Polymer (Korea) Vol. 16, No. 5, pp 563－569 (1992)

메틸비닐케톤을 포함하는 전구체 중합체들의 합성과 삼염화산소산인으로 처리했을 때의 전기전도도

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(1992년 5월 11일 접수)

Syntheses of Precursor Polymers Containing Methyl Vinyl Ketone and Their Electrical Conductivities on Being Treated with Phosphorous Oxychloride

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(Received May 11, 1992)

요 약 : 메틸비닐케톤(MVK)을 포함하는 중합체들을 합성하고 이들과 삼염화산소산인($POCl_3$)을 반응시켜 얻은 전도성고분자의 전기전도도를 측정하였다. 메틸비닐케톤(MVK)을 3가지 다른 농도의 AIBN을 개시제로 하여 benzene용매하에 50℃에서 7시간 각각 라디칼중합하여 얻은 중합체를 Cannon-Fenske 점도계로 측정한 중합체의 고유점도 [η]와 GPC로 얻은 중량평균분자량($\overline{M}_w$)으로부터 $[\eta]=7.7\times10^{-5}\overline{M}_w^{0.72}$와 같은 관계를 얻었다. 또한 4가지 다른 몰비(0.5~5.0[MVK]/[MA])의 메틸비닐케톤(MVK)과 메틸아크릴레이트(MA)를 AIBN을 개시제로 하여 50℃에서 라디칼 공중합하여 공중합체(poly(MVK-co-MA))를 합성하였다. 이 공중합반응에 대한 단량체 반응성비를 Kelene-Tüdös법으로 결정하였다 ; r_1(MVK)=1.85, r_2(MA)=0.99. PMVK와 poly(MVK-co-MA)를 0℃에서, 클로로포름하에서 $POCl_3$와 반응시켜 전도성고분자인 폴리(아세틸아세틸렌)유도체들을 얻었다. 이들 전도성고분자들은 THF 및 DMF에 용해되었으며 적외선 및 자외선 분광법에 의해 분자내 이중결합이 생성된 것을 확인하였다. 4-point probe DC방법으로 이들의 전도도를 측정한 결과 전구체고분자인 PMVK는 분자량이 증가할수록 또한 $POCl_3$와의 반응시간이 증가할수록 전도도는 증가하였는데 $10^{-7}\sim10^{-9}$ Scm^{-1} 정도의 값을 보였다. $POCl_3$와 반응시킨 공중합체의 경우는 PMVK에 비해 약간 낮은 값을 보였으며, 공중합체내 MA단위의 함량이 증가할수록 전도도는 감소하였다.

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Abstract : Electrical conductivities of polymers containing methyl vinyl ketone(MVK) on being treated with phosphorous oxychloride, were investigated. Poly(methyl vinyl ketone)(PMVK)s were synthesized with three different concentrations of AIBN in benzene at 50℃ ; Intrinsic viscosity(η) of PMVK measured with a Cannon-Fenske viscometer was correlated with weight-average molecular weight by GPC as the following Mark-Houwink-Sakurada relationship ; $[\eta]=7.7\times10^{-5}\overline{M}_w^{0.72}$. Four types of copolymers with MVK and methyl acrylate(MA), poly(MVK-co-MA)'s having different monomer feed ratios(0.5~5.0[MVK]/[MA]) were obtained by radical copolymerization with 3.7×10^{-4}M of AIBN at 50℃. The reactivity ratio of each monomer was determined by the Kelen-Tüdös method as follows ; r_1(MVK)=1.85, r_2(MA)=0.99. Poly(acetylacetylene) derivatives were obtained by reacting PMVK or poly(MVK-co-MA) with phosphorous oxychloride in chloroform at 0℃ under various reaction times. The conductive polymers were soluble in THF and DMF. The formation of double bond in the polymers was identified by IR and UV spectra. Their conductivities were measured by 4-point probe DC method. The conductivity of the poly(acetylacetylene) lay in the range of $10^{-7}\sim10^{-9}$ Scm^{-1} and increased with increasing molecular weight of PMVK and $POCl_3$ treatment time. It was found that the conductivity of the $POCl_3$-treated copolymer was slightly lower than that of PMVK and decreased with increasing MA content in the copolymers.

INTRODUCTION

The electrically conductive polymers have attracted much interests from theoretical and practical standpoints.[1~4] Among them, polyacetylene has been extensively studied because of its high electrical conductivity and ease of synthesis.[5~8] Polyacethylene is,however, unstable in air, is insoluble in the usual organic solvents, and decomposed before melting.

Therefore, studies of the syntheses and properties of substituted polyacetylene, polyarylenes or poly(arylenevinylene)s, etc. have been intensively made.[9~17] Ogawa et al.[18,19] reported on the reaction of poly(alkyl vinly ketone)s with active chlorides such as phosphoryl chloride to obtain the electrical conductive poly(acylacetylene) films.[18,19] The conductivities of polyacetylenes are dependent on the number of duble bonds such as the degree of polymerization of the starting material, poly(alkyl vinyl ketone) and the regularity of the repeating unit.

Of great importance is the fact that poly(methyl vinyl ketone)(PMVK) can be used as a precursor polymer to obtain a novel semiconductor material since it shows high conductivity on being treated with phosphoryl chloride or phosphorous oxychloride.[19] However, it is not clear as yet whether the high conductivity of PMVK reacted with active chlorides is inherent property of PMVK or not. Thus, more detailed studies on the characterization and electrical conductivities of homopolymer of methyl vinyl ketone(MVK) and its copolymers should be continued.

In this connection, we synthesized several PMVK's using 2,2'-azobisisobutylonitrile(AIBN) as an initiator at 50℃ and studied the effets of molecular weights of the precursor polymers on the electrical conductivities after being reacted with phosphorous oxychloride. We also prepared a copolymer with MVK and methyl acrylate(MA), (poly(MVK-co-MA)), by radical copolymerization and determined the monomer reactivity ratios by the Kelen-Tüdös method. We report their conductivities after being treated with phosphorus oxychloride and the effects of the compositions of the precursor copolymers on the conductivities. Electrical conductivity of the polymers was measured by 4-point probe DC method.

EXPERIMENTAL

Materials

Methyl vinyl ketone (MVK ; Merck) was dehydrated with calcium chloride and fractionally distilled. Methyl acrylate(MA ; Tokyo Kasei) was washed with 5% aqueous solution of sodium hydroxide two times and dehydrated with calcium chloride, followed by fractionally distillation. 2,2'-Azobisisobutylonitrile (AIBN ; Wako) was recrystallized from dehydrated ethanol and 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.

Preparation of Materials

Synthesis of poly(methyl vinyl ketone), PMVK

3.7M of MVK was dissolved in benzene and then added with three different concentrations of AIBN, ranged from 3.7×10^{-3} to 3.7×10^{-6} M, in polymerization tubes. The tubes were sealed after charging with nitrogen and polymerizations were carried out for 7 hrs at 50℃. After polymerization, the contents were poured into methanol with stirring ; the precipitates were filtered and dried in vacuo to constant weight. The polymers were identified by I.R. spectroscopy(Perkin-Elmer 1330).

Synthesis of Poly(MVK-co-MA)

The copolymer, poly(methylvinylketone-co-methylacrylate) (poly(MVK-co-MA)) was prepared by reacting a mixture of MVK and MA with 1.2×10^{-3} M of AIBN at 50℃ by the similar method described for preparation of PMVK, except the copolymerization was carried out in bulk. A series of copolymerizations, in which the feed ratios of MVK (M_1) to MA(M_2) were varied in the range of 0.5 to 5.0 by mol. %, yielded copolymers over a wide range of compositions. The copolymerizations were stopped before 10% conversion was reached.

Analysis of Copolymer Compositions

The copolymer composition was determined by using UV spectrophotometer(Shimadzu 200A). The specific absorptivities of polymers were measured at 288 nm in THF.

Treatment of Polymers with $POCl_3$

1 g of PMVK was dissolved in 100 ml of chloroform and 8.225 g of $POCl_3$ were added to a three-necked flask equipped with a stirrer, a gas inlet and outlet and the mixture was kept in an ice bath with stirring for a required time(5~72 hrs). 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.

Treatment of Poly(MVK-co-MA) with $POCl_3$

poly(MVK-co-MA) was treated with $POCl_3$ by the same method as described for PMVK, except that the treatment time is fixed at 60 hrs.

Measurements

Molecular weight : The molecular weights of PMVKs synthesized with various AIBN concentrations were determined by gel permeation chromatography(GPC)(Waters-244). The measurements were conducted in THF and the apparatus was calibrated with PS standards. Intrinsic viscosity was measured at 20± 0.01℃ with a Cannon-Fenske viscometer in THF.

Glass transition temperature(T_g) : T_g of PVMK was measured with differential scanning calorimetry(DSC)(Perkin-Elmer DSC 4). The heating rate was 10℃/min and the onset of heat jump in DSC thermogram was taken as T_g.

Electrical conductivities : For the 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 4-point probe DC method in a vacuum of 10^{-3} torr.

RESULTS AND DISCUSSION

Characterization of PMVK

The polymerization rate of MVK followed the one-half order kinetics for the initiator concentrations and first order kinetics for the monomer

concentrations.

The weight average molecular weights of PMVK's($\overline{M}_w$) ranged from 57,000 to 76,000(see Table 4). From the measurement of intrinsic viscosities(η) of the polymers, we can correlate it with the $\overline{M}_w$,obtained from GPC, as the following modified Mark-Houwink-Sakurada equation :

$$\eta = 7.7 \times 10^{-5} \overline{M}_w^{0.72}$$

The glass transition temperature of PMVK was given as 307°K. The T_g's of the copolymers with different monomer feed ratio ranged from 282°K to 307°K.

Monomer Reactivity in Poly(MVK-co-MA)

The copolymer composition in poly(MVK-co-MA) was analyzed by using UV spectroscopy. The UV spectra of PMVK and poly(methylacrylate) (PMA) in THF are shown in Fig. 1, where 288 nm is selected as the characteristic wavelength for analysis because PMA scarcely absorbs the light of the wavelength. The UV spectrum of a copolymer, poly(MVK-co-MA), was also shown in Fig. 1, for comparison. The copolymer sample has mole ratio of 3/1 [MVK]/[MA] in feed. The following equation was derived from the relationship between the specfic absorptivity of copolymer(k) and the weight fraction(x) of monomer unit in copolymer :

$$k = 0.112 + 1.102\,x$$

The copolymer compositions are listed in Table 1, along with other parameters necessary to obtain the reactivity ratios of each monomer by the Kelen-Tüdös method. From the Kelen-Tüdös plot, r_1 and r_2 values were determined as 1.85(MVK) and 0.99(MA), respectively.

Electrical Conductivity of PVMKs Treated with $POCl_3$

Table 2 shows the solubility of the PMVK's treated with $POCl_3$. In this case, the PMVK was synthesized with 3.7×10^{-4} M of AIBN and the copolymer, poly(MVK-co-MA) was synthesized with the mole ratio of 5/1 [MVK] to [MA] and treated with $POCl_3$ for 60 hrs. The solubility of PMVKs was tested in several polar solvents like chloro-

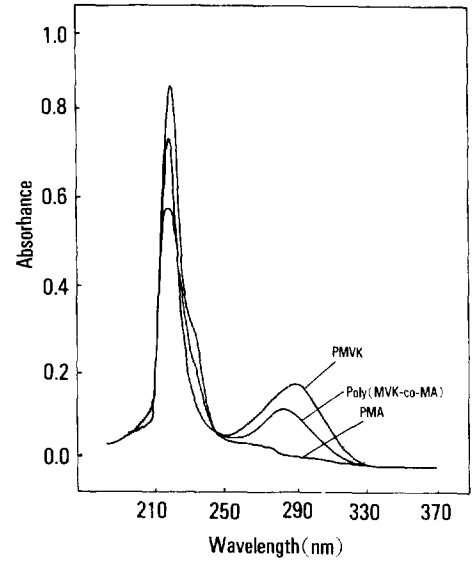

Fig. 1. UV spectra of poly(methyl vinyl ketone), poly (methylacrylate) and poly(methyl vinyl ketone-co-methylacrylate) in THF(3 mg/100 ml) : The copolymer sample has mole ratio of [MVK]/[MA]=3/1 in feed.

Table 1. Determination of Monomer Reactivity Ratios for the Copolymerization of MVK(M_1) and MA(M_2) with AIBN at 50°C [AIBN]=1.2×10^{-3} M, $\alpha = 1.09$

Exp. No.	$X = M_1/M_2$	$Y = m_1/m_2$	X^2	$Y-1$	$F = X^2/Y$	$G = \frac{X(Y-1)}{Y}$	$\alpha+F$	$\eta = G/(\alpha+F)$	$\xi = F/(\alpha+F)$
1	5.06	8.61	25.57	7.61	2.97	4.47	4.06	1.10	0.73
2	3.00	4.89	9.01	3.89	1.84	2.39	2.93	0.82	0.63
3	1.00	1.51	1.01	0.51	0.67	0.34	1.76	0.19	0.38
4	0.50	0.62	0.25	−0.38	0.40	−0.30	1.49	−0.20	0.27

r_1(MVK)=1.85, r_2(MA)=0.99 ; $\alpha = \sqrt{F_{min} \times F_{max}}$.

Table 2. Solubility of PMVKs Treated with $POCl_3$

Treatment time(hr)	Solvents			
	Chloroform	THF	DMF	DMSO
5	++	++		
12	+	+	+	+
36	+	+	+	+
60	+	+	+	+
poly(MVK-co-MA)*		+	+	

++ completely soluble + slightly soluble

* The copolymer was treated with $POCl_3$ for 60 hrs. In this case, the copolymer with monomer feed ratio of 5/1(by mol. %) [MVK]/[MA] was used.

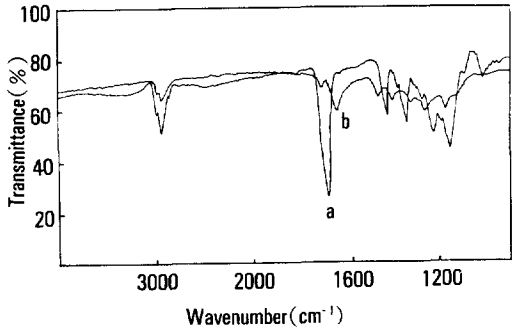

Fig. 2. IR spectra of (a) PMVK and (b) PMVK treated with $POCl_3$ for 60 hrs.

form, THF, 2,2'-dimethylformamide(DMF) and dimethyl sufoxide(DMSO). The PMVK treated with $POCl_3$ for short time was completely soluble in common polar solvents but the PMVK's treated for long time were no longer soluble. As expected, the solubility of PMVK in those solvents decreased with the treatment time.

Fig. 2 shows IR spectra of PMVK(a) and PMVK treated with $POCl_3$ for 60 hrs(b). The absorption band(b) at 1626 cm^{-1} is due to a double bond formed when PMVK was treated with $POCl_3$. Similar result was also reported by Ogawa, et al.[18] UV spectra were obtained to confirm the conjugated double bond of the PMVK treated with $POCl_3$. Fig. 3 shows UV spectra of PMVK(a) and PMVK treated with $POCl_3$ for 24 hrs in THF(b). The characteristic peak of PMVK was observed at 290 nm in

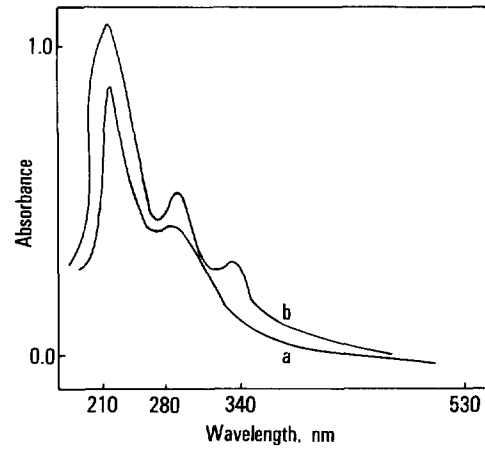

Fig. 3. UV spectra of (a) PMVK and (b) PMVK treated with $POCl_3$ for 24 hrs.

Table 3. Conductivities of PMVKs Treated with $POCl_3$*

Treatment time(hr)	Conductivity (S/cm)
12	1.60×10^{-9}
24	2.96×10^{-9}
36	4.17×10^{-9}
48	1.16×10^{-8}
60	5.30×10^{-7}
72	5.70×10^{-7}
poly(MVK-co-MA)**	8.67×10^{-8}

* The PMVK used were synthesized with 3.7×10^{-4} M of AIBN.

** The copolymer was treated with $POCl_3$ for 60 hrs. In this case, the copolymer with monomer feed ratio of 5/1(by mol. %) [MVK]/[MA] was used. The molecular weight of the copolymer was 59,000.

both cases but a new peak was observed in the longer wavelength region around 340 nm in the case of PMVK treated with $POCl_3$. It may be assumed that the spectrum shown in Fig. 3 suggests that π-conjugation extends along the polymer chains.[20]

The conductivities of all the PMVK treated with $POCl_3$ lay in the range of ca.$10^{-7}\sim10^{-9}$ Scm^{-1}, as shown in Table 3. It was observed that the conductivities were increased with increasing treat-

Table 4. Effect of Molecular Weight of PMVK on the Conductivities

AIBN Concentration [M]	Molecular weight[a] M_n	M_w	Conductivity[b] (S/cm)
3.7×10^{-6}	53,000	76,000	4.70×10^{-7}
3.7×10^{-4}[c]	48,000	64,000	1.16×10^{-8}
3.7×10^{-3}	40,000	57,000	1.55×10^{-9}

[a] Measured by GPC

[b] PMVK was treated with $POCl_3$ for 48 hrs.

[c] This PMVK sample was used to investigate the effect of $POCl_3$ treatment time in Table 3.

ment time with $POCl_3$, due to the formation of more conjugated double bonds. In this case, the PMVK were synthesized with 3.0×10^{-4} M of AIBN. Table 3 also shows that the conductivity of the $POCl_3$-treated copolymer is slightly lower than those of $POCl_3$-treated PMVK's. The result may be due to the less contents of conjugated diene in the copolymer than that in PMVK homopolymer, which results in the less regular coplanar structure of the copolymer compared with PMVK. In this Table, the copolymer with monomer feed ratio of 5/1(by mol. %) [MVK]/[MA] was treated with $POCl_3$ for 60 hrs. The molecular weight of the copolymer was 59,000(The intrinsic viscosity is 0.982 in THF at 20℃).

The effect of molecular weight of PMVK, as a precursor polymer to obtain a conductive polymer on being treated with $POCl_3$, is summarized in Table 4. In Table 4, the PMVKs were synthesized with three different AIBN concentrations and the PMVKs were treated with $POCl_3$ for 48 hrs in THF. The molecular weights of PMVKs decreased with increasing AIBN concentration. One can see that the PMVKs with larger molec ular weight exhibit higher electrical conductivities on being treated with $POCl_3$ under the same treatment condition.

Electrical Conductivity of Poly(MVK-co-MA) Treated with $POCl_3$

Fig. 4 shows IR spectra of poly(MVK-co-MA) and poly(MVK-co-MA) treated with $POCl_3$ for 60 hrs. The IR sepctrum of the copolymer untreated

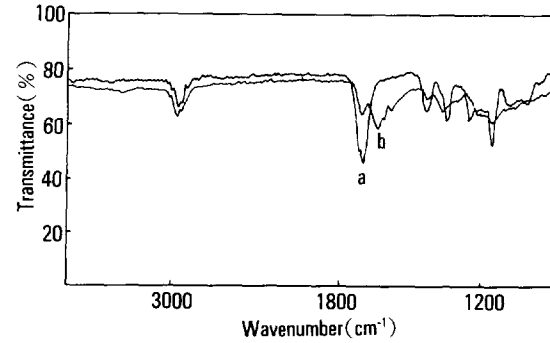

Fig. 4. IR spectra of (a) poly(MVK-co-MA) and (b) poly(MVK-co-MA) treated with $POCl_3$ for 60 hrs.

Table 5. Effect of Mole Ratio of [MA] to [MVK] on the Conductivities of $POCl_3$-treated poly(MVK-co-MA)*

Mole Ratio of [MVK]/[MA] in feed	in copolymer	Conductivity (S/cm)
5.06	8.61	8.67×10^{-8}
3.00	4.89	5.20×10^{-9}
1.00	1.51	1.02×10^{-9}
0.50	0.62	7.30×10^{-10}

* The copolymer was treated with $POCl_3$ for 60 hrs.

with $POCl_3$ shows characteristic absorption peaks at 2810cm^{-1}(C-H), 1660cm^{-1}(C=O) and 1201cm^{-1} (C-O-C). Meanwhile, when the copolymer was treated with $POCl_3$ a new peak at 1616 cm^{-1} appears, meaning again that the conjugate double bond was formed.

Table 5 shows the effect of mole ratio of [MVK] /[MA] on the conductivity of the $POCl_3$-treated poly(MVK-co-MA). The precursor copolymer was reacted with phosphorous oxychloride at 0℃ for 60 hrs. It is seen that the conductivity decreases with decreasing mole ratio of [MVK] to [MA].

CONCLUDING REMARKS

In this work, poly(methyl vinyl ketone) was synthesized by using 2,2'-azobisisobutylonitrile(AIBN) as an initiator in benzene at 50℃. A copolymer of MVK and MA was also prepared by radical copolymerization at 50℃. Molecular weights of poly (methyl vinyl ketone)(PMVK) were measured by

the Cannon-Fenske viscometer and GPC. Plot of intrinsic viscosity(η) versus $\bar{M}_w$ on a double logarithmic graph indicated the following Mark-Houwink-Sakurada relationship ; $[\eta]=7.7\times10^{-5}\bar{M}_w^{0.72}$. In the copolymerizaion of MVK and MA, the reactivity ratio of each monomer was determined by the Kelen-Tüdös method as follows ; r_1(MVK) = 1.85, r_2(MA) = 0.99. Poly(acetylacetylene)s were obtained by the reactions of PMVK or poly(MVK-co-MA) with phosphorous oxychloride in chloroform at 0℃ under various reaction time. Conductivity of samples was measured by 4-point probe DC method. The conductivities of the poly(acetylacetylene) derivatives lay in the range of $10^{-7}\sim10^{-9}$ Scm^{-1} and increased with increasing molecular weight of PMVK and $POCl_3$ treatment time. It was found that the conductivity of the $POCl_3$-treated copolymer was slightly lower than that of PMVK. Their conductivities decreased with decreasing mole ratio of [MVK] to [MA].

Finally, it should be mentioned that the conductivity would be sensitive to the unreacted $POCl_3$ remaining in final conductive polymers, if any. It was observed that the effect of traces of unreacted $POCl_3$ in the final product on the conductivity is negligible if the product is washed with excess methanol for 120 min or longer.[21] The amount of the $POCl_3$ residues after washing for 120 min in the product was anlyzed by ^{31}P-NMR spectroscopy. In fact, the amount of remaining $POCl_3$ was extremely small, ca. 0.000030 g.(Note that the amount of initial $POCl_3$ before reaction was 8.225 g).

Acknowledgements : We wish to express our sincere thanks to Prof. S. Saito, Graduate School of Engineering Sciences, Kyushu University, Japan, for his help in measuring conductivities of samples and for his valuable comments on the experimental results. This work was financially supported by the Korea Science and Engineering Foundation.

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