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The Temperature Dependence of Copolymerization Reactivity Ratios

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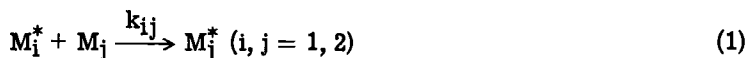
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NEW INTERPRETATIONS

The Temperature Dependence of Copolymerization Reactivity Ratios

In the copolymerization of vinyl monomers, four (and only four) reactions are usually required to describe the propagation:



The instantaneous composition of polymer formed is then given as

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2f_1 f_2 + f_2 f_2^2) \quad (2)$$

where F_i and f_i are mole fractions of monomer i in the polymer and feed, respectively, and r_1 and r_2 are the reactivity ratios defined as:

$$r_1 = k_{11}/k_{12}; r_2 = k_{22}/k_{21} \quad (3)$$

These reactivity ratios are functions of (a) the monomers used, (b) the mechanism of polymerization, and (c) the conditions of the polymerization.

For constant (a) and (b), the questions arise: How strong a function of polymerization conditions are the numerical values of r_1 and r_2 ? Can one alter reactivity ratios for a given monomer pair by changing reaction condition?

For ionic copolymerizations, solvent and/or counter-ion changes often provide convenient means of doing this, but for free radical copolymerizations temperature and pressure are almost the only significant experimental variables. Since high pressure presents numerous experimental problems, temperature is often considered as a simple means of effecting changes in reactivity ratios. Therefore, let us consider its influence on reactivity ratios for simple systems which follow Eqs. (1) and (2).

Begin by considering a reactivity ratio as the ratio of two Arrhenius expressions

$$r_1 = \frac{A_{11} \exp(-E_{11}/RT)}{A_{12} \exp(-E_{12}/RT)} \quad (4)$$

Invoke the experimental fact that entropies of polymerization are approximately equal, and extrapolate this to the reasonable assumption that entropies of activation are approximately equal. Therefore A_{11} approximately equals A_{12} and Eq. (4) becomes

$$r_1 = \exp[-(E_{11} - E_{12})/RT] \quad (5)$$

$$\ln r_1 = -(E_{11} - E_{12})/RT \quad (6)$$

The temperature dependence of the reactivity ratio can then be written as

$$\frac{d \ln r_1}{d 1/T} = - \frac{(E_{11} - E_{12})}{R} \quad (7)$$

Combining Eqs. (6) and (7) we see that

$$\frac{d \ln r_1}{d 1/T} = T \ln r_1 \quad (8a)$$

Similarly

$$\frac{d \ln r_2}{d 1/T} = T \ln r_2 \quad (8b)$$

The term $(-RT \ln r)$ is the apparent activation energy for r . Since the value of r itself appears in its activation energy, only large values of r (or of $1/r$) will have strong temperature dependencies.

Equation (8) predicts that a reactivity ratio greater than unity will decrease with increasing temperature and vice versa. A value of unity will always be approached for r with increasing temperature, as shown in Fig. 1. Therefore, the tendency toward random copolymerization is enhanced by an increase in temperature. Conversely, the tendency toward alternating copolymerization is reduced by an increase in temperature. However, the effect of temperature is so small that the change in a reactivity ratio with a reasonable change in temperature will be experimentally significant only for those reactivity ratios which are very large or very small. If we take "very large" to be a value greater than 10 (and "small" less than 0.1), it can be seen from inspections of tabulated reactivity ratios that only about one-fourth of the systems which have been studied can be expected to have significant temperature dependencies for one or both reactivity ratios. Most such systems

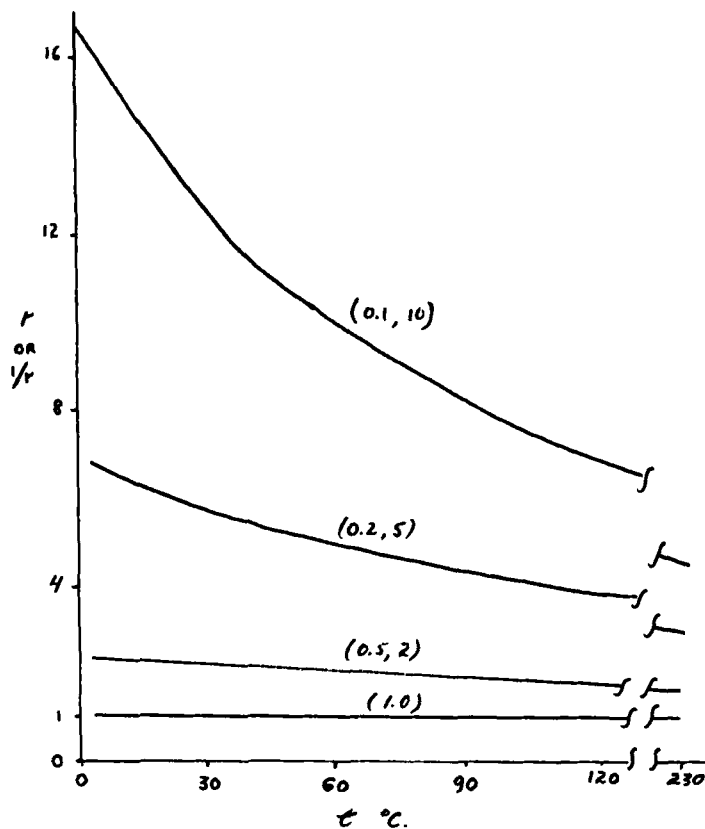


Fig. 1. Calculated variation of reactivity ratios with temperature according to Eq. (8). Values on curve are of r at 60°C .

involve a conjugated and an unconjugated monomer pair, such as styrene-vinyl acetate.

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