Relationship between Polymer Concentration and Molecular Weight in the Viscosity Behavior of Concentrated Solution

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With 9 figures and 1 table

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Introduction

At the present it is a well known fact that when a double logarithmic plot is made for viscosity of polymer melt or solution at a given concentration and solute molecular weight, these data points can be fit by two straight lines with different slopes (1). The similar trends have been observed for relationships between viscosity and concentration of polymer solution in higher concentration regions (2). For the points at which the two straight lines in the former and the latter plot meet, a critical molecular weight, $M_c$, and a critical concentration, $C_c$, have been defined, respectively. The existence of these critical quantities have been discussed in terms of the entanglements among polymer chains (3, 4).

A number of authors have been engaged in finding the relationship between polymer concentration and molecular weight at these critical points. Among these studies, Porter and Johnson (5) reported that the product, $M_c \cdot C$, remained constant, so far as a given polymer homologous series is concerned. This result is in contrast with that of Onogi and his coworkers (2) as well as that of Ferry and his coworkers (6); the former and the latter authors deduced $C_c \cdot M^{0.5} \approx \text{const.}$ and $C_c \cdot M^{0.68} \approx \text{const.}$, respectively. The present authors have also presented a relationship different from any one of the above (7).

More recently, a somewhat general relationship was proposed by Cornet, which is approximated by $C_c \cdot M^a \approx \text{const.}$ (8). The exponent, $a$, in this equation is not a constant independent of molecular weight but is found to be 0.5 and 1.0 within enough of a high and a low molecular weight range, respectively. Thus the present situation of studying this problem is that there are diverse opinions.

This paper deals experimentally with the relationship between polymer concentration and molecular weight at the critical point appearing in the viscosity behavior of acrylonitrile copolymer solutions. An analogous relationship as proposed by Cornet is deduced. However, the exponent, $a$, is found to vary with the range of concentration in a different fashion from that of the above author, and this is discussed considering the excluded volume effect in polymer coils.

Experimental

All samples studied were acrylonitrile-methacrylate copolymers (90/10) which were prepared by suspension polymerization at 60 °C in a three necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel. Azo-bis-isobutyronitrile and polyvinylalcohol were used as a catalyst and a suspension stabilizer, respectively. Molecular weights of each samples were regulated by

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using monoethanolamine as a chain transfer agent. The molecular weights of samples determined by intrinsic viscosity in dimethylformamide were 32,000 to 1,285,000 using the following equation:

$$\eta = 6.59 \times 10^{-4} M_w^{0.66}$$ in D.M.F. at 30 °C.

Reagent-grade sodium thiocyanate and deionized water were used in the preparation of polymer solutions. Polymer solutions were prepared by mixing dried polymer and 50 wt%, 55 wt%, 57.5 wt%, 60 wt% NaSCN aq.-solution, or γ-butyrolactone, and dissolving them at 80 °C. The concentration range covered was between 30 wt% and 0.1 wt% solid.

Steady-flow viscosity was measured by means of a capillary viscometer with continuously varying head, described by Maron et al. (9). The measuring techniques were entirely the same as theirs. The zero shear viscosity was estimated by the extrapolation of double logarithmic plots between viscosity and rate of shear to the low shear rate regions. Fig. 1 shows examples of rate of shear dependence of the viscosity at different concentrations.

Experimental Results

Figs. 2–6 show the double logarithmic relationship between zero-shear viscosity $\eta_0$ and polymer concentration of solutions of acrylonitrile copolymer having different molecular weights in various solvents such as 50 wt%, 55 wt%, 57.5 wt%, 60 wt% NaSCN aq.-solutions, and γ-butyrolactone. As seen from these figures, the double logarithmic plots can be fit by two straight lines intersecting at the critical concentration $C_e$.

![Fig. 1. Rate of shear dependence of viscosity of acrylonitrile-copolymer solutions at 30 °C, in different polymer concentrations](image)

![Fig. 2. Double logarithmic plot between zero-shear viscosity and concentration for the solution of acrylonitrile copolymer with various molecular weights in 50 wt% NaSCN aq.-solution at 80 °C](image)

![Fig. 3. Double logarithmic plot between zero-shear viscosity and concentration for the solution of acrylonitrile copolymer with various molecular weights in 55 wt% NaSCN aq.-solution at 30 °C](image)