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The Electric Conductivity of Poly(Ethyl Vinyl Ketone) Film Reacted with Phosphoryl Chloride

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SUMMARY

The reaction of poly(ethyl vinyl ketone) with active chlorides in petroleum ether was followed by the electric conductivity measurement. Phosphoryl chloride was found to be an effective reagent to produce a highly conjugated system with an apparent specific conductivity of the order of $10^{-2}\,\Omega^{-1}cm^{-1}$ in petroleum ether. The reaction temperature seems to be important for the electric conductivity of the product, the higher the reaction temperature, the lower the electric conductivity of the reacted film.

INTRODUCTION

Previously(1) we have reported the formation of poly(acyl acetylene) derivatives by the reaction of poly(alkyl vinyl ketone)s with active chlorides such as phosphoryl chloride, at room temperature. It was found that the reaction product from poly(methyl vinyl ketone) had an apparent specific electric conductivity of the order of about $10^{-5}\,\Omega^{-1}\,cm^{-1}$, when reacted at room temperature in solution or in the form of a film in non-solvent. In this paper, the changes in the electric conductivity of poly(ethyl vinyl ketone) film during the reaction, are reported.

EXPERIMENTAL

Materiala: Ethyl vinyl ketone (EVK) was prepared by the following reaction(2):

$$CH_3CH_2COCl \;+\; CH_2{=}CH_2 \xrightarrow[\text{in } CHCl_3]{AlCl_3} CH_3CH_2COCH_2CH_2Cl$$

$$\xrightarrow{\text{diethylaniline}} CH_3CH_2COCH{=}CH_2$$

EVK thus obtained was purified by distilling twice under a reduced pressure, and polymerized in bulk at 60° using 2,2'-azobisisobutyronitrile as an initiator. The poly(EVK) was purified by reprecipitaing from a chloroform-petroleum ether system. The intrinsic viscosities of poly(EVK) used for the reaction were o.25 and 0.50. A

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chloroform solution of poly(EVK) was then cast on a mercury surface and the film was dried at room temperature. The films used had a thickness of about 0.2 - 0.4 mm.

The reaction and electric conductivity measurement: A small piece of the poly(EVK) film, 5 x 8 mm, was connected to thin gold wires or tapes using a colloidal carbon "Aquadaq" as an adhesive, and the glass apparatus shown in Fig. 1 was used for the reaction and conductivity measurement(a four-probe method). The electric conductivity was measured by both

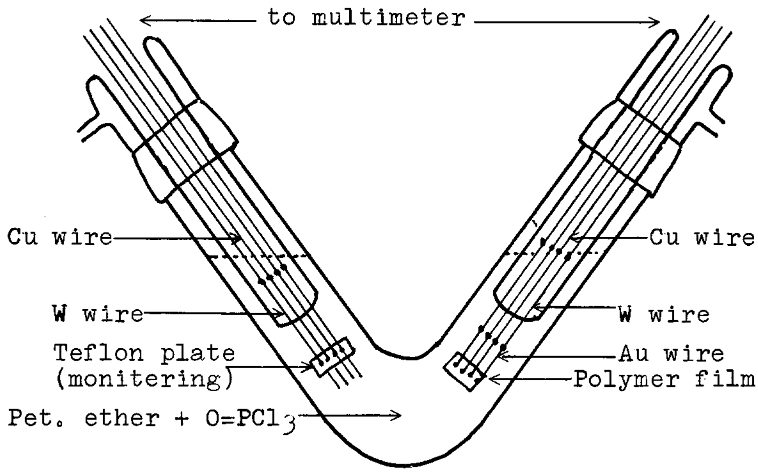

Fig.1. Apparatus for the reaction and conductivity measurement.

DC and AC, but because of polarization in the case of DC, most measurements were carried out with AC of less than 20 Hz, but there was no significant difference in data between the measurements with DC and AC.

In the apparatus shown in Fig. 1, were placed dried petroleum ether and a required amount of active chloride, and the apparatus was mounted in a constant temperature bath. It was found that there was only negligible conductivity at the reference side during the reaction, and therefore monitoring was found to be not necessary for this non polar system.

RESULTS AND DISCUSSION

Fig. 2 shows the changes in the electric conductivities with reaction time. The conductivity increased rapidly over the first few hours but after about 10 hours it levelled out, and started to decrease slightly. The maximum conductivity was about $10^{-4}\Omega^{-1}$ cm^{-1} for the case of phosphoryl chloride at 40°C. As can be seen from the figure phosphorus trichloride and methyl trichlorosilane did not give electrically conductive material. Other chlorides such as benzoyl chloride and toluene sulphonyl chloride did not react with poly(EVK) under the condition of this work. A detailed study on the screening of various active chlorides for this reaction is being made and the results will be reported in future.

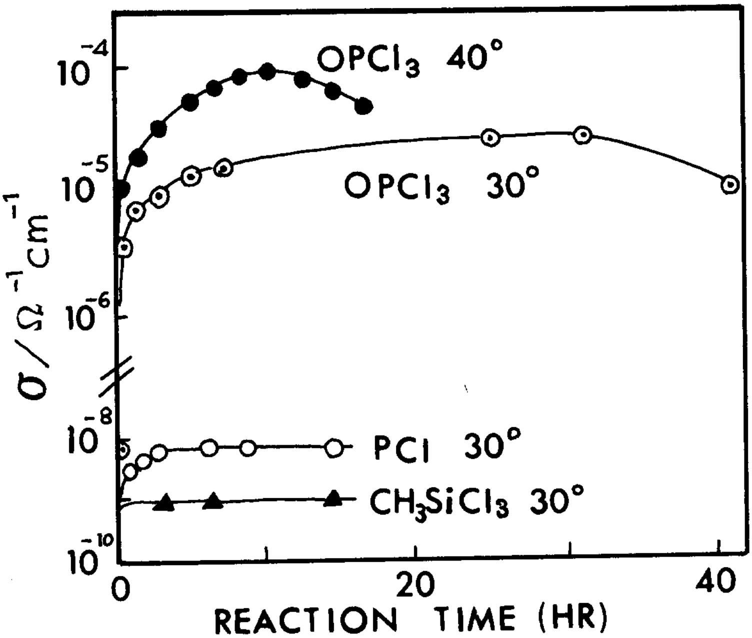

Fig. 2. Conductivity changes with reaction time in petroleum ether. $(O{=}PCl_3)/(P.Ether)=2/25$ v/v.

Fig. 3 shows some of the typical curves for the reaction of poly(EVK) films at 0°C. It can be seen that the conductivities of the final products are much higher than those at 30 and 40°C, although the reaction is slower at 0°C, being about $10^{-2}\Omega^{-1}$ cm^{-1} in average. We cannot yet explain the effect of reaction temperature on the conductivity, but believe that the following reactions which take place depending on temperature influence the conductivity;

(i) the formation of C=C double bond in the chain.

(ii) the consumption of C=O group by the acid-catalyzed Aldol condensation, which produce the units without C=C double bonds in the polymer chain.

(iii) the addition of acids to the C=C double bonds formed, which breaks the conjugation.

(iv) absorption of HCl, $O=PCl_3$, etc. on the polyene.

The poly(EVK) films reacted at 30 and 40°C were no longer soluble in chloroform while that reacted at 0°C was still soluble. This suggests that the cross-linking of polymer chains by the acid-catalyzed Aldol condensation(reaction ii) takes place at higher temperature.

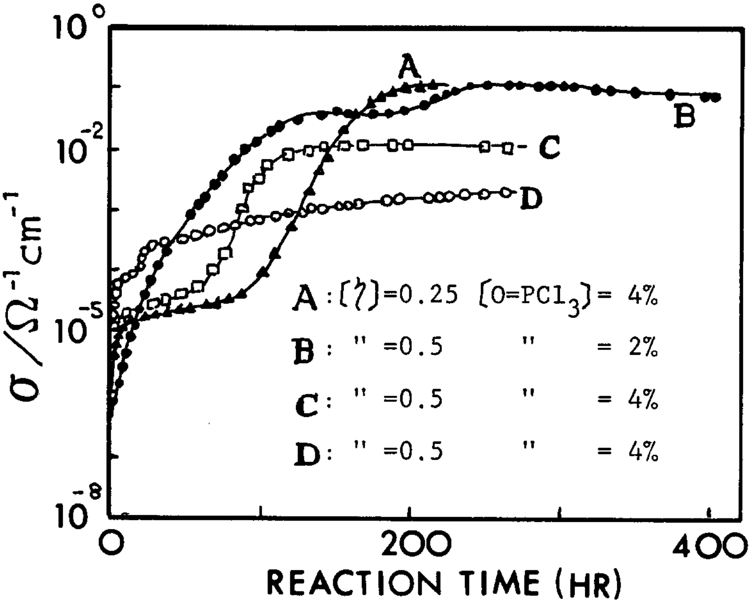

Fig. 3. Conductivity changes with reaction time in petroleum ether at 0°C using $O=PCl_3$.

It can be seen from the figure that the conductivity jumps after a certain reaction time, although the time and scale of jumping are not consistent for each sample. The cause for this jumping is not yet clarified. The samples reacted first at 0°C for 50 hours, at which the conductivity reached to $10^{-5}\Omega^{-1}$ cm^{-1}, were then heated at 45°C. It was found that no jumping took place and the conductivity started to decrease slowly. The film reacted at 0°C, whose conductivity reached to 10^{-2} $\Omega^{-1}cm^{-1}$, was ten heated to 45°C, and left to stand for 50 hours at this temperature. The conductivity decreased and it did not return to the original value even when cooled to 0°C again. From these experimental results, it seems likely that the reaction(iii) takes place at higher temperatures. The effects of reaction temperature are being investigated in more detail, and we hope to clarify the problems soon.

The concentration of phosphoryl chloride and the molecular weight of poly(EVK) seemed to have insignificant effect on the conductivity.

Fig. 4 shows the temperature dependency of the conductivity of the reacted poly(EVK) film. The activation energy of the conductivity was found to be 1.1 eV for the samplereacted at 30°C, and 0.50 eV for that reacted at 0°C. For this measurement, the reacted films were washed rapidly with methanol containing small amounts of triethylamine and dried for 24 hours in vacuum at 40°C. By this treatment the conductivity of the sample somewhat decreased; for example from 10^{-2} to 10^{-4} $\Omega^{-1}cm^{-1}$ for the sample reacted at 0°C.

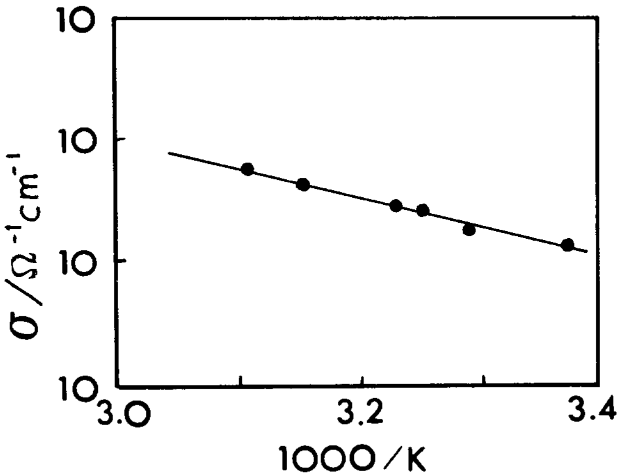

Fig. 4. Temperature dependency of conductivity of poly(EVK) reacted at 30°C.

The nature of the electic conductivity for this system has not been clarified yet. It is thought that the specific conductivity of the order of $10^{-5}\Omega^{-1}cm^{-1}$ is due to electronic conductivity within the conjugated system, because the poly(EVK), poly(methyl vinyl ketone) and poly(phenyl vinyl ketone) reacted in solution, precipitated, washed with methanol containing triethylamine and dried in vacuum at 40 - 50°C, all had a specific conductivity of about $10^{-5}\Omega^{-1}cm^{-1}$ when measured at room temperature in vacuum in the form of compressed pellets(3). The higher conductivity of 10^{-2} and above for poly(EVK) reacted at 0°C could be partly ionic nature due to the acid protons on the film surface. It is known that polyacetylenes also increase their conductivities by absorbing various suabstances (4). In any case it can be said that if there was no conjugated system, the conductivity could not be enhanced by absorption. We admit that it is almost impossible to measure the intrinsic conductivity for this system.

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