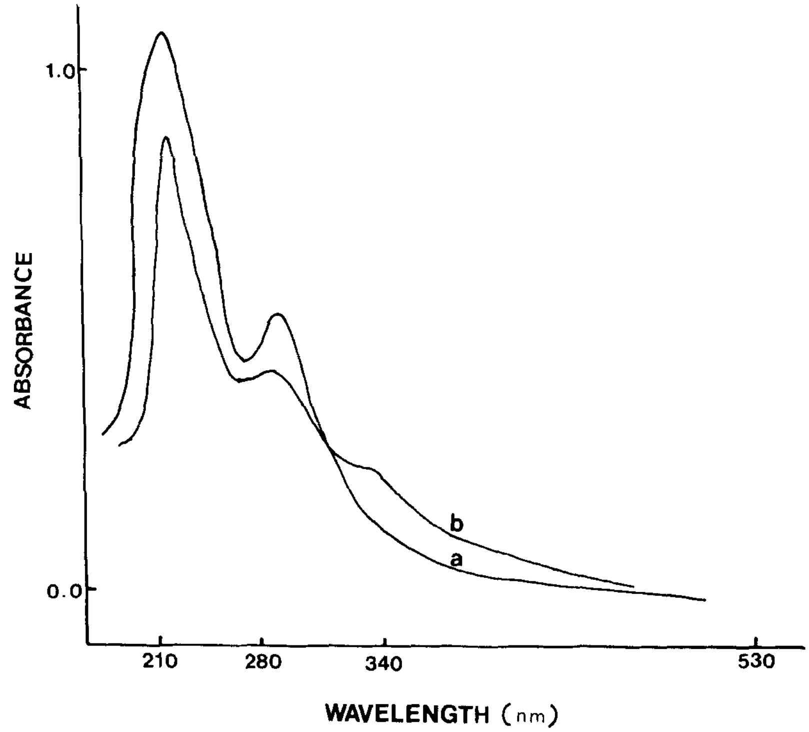


FIG. 2. UV spectra of poly(vinyl methyl ketone) (a) and poly (acetyl acetylene) (b) in THF. Reaction time 24h.

2). The results differed greatly from those reported by Ogawa et al. They measured the conductivities of samples by using alternating current in the solution or in air. The samples they measured were most likely doped with $POCl_3$. It should be pointed out that their high conductivities might not be intrinsic properties in the polymers. Of great importance is the fact that the measurement must be carefully carried out under a vacuum in order to determine the intrinsic conductivity of a sample. The conductivities of polymers containing conjugated structures are very sensitive to contamination. In fact, it was observed that the conductivities of the pellets were two to three orders of magnitude higher in air than in a vacuum. Similar results were also observed in case of $POCl_3$-treated poly(MVK-co-MMA).

The doping of conjugated polymers increases conductivity by oxidation or reduction with electron acceptors or donors, respectively. Among various dopants, iodine has been widely used [22]. Table 3 shows the conductivities of the powdery or pellet types of MVK-containing polymers, which were doped with iodine. It can be seen from this table that the highest value of 10^{-4} S/cm was achieved in some samples. However, no clear difference in conductivities of these doped samples was found. The conductivity decreased two or three orders of magnitude from the initial value after 24 h. This decrease of conductivity is attributable to the stability of the samples. It has been reported that the decreasing stability of conducting polymers exposed to air is due to oxidation, which increases with time [23, 24].

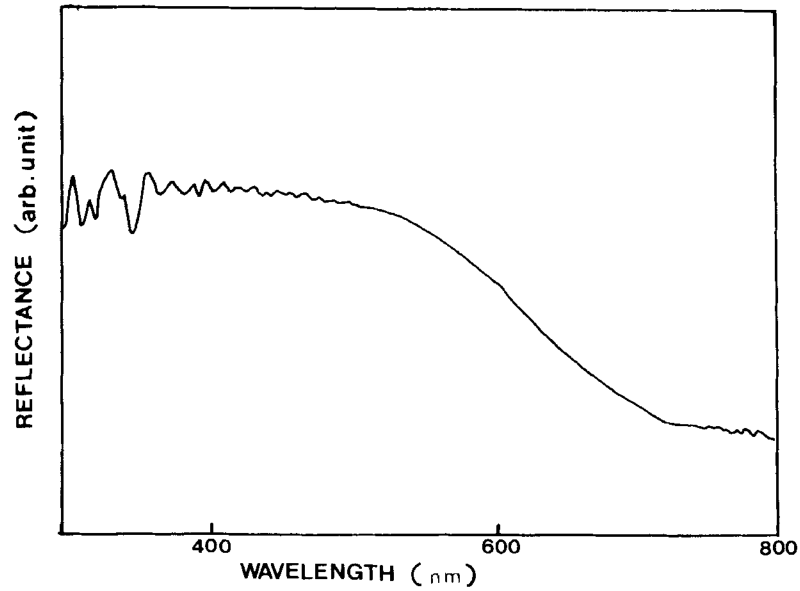


FIG. 3. Visible reflectance of pellet of PMVK treated with $POCl_3$ for 72 h. The reflectance was measured by using an integration sphere apparatus.

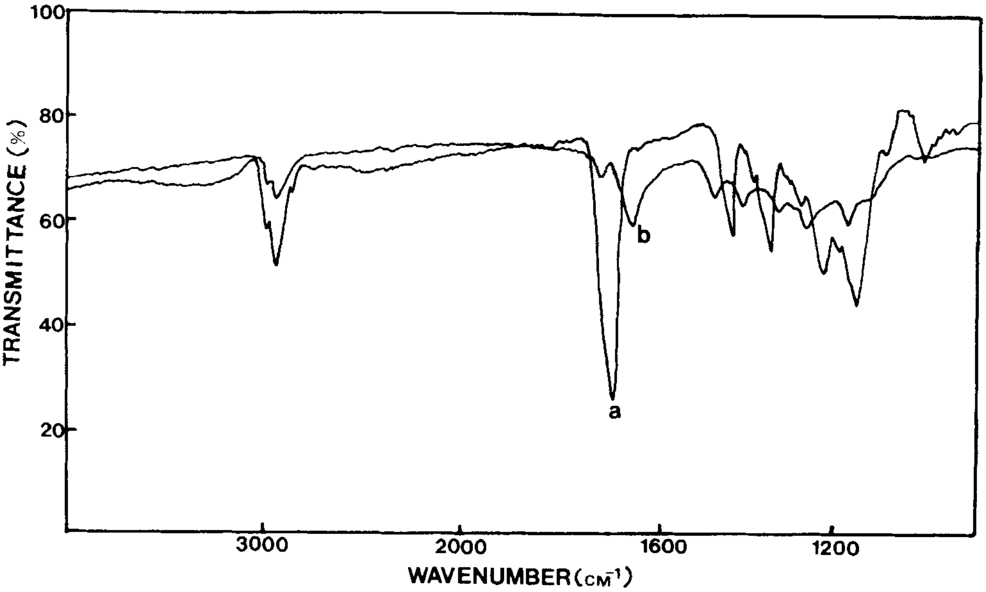


FIG. 4. IR spectra of KBr pellet of (a) poly(MVK-co-MMA) and (b) $POCl_3$-treated poly(MVK-co-MMA) for 60 h.

TABLE 2. Conductivities of PMVKs Treated with $POCl_3$ for Various Periods of Time

Reaction time (h)	Conductivity (S/cm)
12	1.5×10^{-17}[a]
	7.5×10^{-15} (in air)
36	1.6×10^{-17}[a]
60	2.9×10^{-17}[a]
72	1.5×10^{-17}[a]
	1.3×10^{-14} (in air)
Poly(MVK-co-MMA)	4.8×10^{-18}[a]

[a] In vacuum.

It was found that the conductivity of the powdery copolymer sample doped with iodine was slightly lower than that of PMVK doped with iodine under the same doping condition. The result may be due to the smaller content of conjugated diene in the copolymer than in PMVK homopolymer, which results in the less regular coplanar structure of the copolymer compared to PMVK.

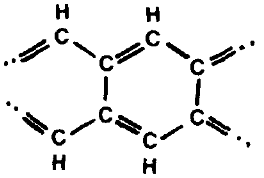
Finally, it should be stated that if one can synthesize polymer "1" from PMVK, the polymer must show a metallic conductivity in a nondoped state. Bredas et al. [25] reported that polymer 1 "polyacene" was no band gap, low ionization potential and wide band width. Synthesis of the polymer having structure 1 has not yet been attempted. Further studies on this subject are now underway and will be reported in the near future.

TABLE 3. Conductivities of Samples Doped with Iodine

Reaction time (h)	Conductivity (S/cm)	Doping method
12	1.8×10^{-4}(1)[a]	a
36	1.3×10^{-5}	a
	2.3×10^{-4} (0.45)	b
60	1.2×10^{-5}	a
	1.3×10^{-5}	b
72	2.4×10^{-4}(2)[a]	a
Poly(MVK-co-MMA)	3.0×10^{-6}	a

[a] Conductivity decreased to (1) 7×10^{-6} S/cm and (2) 2.4×10^{-5} S/cm after 24 h.

Doping was carried out in (a) powder and (b) pellet. ( ); Moles of I_2 per structural unit.



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CONCLUSIONS

In this article, we characterized poly(methyl vinyl ketone) and its copolymer with methyl methacrylate after being reacted with phosphorous oxychloride by IR and UV spectroscopies. We measured the conductivities of the polymers containing methyl vinyl ketone by using the four-point probe DC method. The spectral studies showed that conjugate double bonds were formed by the reaction of those polymers with $POCl_3$ for PMVK and poly(MVK-co-MMA). The conductivities of all the PMVK pellets treated with $POCl_3$ were very low, ca. 10^{-17} S/cm, regardless of the treatment time, even though the conductivity of the polymers was closely related to the formation of double bond in polymer backbone by treatment with $POCl_3$. The solubility of the polymers in common polar solvents like chloroform and THF was decreased with increasing $POCl_3$ treatment time. The conductivity of the copolymer was slightly lower than that of PMVK.

It was found that the conductivities of $POCl_3$-treated MVK-containing polymers are in the range of the order of 10^{-5} S/cm when doped with iodine and are much higher than those of polymers containing MVK treated only with $POCl_3$, being in order of 10^{-17} S/cm. It was suggested that the high conductivity of the $POCl_3$ -treated PMVK reported by Ogawa et al. might not be an intrinsic property of PMVK.

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