2. Filippova, K. B., *Izvest. Akad. Nauk S.S.S.R.* (*Ser. Fiz.*), **22**, 330 (1958).

3. Gross, B., *J. Chem. Phys.*, **17**, 866 (1949).

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A New Method for Determining Effective Tensile Gage Length

It has been shown by a photographic method that crosshead displacement can be used to calculate the elongation for a dumbbell specimen in tensile extension by using an effective gage length.[1] We wish to report here a convenient method for determining this effective gage length from tensile data at different crosshead speeds *without actually measuring the gage length* and to show that this method can be applied to dumbbell specimens as well as specimens of film strips.

It has been shown[1] that at constant temperature the true stress αS, measured at different strain rates R, is related to experiment time t in the following manner

$$\alpha S/R = f(t) \tag{1}$$

where α is the extension, S the stress based on the original cross-sectional area of the specimen, and $f(t)$ a function of t. By definition

$$\alpha = 1 + \gamma = (L_e + D)/L_e \tag{2}$$

$$R = V/L_e \tag{3}$$

where γ is the elongation, L_e the effective gage length, and V and D are the speed and displacement of the crosshead respectively. Substitution of (2) and (3) into (1) and transposing gives

$$D = f(t)V/S - L_e \tag{4}$$

When the crosshead displacements at constant value of time t are plotted against the ratios of crosshead speed V to apparent stress, the result will be a straight line, since $f(t)$ is a function of t only. The intercept of this line with the ordinate will give the value of $-L_e$. Since L_e does not change with t, all lines of constant t should converge to the same $-L_e$ on the ordinate.

An example of this kind of D vs. V/S plot is reproduced in Figure 1. Figure 1 is based on tensile data obtained from specimens of rectangular strips of a commercial polyisobutylene (Vistanex 120) at 24°C. and using crosshead speeds of 5 to 50 in./min. with an initial jaw separation of 1 in. The actual isochronic lines do not intercept the D axis at the same point of $-L_e$. However, the variation is within experimental error. The isochronic lines shown in Figure 1 were drawn through the average of $-L_e$ which is 0.93 in. for 1 in. jaw separation to compare with the experimental points which are shown as dots. The excellent agreement shows that this method is adequate for the determination of effective gage length. Another experiment on the same
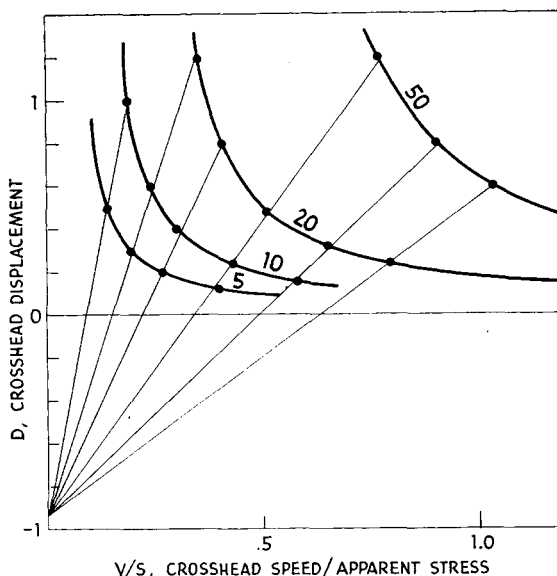

Fig. 1. The D vs. V/S curves for a polyisobutylene. The numerals indicate the crosshead speeds in in./min.

material but with a jaw separation of 2 in. gives an effective gage length of 1.85 in.

This method was applied to the stress-strain data on NBS polyisobutylene obtained[1] with dumbbell specimens, to which an effective gage length correction had been already applied. For this case eq. (4) can be modified to

$$\gamma = f(t)R/S - 1$$

The intercept of isochronic lines should, therefore, be -1, instead of $-L_e$. This was the actual result. Therefore, this method is applicable to dumbbell specimens as well.

In the region of small crosshead displacement where the hyperbolic D vs. V/S curve is almost flat, a small experimental error would cause a considerable error in L_e. At the other end of the curve, i.e., at large displacement, eq. (1) may not hold. The application of this method for determining effective gage length is probably, therefore, limited to a region from 20 to 120% nominal elongation.

Reference

1. Smith, T. I.., *J. Polymer Sci.*, **20**, 89 (1956).

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Reactions of Primary Amines with Epoxides

The advent of epoxy resin technology has created considerable interest in the reactions of amines with epoxides.[1] The reactions of ammonia and primary amines with epoxides are competitive consecutive processes and present con-
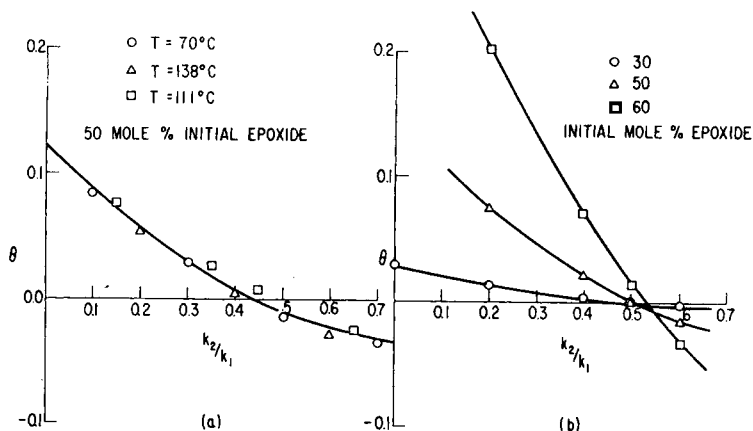
Fig. 1. Propylene oxide–butylamine reaction. Plots of θ versus k_2/k_1 for the function

$$\theta = k_2/k_1 \log (B_\infty/B_0) - \log \{(B_\infty/B_0) + (C_\infty/B_0)(1 - k_2/k_1)\}.$$

siderable problems in chemical and kinetic analysis.[2] Although the three-step reaction of ammonia with epoxides is inevitably mathematically complex, the two-step reaction of primary amines can be treated fairly simply.

For the reactions:

$$A + B \xrightarrow{k_1} C \qquad (1)$$

$$A + C \xrightarrow{k_2} D \qquad (2)$$

$$-d[C]/d[B] = 1 - \alpha[C]/[B] \qquad (3)$$

where $\alpha = k_2/k_1$.

Solution of this equation yields

$$\alpha \ln \frac{[B]}{[B_0]} = \ln \{[B]/[B_0] + ([C]/[B_0])(1 - \alpha)\} \qquad (4)$$

where $[B_0]$ is the initial concentration of [B] and the other concentration terms refer to any time throughout the course of the reaction. The same result may be obtained by using the "static" treatment of Fuoss.[3] Since this equation holds for the complete course of the reaction, it should be possible to evaluate α from measurements of [B] and [C] after the reaction has virtually gone to completion.

We have applied this treatment to the reaction of propylene oxide with n-butylamine, where a series of different substoichiometric amounts of propylene oxide reacted in Carius tubes with butylamine to virtual completion. The reaction products were analyzed by vapor phase chromatography on a 2-ft. silicone rubber column programmed at 7.9°C./min. and starting at 80°C. Under these conditions the three end products were well separated and their mole fractions calculated from calibration curves obtained with mixtures of known composition.

The results of several experiments at different compositions and temperatures are shown in Figure 1. From eq. (4) it can be seen that the intercepts $\theta = 0$ in Figure 1 represent the true values of k_2/k_1.

It can readily be seen that k_2/k_1 is virtually independent of temperature and composition over a considerable range of both, and has a value of 0.49 ± 0.05. It is expected that this figure will be fairly independent of the substituents on either reactant for the epoxide–primary amine reaction,

and the value of 6:4 obtained by Potter and McLaughlin[2] for the competition of mono- and diethanolamine for ethylene oxide supports this contention.

Extrapolating these conclusions to primary amine-cured epoxy resins, one may conclude that gelation should generally occur at higher conversions than those predicted by the Flory-Stockmayer[4] theory because of the unequal activity of the amine functions. Second, the branching coefficient should be independent of temperature. This means there should be no temperature-dependent chemical influence on the structure of the network. The possibility of temperature-dependent physical influences is, of course, considerable.

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References

1. Smith, I. T., *Polymer*, **2**, 95 (1961).

2. Potter, C., and McLaughlin, R. R., *Can. J. Res.*, **25B**, 405 and 415 (1947).

3. Fuoss, R., *J. Am. Chem. Soc.*, **65**, 2406 (1943).

4. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, 1953, p. 353.

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Water Vapor Transmission Through Porous Films

The usefulness of porous plastic films in many applications—for example, wearing apparel—depends to a large degree on their capability of transmitting water vapor. The variety of commercially available porous plastic sheets and films is increasing, while the methods of evaluating water vapor transmission of such films leave much to be desired. In general, water vapor transmission rates (WVTR) are measured by placing a sample between two layers of air at different humidities. The comparison of data obtained