

Viscosity of Concentrated Styrene Solutions of Polystyrene

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Synopsis

Viscosities of concentrated solutions of polystyrene of different intrinsic viscosities were measured at varying polymer concentration and temperature. By modifying Martin's equation, an empirical equation correlating the viscosity of the solution as a function of the polymer concentration, the intrinsic viscosity of the polymer, and temperature was obtained.

Viscosities of dilute solutions of polymers have been widely studied theoretically and experimentally. There have been, however, few investigations on the viscosity of concentrated solutions because of the complexity of the mechanism.

In connection with the kinetic study on bulk polymerization of styrene at high conversion, where the viscosity of the system plays an important role in the reaction mechanism since the reaction is diffusion-controlled, a quantitative evaluation of the viscosity of styrene solutions of polystyrene is required.

The present paper is concerned with the correlation of the bulk viscosity of polystyrene solutions with the polymer concentration, intrinsic viscosity $[\eta]$, and absolute temperature T . In the present correlation, the intrinsic viscosity in toluene rather than in styrene is introduced, since correlation between the average molecular weight of polystyrene and the intrinsic viscosity in toluene has been well studied.¹ Spencer and Williams² have measured the viscosities of isopropylbenzene solutions of polystyrene η (in poise) in the high concentration range and obtained the following empirical equation:

$$\eta = 3.63 \times 10^{-10} \exp \{0.0572 M^{1/2} + C^{1/2} (22.54 - 0.045 M^{1/2} + 5000/T)\} \quad (1)$$

where M and C are the molecular weight and polymer weight fraction, respectively. Equation (1), however, does not necessarily hold over the whole range of the polymer concentration, C . For example, eq. (1) gives an extremely small value of the viscosity for polymer concentrations less than 0.1 g./g. In addition to this, there is a difficulty in applying eq. (1)

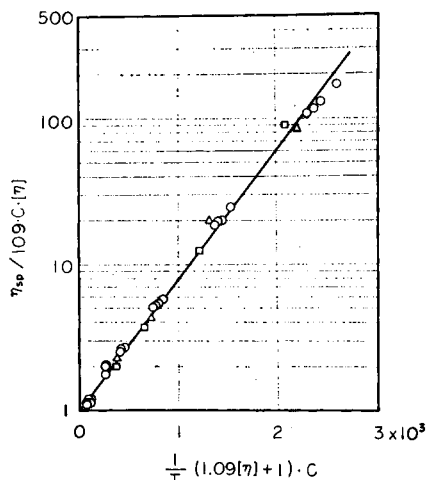


Fig. 1. Correlation of viscosity of concentrated styrene solutions. See Table I for code.

directly to the kinetic study of the bulk polymerization of styrene, where the solvent is different.

Three different types of polystyrene were dried for over 48 hr. and dissolved into distilled styrene to make solutions of various concentrations; the viscosities of these solutions were measured by means of Ostwald-type viscometers under very low shear rate conditions, i.e., 500 sec.⁻¹ at most. The experimental conditions are summarized in Table I.

Martin³ has proposed an equation [eq. (2)] to give the viscosity of concentrated solutions of polymers in terms of the specific viscosity.

$$\eta_{sp}/C = [\eta] \exp \{K' [\eta] C\} \quad (2)$$

It is seen that the noted equation of Huggins concerning the viscosity of dilute solutions,

$$\eta_{sp}/C = [\eta] + K [\eta]^2 C \quad (3)$$

can be deduced from eq. (2) by expanding the exponential term and neglecting terms higher than the third order. If it is assumed that the coefficient K' in eq. (2) depends only on the intrinsic viscosity and the reciprocal of the absolute temperature, eq. (2) can be generalized in the form

$$\ln (\eta_{sp}/[\eta] C) = g([\eta], 1/T)C \quad (4)$$

TABLE I
Experimental Conditions

| Type | Symbol in Fig. 1 | $[\eta]$ (30°C., toluene) | Temperature, °C. | Concentration range, g./g. |
|------|------------------|---------------------------|------------------|----------------------------|
| A | ○ | 0.84 | 30, 50, 60, 70 | 0.0074–0.303 |
| B | △ | 0.77 | 70 | 0.051–0.303 |
| C | □ | 0.65 | 70 | 0.052–0.303 |

When $\ln (\eta_{sp}/C)$ was plotted against C , a group of straight lines with different slopes depending on the temperature and $[\eta]$ were obtained. By plotting the slopes against $1/T$ and $[\eta]$, the function g was determined as

$$g([\eta], 1/T) = 2790 (1.09 [\eta] + 1) (1/T) \quad (5)$$

It was found that the intercept of the straight line in the plot of $\ln \eta_{sp}/C$ versus C is equal to a value of 109 times $[\eta]$ measured in toluene.

Consequently the final form of the correlation is, as shown in Figure 1, expressed in the form:

$$\eta_{sp}/C = 109 [\eta] \exp \{ 2790C(1.09 [\eta] + 1)/T \} \quad (6)$$

where $[\eta]$ is defined, as usual, as $\lim_{C \rightarrow 0} (\eta_{sp}/C)$ in units of deciliters/gram.

Therefore the relative bulk viscosity is calculated as $\eta_r = (\eta_{sp} + 1)$, where η_{sp} is viscosity in styrene.

References

1. T. Alfrey, A. Bartovics, and H. Mark, *J. Am. Chem. Soc.*, **65**, 2319 (1943).
2. R. S. Spencer and J. L. Williams, *J. Colloid Sci.*, **2**, 117 (1947).
3. A. F. Martin, paper presented at American Chemical Society Meeting, Memphis, April 1942.

Résumé

Des viscosités de solutions concentrées de polystyrène avec différentes viscosités intrinsèques ont été mesurées en faisant varier la concentration en polymère et la température. En modifiant l'équation de Martin on a obtenu une équation empirique qui relie la viscosité de la solution à la concentration en polymère, la viscosité intrinsèque du polymère et la température.

Zusammenfassung

Die Viskosität konzentrierter Lösungen von Polystyrol mit verschiedener Viskositätszahl wurde bei variierter Polymerkonzentration und Temperatur gemessen. Durch Modifizierung der Martin-Gleichung erhielt man eine empirische Gleichung, die die Viskosität der Lösung als Funktion der Polymerkonzentration, der Viskositätszahl des Polymeren und der Temperatur beschreibt.

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