SHORT COMMUNICATIONS

The Polymerization of Vinyl Acetate Catalyzed by Iodine

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Recently it was reported by the present authors[1] that α-methylstyrene (αMS) could be polymerized with iodine, making an example of iodine-catalyzed high-polymerization in addition to vinylether[2]. Now, it has been confirmed that vinyl acetate (VAc) also belongs to another monomer of this kind. Since the polymerization of this monomer, however, is slightly different from those of αMS and vinylether, and moreover, the peculiar behavior of iodine in polymerizing VAc was not mentioned at all by Bartlett et al.[3] who studied rather the role of iodine as inhibitor at its low concentration, essential points of this reaction will be reported.

Vinyl acetate was sealed in glass tubes together with iodine after degassed and dehydrated. The reaction was carried out at room temperature by shaking the tubes, because the reaction system remained heterogeneous in the case of a large amount of iodine. Besides the increase of viscosity the polymerization could be recognized by gradual precipitation of deep violet substance on the wall from the solution, but the precipitation did not occur so rapidly, e. g. it occurred after a day in the solution of 9 wt.% iodine. Such a tendency of separating colored "polymers" was not observed in the case of αMS, where the polymers could be separated by the addition of methanol. Conversions of the monomer obtained at 160 hr. are plotted against the initial concentration of iodine in Fig. 1. Iodine begins to exhibit its polymerizing power at the concentration of 1 wt.% as suggested by the shape of the curve and this fact agrees with the finding of Bartlett and Kwait[3] as mentioned above.

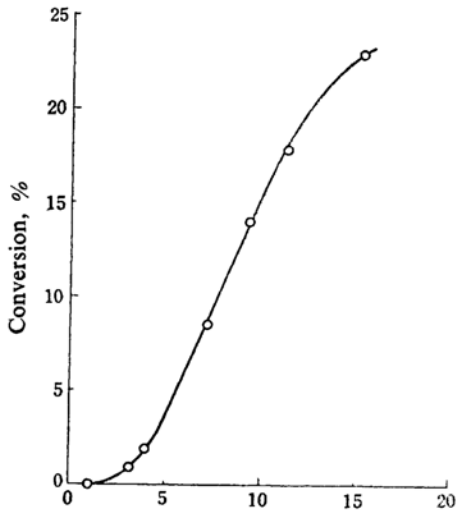

Fig. 1. Conversion of vinyl acetate to the insoluble polymer against the concentration of iodine.

The polymer is hard, brittle and amorphous, according to the X-ray pattern. It does not melt below 310°C. Iodine content is about 14~18%, though the concentration of iodine in the solution is varied from 4~15%. Infrared spectrum of the polymer shows that this polymer includes carbonyl and methyl groups. It is insoluble in ordinary organic solvents*, and hardly soluble even in aqueous potassium iodide solution at 80°C, suggesting that iodine is firmly occluded or bonded to the polymer. The molecular weight therefore can not be determined yet. This result presents a sharp contrast to the case of vinylether. According to preliminary measurement, this polymer seems to have specific resistance of about the order of 10^8~10^9 ohm/cm.

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1) K. Hirota, G. Meshitsuka, F. Takemura and T. Tanaka, This Bulletin, 33, 1316 (1960).
2) D. D. Eley and A. W. Richard, *Trans. Faraday Soc.*, 45, 425 (1949).
3) P. D. Bartlett and H. Kwait, *J. Am. Chem. Soc.*, 72, 1051 (1950).

* Besides the main polymer as described, a small amount of polymerized product which was soluble in petroleum benzine could be obtained.

X-ray measurement of the samples, and also to Mrs. Kiyoko Kishi for the help of the experiment.

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