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COMMENTS ON REHNER'S PROPOSED METHOD FOR ESTIMATING POLYMER MOLECULAR WEIGHT DISTRIBUTION WITHOUT FRACTIONATION

Rehner (1) used an empirical molecular weight distribution function proposed by one of us and derived an expression which enabled one to estimate the molecular weight distribution of the original polymer from its crosslink density and gel-sol ratio upon vulcanization or other crosslinking reactions. He later found a mathematical error in his derivation (2). The corrected expression, however, did not give acceptable results when actual crosslinking data were used. Using Rehner's notations the empirical molecular distribution equation used is

$$w_y = ab\, M_0^b\, y^{b-1} \exp\{-a\, M_0^b\, y^b\} \tag{1}$$

In his first paper this equation was erroneously written as

$$w_y = ab\, M_0^{b-1}\, y^{b-1} \exp\{-a\, M_0^b\, y^b\} \tag{1'}$$

where a and b are two adjustable constants, M_0 is the molecular weight of the monomer, y is degree of polymerization, and w_y is the weight fraction of y-mer. He then considered the possibility that eq. (1) might be responsible for the unacceptable results.

On examination of his derivation, we have found additional errors, particularly in the steps leading to his eq. (10′) (2).

$$w_s = \{a^{1/b}\, b\, M_0 \Gamma\, [2 - (1/b)] - b\rho\}/(M_0 - b\rho) \tag{10'}$$

(where w_s is the weight fraction of sol and ρ is the crosslink density). Also, we do not believe it is permissible to ignore the higher terms in the expansion of the term

$$[1 - \rho\,(1 - w_s)]^{(x/aM_0^b)^{1/b}}$$

in his eq. (8).

$$w_s = a^{1/b}\, b\, M_0^{b-(1/b)} \sum_{y=1}^{\infty} x^{[1-(1/b)]}$$

$$[1 - \rho\,(1 - w_s)]^{(x/a\, M_0^b)^{1/b}} \exp\,[-x].$$

However small the value for $\rho\,(1 - w_s)$, as long as the group $(x/aM_0^b)^{1/b}$

is allowed to vary from 1 to infinitely large, the higher terms in the binominal expansion cannot be ignored. Taking these points into consideration, we have derived an expression for w_s.

$$w_s = \int_0^\infty \exp\{-[x + \frac{\rho(1 - w_s)}{a^{1/b} M_0} x^{1/b}]\} dx \qquad (2)$$

Equation (2) can only be solved numerically. Thus, Rehner's method starting from eq. (1) is not any simpler than the method proposed by Bueche and Harding (3).

Rehner started also with Schulz's distribution function and arrived at an explicit expression for w_s. He could not, however, obtain reasonable coefficients for Schulz's equation from the SBR data listed in Table I of his paper. In the first set of SBR data, we feel that the corrected crosslinked density value of 0.83 might be an overcorrected one resulting from the use of Rehner's eq. (13). In this case, the correction reduced ρ to one-fourth of its uncorrected value. If the corrected value were only about 25% larger, a positive value of k (Schulz's coefficient) would have resulted. The second set of SBR data involve a zero sol fraction w_s which is hardly a usable condition for the determination of molecular weight distribution of the original sample.

Because of the uncertainties involved in obtaining correct values for crosslink density and gel-sol ratio, we feel that the present method at best can give only relative comparison of molecular weight distributions even when crosslinking is not carried too far. When extensive crosslinking is involved as in the case of the above mentioned SBR data, we feel that no reliable result can be expected.

References

(1) Rehner, John, Jr., J. Appl. Polymer Sci., 4, 95 (1960).

(2) Rehner, John, Jr., J. Appl. Polymer Sci., 5, S20 (1961).

(3) Bueche, F., and S. W. Harding, J. Appl. Polymer Sci., 2, 273 (1959).

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