Notes to the Editor

Rate of condensation polymerization for monomers having reactivities different from their polymers

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(Received 1 November 1976)

INTRODUCTION

Several monomers, specially containing aromatic rings, undergoing condensation polymerization exhibit reactivities different from those of higher homologues. For example, for phenylene sulphide by Lenz *et al.*[1] showed that the monomer molecules have much lower reactivities than the dimer, trimer, etc. which all react at the same rate. Challa[2–4] from studies of the equilibrium kinetics of the formation of poly(ethylene terephthalate) by the ester-interchange reaction, also found the monomer having a lower reactivity than the polymer molecules. A similar phenomenon was found by Hodgkin[5] for polyimide formation. In contrast to monomers discussed previously, in the latter case, when one of the amino groups has reacted, the residual group has a lower reactivity. Indeed, there are several imide monomers for which the reactivity changes are large enough to prevent polymerization[5].

In the case of aromatic diisocyanates, the reactivity of the residual isocyanate groups depends upon the electron – withdrawing nature of its substituent[6], and consequently, the functional group reactivity changes as the polymerization progresses[7].

The reaction rate model presented in this work takes into account the difference in reactivity between monomers and polymer molecules. Equations developed herein can be applied to the initial region of condensation polymerization, where the equal reactivity hypothesis is strictly not valid[8] and can be easily adapted to diisocyanate polymerization.

THEORY AND DISCUSSION

Condensation polymerization is represented schematically as a set of infinite elementary reactions:

$$P_m + P_n \xrightarrow{k_{p_{m,n}}} P_{m+n}$$

$$m, n = 1, 2 \ldots \tag{1}$$

and reaction rates are normally evaluated using the equal reactivity hypothesis[9,10]:

$$\begin{aligned} k_{p_{m,n}} &= k_p \qquad m \neq n;\, m, n = 1, 2 \ldots \\ &= k_{p/2} \qquad m = n \end{aligned} \tag{2}$$

$$r_p = \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}t}[-\mathrm{B}] = \frac{k_p}{2}[-\mathrm{A}]\,[-\mathrm{B}] \tag{3}$$

However, when the monomer reacts at different rate, then

$$k_{p_{1,1}} = k_{11}/2$$

$$\begin{aligned} k_{p_{m,n}} &= k_p \text{ for } m \neq n \\ &= k_p/2 \text{ for } m = n > 1 \end{aligned} \tag{5}$$

if it assumed that all polymer homologues react at the same rate and

$$\frac{\mathrm{d}}{\mathrm{d}t}[P_1] = -(2\frac{k_{11}}{2}[P_1]^2 + k_p[P_1]\,[P_2] + k_p[P_1]\,[P_3] + \ldots)$$

$$= -(k_{11} - k_p)[P_1]^2 - k_p[P_1]\,[P] \tag{6}$$

where $[P] \equiv [P_1] + [P_2] + \ldots$

Similarly writing equations for $\mathrm{d}[P_2]/\mathrm{d}t$, $\mathrm{d}[P_3]/\mathrm{d}t$ etc. and summing the equations for all values of n, one finds that:

$$\frac{\mathrm{d}[P]}{\mathrm{d}t} = -\frac{1}{2}(k_{11} - k_p)[P_1]^2 - \frac{1}{2}k_p[P]^2 \tag{7}$$

Equations (6) and (7) can be rewritten in the following dimensionless form

$$\frac{\mathrm{d}Y}{\mathrm{d}X} = -\frac{1}{2}(R - l)Z^2 - \frac{1}{2}Y^2 \tag{8}$$

$$\frac{\mathrm{d}Z}{\mathrm{d}X} = -(R - 1)Z^2 - YZ \tag{9}$$

where

$$R = \frac{k_{11}}{k_p},$$

$$X = k_p[P]_0 t,$$

$$Y = [P]/[P]_0$$

$$\text{and } Z = [P]_1/[P]_0 \tag{10}$$

The initial conditions for equation (9) and (10) are:

$$Y = Z = 1 \quad \text{at } X = 0 \tag{11}$$

Equations (8) and (9) may be solved numerically to give the extent of conversion, $p(= 1 - Y)$, as a function of

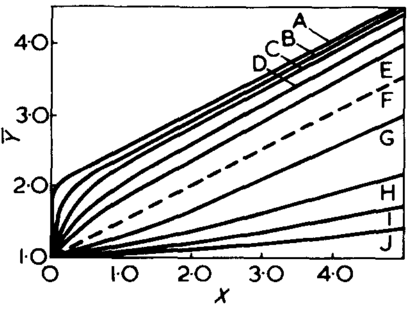

Figure 1 *1/Y versus X* for different values of *R:* A, 100; B, 25.0; C, 10.0; D, 4.0; E, 2.0; F, 1.0; G, 0.50; H, 0.20; I, 0.10, J, 0.05

the dimensionless time, X, for different values of R. *Figure 1* gives the results. The plot for $R = 1$ has been obtained by integrating equation (3):

$$\frac{1}{Y} = \frac{[P]_0}{[P]} = 1 + \frac{1}{2}k_p[P]_0t$$

$$= \left(1 + \frac{X}{2}\right) \qquad (16)$$

According to equation (8), the slope of the 1/Y *versus* X curve for $X \rightarrow 0$ is equal to $R/2$. For small values of X, there is a curvature and as X approaches large values, $1/Y$ (= $\overline{DP}$) *versus* X becomes linear with a slope of 0.5, independent of the value of R. The curvature increases as R increases and the smaller the value of R, the larger is the time taken to reach the linear region. In the linear region, (*Figure 1*) there is a set of parallel lines corresponding to different values of R. This is expected physically because the larger the value of R, the faster is the monomer consumed and the linear region starts from the values of X when the monomer is almost completely consumed. For curves for $R = 25$ and above, only small differences in the behaviour are observed.

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Crystallinity and fusion of low molecular weight poly(ethylene oxide): effect of end-group

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(Received 23 March 1977)

Many interesting observations have been made on low molecular weight fractions of α,ω-hydroxy-poly(ethylene oxide), notably by Kovacs, Skoulios, Spegt and coworkers at Strasbourg[1–4]. Fractions of $\bar{M}_n < 3000$ when crystallized from the melt at (say) 25°C typically form stacked lamella structures[2–5] in which the polymer chains are unfolded [3–5]. In these extended chain crystals the end-groups of the poly(ethylene oxide) chains are concentrated in the surface layers of the lamella crystals. It has been argued[1,6] that the formation of hydroxy–hydroxy hydrogen bonds in the surface layers of the crystalline lamellae is an important factor in determining the mode of crystallization and the stability of the crystals. Our experiments with poly(ethylene oxide) fractions having a variety of end-groups (e.g. alkoxy[7,8], acetoxy[9]) lead us to the view that the experimental results obtained with hydroxy-ended fractions are not unique. (We note a similar viewpoint expressed in ref 2.) Our intention here is to promote this view by the presentation of further experimental results obtained with α,ω-methoxy- and α,ω-ethoxy-poly(ethylene oxide) fractions.

Samples of α,ω-hydroxy-poly(ethylene oxide) were obtained from commercial sources: Shell Chemical Co. Ltd (1000, 1500), Hoechst Chemicals Ltd (2000) and Fluka AG (3000). Before use samples were precipitated from dilute solution in benzene by addition of iso-octane and thoroughly dried. The α,ω-methoxy- and α,ω-ethoxy-poly(ethylene oxide) fractions were prepared by the method described elsewhere[10]. Infra-red spectroscopy, elemental analysis and end-group analysis were used to confirm conversions of hydroxy to alkoxy end-groups exceeding 99%. The molecular weights and molecular weight distributions of the fractions were checked against standard samples by gel permeation chromatography (g.p.c.). We denote the samples by their nominal molecular weights and by a suffix H (hydroxy), M (methoxy) or E (ethoxy). The g.p.c. data listed in *Table 1* show that the chain length distributions are essentially unchanged by the alkoxylation process.

Melting points (T_m, *Table 1*) were measured by dilatometry[11] for fractions crystallized at several temperatures (T_c, *Table 1*) and were found to be independent of T_c. Only single melting transitions were observed. Specific volumes (ν_{sp}, *Table 1*) were measured at 25°C by picnometry[11] for the 1500 fractions crystallized at 25°C. Lamella spacings (l, *Table 1*) were measured by small-angle X-ray scattering[11] at room temperature (~20°C) for samples crystallized at 25° and 35°C and were found to be independent of T_c. Double maxima were observed for 1000H (T_c = 35°C) and 1000M (T_c = 25° and 35°C): this effect is attributable[4] to fractionation during the crystallization process. Because of this complication, and also because of possible fractionation during the preparative processes (*Table 1*), the following remarks are restricted to fractions with $\bar{M}_n > 1500$.

The evidence of the lamella spacings and the specific volumes is that the stacked lamella structure of these fractions is not affected by the end-groups. Comparison of l with the extended-chain lengths of the fractions [calculated assuming 64×10^{-3} nm/g as for the 7:2 helical poly(ethylene oxide) chain[12]] listed in *Table 1* shows that the lamellae contain extended chains. Comparison of ν_{sp} with that of perfectly crystalline poly(ethylene oxide), i.e. 0.813 cm^3/g at 25°C[12], shows that the stacked lamella structures contain a significant amount of non-crystalline material.

In *Table 1* the melting points for a given molecular weight are practically identical. The stability of a stacked lamella polycrystal is measured by its free energy of formation from the