Dilute Solution Viscosity of Polyacrylonitrile in N,N-Dimethylformamide

INTRODUCTION

When reduced viscosity is plotted against polymer concentration, an abnormal phenomenon is often observed in the region of extremely dilute solution for several polymers.[1-5] This phenomenon is due to polymer adsorption on the glass wall of the capillary.

Such a phenomenon was also confirmed in our experiments in the polyacrylonitrile (PAN)-N,N-dimethylformamide (DMF) system, when the measurement was done in air. However, since DMF is highly hygroscopic, more accurate measurements are needed to determine such viscometric properties. On the other hand, in modern GPC, the molecular weight of the eluted polymer is determined from the reduced viscosity in each elution count by means of an autoviscometer. The viscosity is usually determined in an efflux time within about 5 min in the region of extremely dilute solution. Accordingly, the above-described viscosity measurement requires further study.

EXPERIMENTAL AND RESULTS

A double-walled bath was designed and constructed with temperature control systems. The bath provides a constant temperature of $20 \pm 0.005°C$. A modified Ubbelohde viscometer, the efflux time of which is 140 sec for water at 20°C, was used. To remove superficial dust and foreign particles, solvent and solutions were filtered with ultrafine filters, with pore sizes of 0.45 μm (Alpha-6, Gelman Instrument Co.). A Hewlett Packard model 5901 autoviscometer was used with modified Ubbelohde viscometers. Efflux times were measured with a transistorized electronic counter using a quartz-crystal oscillator as a time-base reference and read to 0.001-sec resolution. An efflux time of the solvent was filled in the same bottle. Despite the above controls, the plot of η_{sp}/C against C was curved upward at concentrations below 0.05 g/dl for DMF solutions of PAN, (Fig. 1). Moreover, efflux times of the solvent increased with the number of measurements [Fig. 2(a)]. The efflux time in 70 repeated measurements increased 0.2 sec from that of the first measurement.

We anticipated that the efflux times of the solvent would increase by absorbing water from the air during measurements. Thus efflux times were measured with DMF in which water had been added in advance, and the times increased considerably with water content (Fig. 3). In order to minimize the effect of water, the column packed with drying agents such as $CaCl_2$ and porous silica gel particles was mounted at one end of the glass tubes of a viscometer, and long rubber tubes were mounted at the other end. Thus the solvent in the viscometer was not in direct contact with air.

Under these conditions, efflux times varied within 0.04 sec in 75 repeated measurements [Fig. 2(b)]. The increase of 0.2 sec in efflux time corresponds to that of 0.02% water in DMF. Further-
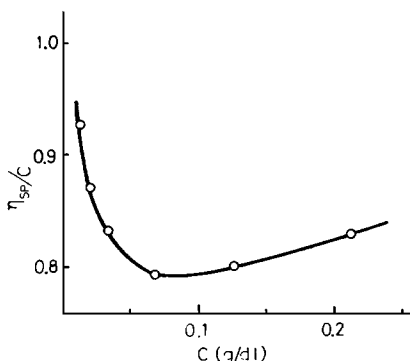

Fig. 1. Plot of η_{sp}/C against C obtained by the method of successive dilution.
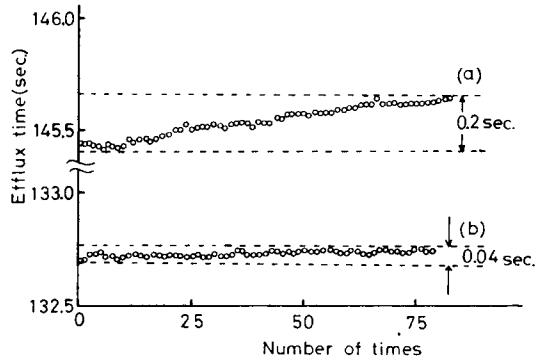
Fig. 2. Increase in the efflux times obtained in (a) air and (b) under such a condition that the effect of water was minimized.
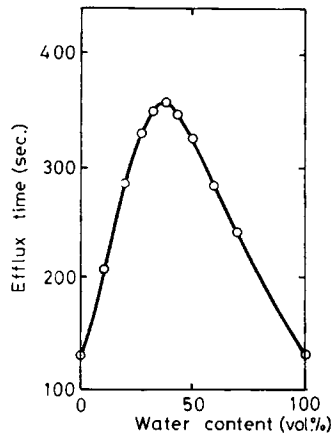

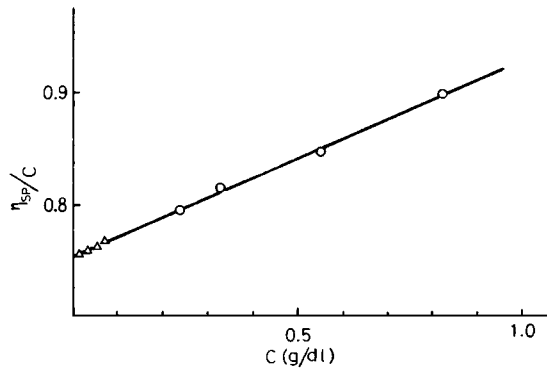Fig. 3. Efflux times in DMF-water system at 20°C.

Fig. 4. Plot of η_{sp}/C against C under recommended conditions: (O) experimental points measured at ordinary conditions, (△) in extremely dilute solution at recommended conditions.

more, Figure 4 shows that the data points of η_{sp}/C at concentrations below 0.1 g/dl fall on the straight line prepared drawn by the data of η_{sp}/C at higher concentrations.   The increase in η_{sp}/C at extremely dilute solution (Fig. 1) is completely due to the absorption of water by DMF.   If we prevent water from being absorbed in DMF, we will be able to determine the η_{sp}/C of eluents by GPC with a high degree of reliability and to calculate the molecular weight of polymers with the Mark-Houwink equation.

References

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