Abnormal Viscosity of Polyvinyl Chloride in Extremely Dilute Solutions

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With a view to determine the intrinsic viscosity of polyvinyl chloride(1) in solutions of some plasticizers, we have measured the viscosity in extremely dilute solutions of unfractionated polyvinyl chloride in dioctyl phthalate as well as in tricresyl phosphate by means of an Ostwald viscosimeter. The solutions were prepared by dispersing the sample in the plasticizer two days at room temperature and by heating four hours at 90°C. The results are shown in Fig. 1,(2) from which, however, the intrinsic viscosity cannot be calculated, since the relation between the specific viscosity divided by concentration (η_{sp}/C) and the concentration (C) dons not conform with the empirical equation of Huggins.(3) Besides, we have observed a similar abnormal behavior in cyclohexanone at extreme dilution, whereas, at higher concentrations no anomaly has ever been observed in this solvent, as reported in our previous paper.(4) In general, it has been found that the value of η_{sp}/C of polyvinyl chloride in extremely dilute solutions shows a minimum at a certain concentration, and then increases with further dilution. Such behavior has never been found with non-electrolytic high polymers, such as polyvinyl chloride, although similar abnormal phenomena have already been observed with high-molecular electrolyte.(5)

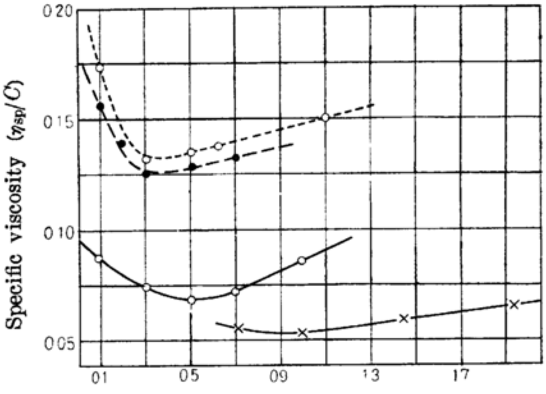

Fig. 1.—Viscosity of polyvinyl chloride in extremely dilute solution: × Sample 1 (average polymerization degree 600), ○ Sample 2 (*ditto* 1500), ● Sample 3 (*ditto* 2900), —— tricresyl phosphate, ………… dioctyl phthalate, – – – – cyclohexanone. Temperature: 80°C.

This somewhat unexpected phenomenon may be of particular interest in two respects. First, it is expected that the true intrinsic viscosity of chain polymer is estimated from these experimental results, the value of which is now frequently used for the estimation of the size and shape of chain polymers in solution by the aid of theories. Secondly the concentration of the minimum value of η_{sp}/C changes with the molecular weight of chain polymers and the nature of solvents, which is evident from Fig. 1. Thus, these phenomena together with theoretical considerations suggest that there may exist a certain special interaction between the polymer molecules in such dilute solutions.

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(1) Supplied by the Mitsui Chemical Industrial Company, and purified by precipitating once from a cyclohexanone solution with methanol.

(2) From the flactuation of measured flow times of solution, the probable error of η_{sp}/C is estimated to be ±1% in the most dilute solution of cyclohexanone, ±3.5% in the most dilute solution of dioctyl phthalate and ±8% in the most dilute solution of tricreesyl phosphate.

(3) M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1942).

(4) Takeda and Turuta, *J. Phys. Soc. Japan*, **6**, 525 (1951).

(5) Fuoss, *J. Polymer Science*, **3**, 602 (1948).