# LETTERS TO THE EDITORS

## *A Comment on Solomon and Ciută's Single-Point Method for Determining Intrinsic Viscosity*

Solomon and Ciută[1] recently proposed a single-point method of determining intrinsic viscosities, in which it was supposedly unnecessary to know the appropriate value of the well-known Huggins' constant,[2] $k'$, or of any related solvent-polymer interaction parameter. Their equation was:

$$[\eta] \approx (\sqrt{2}/C)\sqrt{\eta_{sp} - \ln \eta_{rel}} \tag{1}$$

where the quantities have their usual significance.

Some justification for this expression was given by expanding $\ln \eta_{rel}$ in a series, resulting eventually in an expression which was, essentially,

$$[\eta] \approx (\eta_{sp}/C)\sqrt{1 - {}^2/_3\eta_{sp} \ldots +} \ldots \tag{2}$$

They then pointed out that, at low enough concentrations, ${}^2/_3\,\eta_{sp} \to 0$, so that $[\eta] = \lim_{C\to 0} (\eta_{sp}/C)$, as it is usually defined. This, however, is merely proof that their approximate expression, like many other linear combinations of $\eta_{sp}/C$ and $\eta_{inh}(= \ln \eta_{rel}/C)$, will extrapolate to $[\eta]$ at infinite dilution. Their further proof of the approximation consisted of a number of experimental examples showing good agreement between approximated and extrapolated values of $[\eta]$.

A slightly more sophisticated analysis of their approximation may be obtained as follows: Let us assume, for mathematical simplicity, that the true concentration-dependence of solution viscosity is given by

$$\eta_{inh} = [\eta] - \beta[\eta]^2C \tag{3}$$

where $\beta = {}^1/_2 - k'$.

Then it is readily shown that

$$\eta_{sp}/C = [\eta] + k'[\eta]^2C + ({}^1/_6 - \beta)[\eta]^3C^2 + \ldots \tag{4}$$

Hence

$$(\eta_{sp} - \ln\eta_{rel})/C = {}^1/_2[\eta]^2C + (1/6 - \beta)[\eta]^3C^2 + \ldots \tag{5}$$

When this quantity is substituted into the right hand side of eq. (1), we find that

$$[\eta] \approx [\eta][1 + (1/6 - \beta)[\eta]C + \ldots] \tag{6}$$

The two sides of the expression will become equal when $\beta = 1/6$ or $k' = 1/3$. Otherwise, the relative error of Solomon and Ciută's approximation is given by

$$\%\ \text{error} = 100\ [\eta]C(1/6 - \beta), \tag{7}$$

which will become more significant as $[\eta]$ and concentration increase, of course. Solomon and Ciută's approximation conceals the assumption that $k' = 1/3$, whereas experimental values usually range from 0.25 to 0.50, and often lie outside these limits.

It should be noted in passing that the hoped-for single-point method without the use of Huggins' constant is chimerical, for sound algebraic reasons. No matter what the true concentration-dependence may be, the well-established fact that Huggins' constant does vary between polymers if not also between solvents necessitates experimental determination of $k'$, $\beta$, or some related parameter before single-point methods may be used.

**References**

1. Solomon, O. F., and I. Z. Ciută, *J. Appl. Polymer Sci.*, **6**, 683 (1962).
2. Huggins, M. L., *J. Am. Chem. Soc.*, **64**, 2716 (1942).

E. H. CATSIFF

Thiokol Chemical Corporation
Trenton, New Jersey

Received April 4, 1963

## *Investigation of the Effect of Chloronitroso Compounds on Polymers Irradiated with UV Light*

The investigations of Hammick and Lister,[1] of Mitchell, Schwarzwald, and Simpson[2] and others have shown that in the presence of UV light chloronitroso compounds are decomposed easily with the formation of H and Cl radicals. The presence of strongly

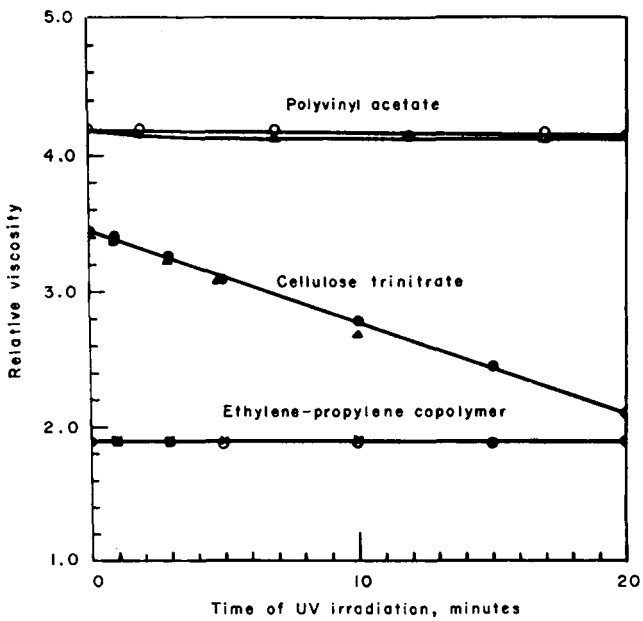


Fig. 1. *Polyvinyl acetate* (the solvent was ethanol): (△) Polyvinyl acetate with (I), and (○) polyvinyl acetate without (I). Weight concentration of (I) in solution was 0.117%, and the weight concentration of polyvinyl acetate in solution was 2.36%. Molar ratio (I): vinyl acetate mer = 0.029. *Cellulose trinitrate* (the solvent was acetic acid): (▲) Cellulose trinitrate with (I), and (●) cellulose trinitrate without (I). Weight concentration of (I) in solution was 0.09% and the weight concentration of cellulose trinitrate in solution was 0.906%. Molar ratio (I): cellulose trinitrate mer = 0.232. *Ethylene-propylene copolymer* (the solvent was benzene): (×) Ethylene-propylene copolymer with (I), and (○) ethylene–propylene copolymer without (I). Weight concentration of (I) in solution was 0.12%, and the weight concentration of ethylene–propylene copolymer in solution was 1.88%. Unknown composition of the copolymer.