

## LETTERS TO THE EDITORS

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

Solomon and Ciută<sup>1</sup> 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,<sup>2</sup>  $k'$ , or of any related solvent-polymer interaction parameter. Their equation was:

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

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,

$$[\eta] \approx (\eta_{sp}/C)\sqrt{1 - \frac{2}{3}\eta_{sp} \dots} \quad (2)$$

They then pointed out that, at low enough concentrations,  $\frac{2}{3}\eta_{sp} \rightarrow 0$ , so that  $[\eta] = \lim_{C \rightarrow 0} (\eta_{sp}/C)$ , 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

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

where  $\beta = 1/2 - k'$ .

Then it is readily shown that

$$\eta_{sp}/C = [\eta] + k'[\eta]^2C + (1/6 - \beta)[\eta]^3C^2 + \dots \quad (4)$$

Hence

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

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

$$[\eta] \approx [\eta][1 + (1/6 - \beta)[\eta]C + \dots] \quad (6)$$

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

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

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).

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

The investigations of Hammick and Lister,<sup>1</sup> of Mitchell, Schwarzwald, and Simpson<sup>2</sup> 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

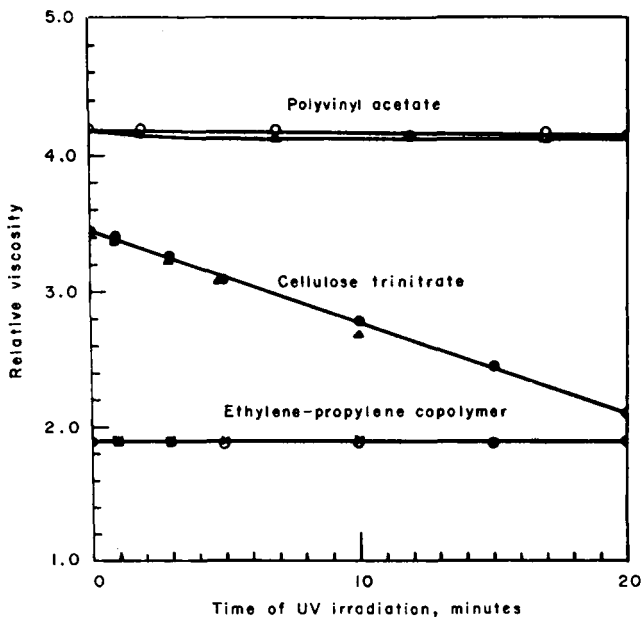


Fig. 1. *Polyvinyl acetate* (the solvent was ethanol): (Δ) Polyvinyl acetate with (I), and (O) polyvinyl acetate without (I). Weight concentration of (I) in solution was 0.117%, and the weight concentration of polyvinyl acetate in solution was 2.36%. Molar ratio (I): vinyl acetate mer = 0.029. *Cellulose 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): (X) Ethylene-propylene copolymer with (I), and (O) 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.