

DISTRIBUTION  
OF ACTIVATION ENERGIES  
IN THE LOW-TEMPERATURE DISPERSION  
OF POLY(2-HYDROXYETHYL METHACRYLATE)

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Dispersions of glassy polymers are characterized by a wide distribution of relaxation or retardation times, similarly to the main transition from glassy to rubbery state. If the relaxation time,  $\tau$ , is expressed in the standard form, that is,  $\tau = \tau_0 \exp(U/RT)$ , it can be seen that the distribution of relaxation times,  $G(\tau)$ , can generally be a consequence (*cf.*<sup>1-3</sup>) of the distribution of the pre-exponential factor,  $\tau_0$ , or activation energies,  $U$ , or else a consequence of the combination of both these distributions ( $R$  being the gas constant and  $T$  being absolute temperature). For the main transition region, the applicability of the time-temperature superposition is a characteristic feature, which means (*cf.*<sup>4</sup>) that  $\tau_0$  is the distributed quantity. From the viewpoint of the conventional theory of thermally activated rate processes, activation entropy<sup>5</sup> is therefore the distributed term (in the notation used this term is comprised in  $\tau_0$ ). Lately, an attempt<sup>6</sup> has been made at a phenomenological description, which considers the distribution of activation energies in the main transition region; however, this alternative approach has not yet been verified in a more general manner.

Dispersions of polymers in the glassy state are generally characterized by changes in the shape of frequency (time) dependences of both components of the complex modulus of elasticity due to a change in temperature, so that the ordinary time-temperature superposition cannot be used. Different temperature dependences of the individual relaxation times indicate that the activation energy is a distributed term. At the same time, for relaxation motions of short segments<sup>7,8</sup> or side chains<sup>9</sup>,  $\tau_0$  can be regarded as a temperature-independent constant. This assumption, *i.e.* the same values of  $\tau_0$  for all  $\tau$ , has been applied in our earlier work<sup>10</sup>, in which isochronal temperature dependences of the components of the complex modulus of elasticity were used to calculate the activation energies,  $U$ , and distribution parameters,  $Q$ , of the Fuoss-Kirkwood equation<sup>11</sup> for the low-temperature dispersion of poly(2-hydroxyethyl methacrylate) and its homologues. The  $U$  and  $Q$  values thus obtained are in good correspondence with those following from isothermal dielectric measurements, so that, in the first approximation,  $\tau_0$  can be considered a constant, and the distribution of the relaxation times  $\tau$  can be assigned to the distribution of the activation energies  $E(U)$ . It has been an objective of the present work to determine the distribution  $E(U)$  which would correspond to the previously calculated<sup>10</sup> parameter  $Q$  and its temperature dependence.

RESULTS AND DISCUSSION

The use of the Fuoss-Kirkwood equation<sup>11</sup> in the description of the relaxation processes means that the corresponding distribution function of the relaxation times has the form

$$F(s) = (Q/\pi) \cos(\pi Q/2) \cosh(Qs) / [\cos^2(\pi Q/2) + \sinh^2(Qs)], \quad (1)$$

in which  $s = \ln(\tau/\tau_m)$ ,  $\tau_m = \tau_0 \exp(U_m/RT)$  being the most frequent relaxation time, for which the loss modulus assumes its highest value,  $G''_m$ . To calculate the distribution  $E(U)$  from

the distribution  $F(s)$ , the variable  $s$  must be expressed in terms of the activation energies (cf.<sup>2,8</sup>)

$$F(s) ds = \{F[(U - U_m)/RT]/RT\} dU = E(U) dU. \quad (2)$$

It can be seen from Eqs (1) and (2) that for  $T = \text{const.}$ , and thus also  $Q = \text{const.}$ , the distribution functions  $F(s)$ , resp.  $E(U)$  are symmetrical around the most frequent values of  $\tau_m$ , resp.  $U_m$ . These distributions are the broader the lower the parameter  $Q$  ( $0 < Q \leq 1$ ). In the case of isothermal measurements the loss modulus attains the value of  $G_m''$  at a frequency  $\omega_m = 1/\tau_m$ , so that, if Arrhenius' relationship is used, the activation energy will be equal to  $U_m$ .

An example of the calculation of  $E(U)$  has been carried out for the low-temperature dispersion of poly(2-hydroxyethyl methacrylate). We have established in an earlier work<sup>10</sup> that the temperature dependence of the distribution parameter can approximately be described in terms of a single empirical relationship  $Q = K_1 + K_2 T$ , in which  $K_1, K_2$  are constants. After substitution in Eq. (1), the following expression is obtained for the distribution of the activation energies:

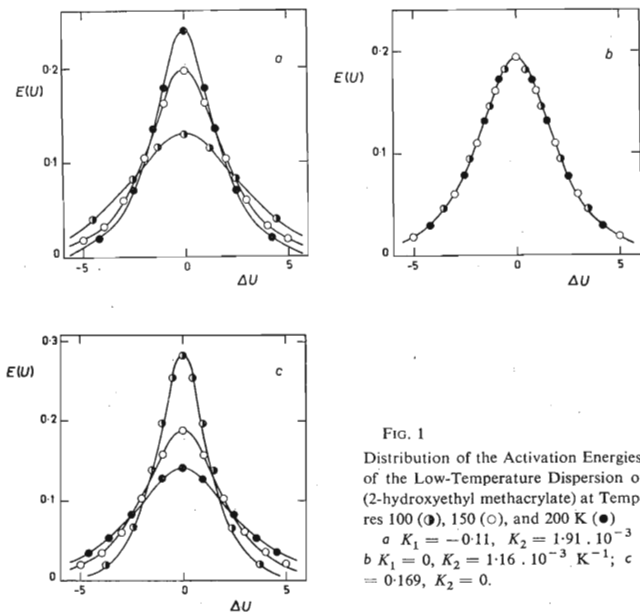


FIG. 1

Distribution of the Activation Energies  $E(U)$  of the Low-Temperature Dispersion of Poly(2-hydroxyethyl methacrylate) at Temperatures 100 (●), 150 (○), and 200 K (●)

a  $K_1 = -0.11$ ,  $K_2 = 1.91 \cdot 10^{-3} \text{ K}^{-1}$ ;  
 b  $K_1 = 0$ ,  $K_2 = 1.16 \cdot 10^{-3} \text{ K}^{-1}$ ; c  $K_1 = 0.169$ ,  $K_2 = 0$ .

$$E(U) = [(K_1/T + K_2)/\pi R] \frac{\cos[\pi(K_1 + K_2T)/2] \cosh[(K_1/T + K_2)(U - U_m)/R]}{\cos^2[\pi(K_1 + K_2T)/2] + \sinh^2[(K_1/T + K_2)(U - U_m)/R]} \quad (3)$$

It is clear from Eq. (3) that the distribution  $E(U)$  will always more or less vary with temperature according to the values which the constants  $K_1, K_2$  assume. We shall calculate the distribution  $E(U)$  for three different temperature dependences of the parameter  $Q(T)$ .  $K_1 = -0.11$  and  $K_2 = 1.91 \cdot 10^{-3} \text{ K}^{-1}$  were found to be the mean constant values for the low-temperature dispersion of poly(2-hydroxyethyl methacrylate)<sup>10</sup>. (For the dispersion temperature  $T_\gamma = 146 \text{ K}$ ,  $Q_\gamma = 0.169$ ). In some cases, for instance if  $K_1$  is subject to a comparably large error, thus losing its justification, the relationship<sup>10</sup>  $Q = K_2T$  is sufficient to describe the temperature dependence of the parameter  $Q$ . At the same time, it can be seen from Eq. (3) that for values  $K_1$  near zero, the changes in  $E(U)$  with temperature will be minimum. We therefore chose as another example the values  $K_1 = 0$  and  $K_2 = 1.16 \cdot 10^{-3} \text{ K}^{-1}$ , which lead — for temperature  $T_\gamma$  — also to  $Q_\gamma = 0.169$ . While treating the results of isochronal measurements in an earlier paper<sup>12</sup>, we used a simplifying assumption, *viz.* that the parameter  $Q$  is temperature-independent; we therefore chose  $Q = K_1 = 0.169$  ( $K_2 = 0$ ) as the third example. For all three cases described above, the distribution  $E(U)$  was calculated in dependence on  $\Delta U = U - U_m$  ( $U_m$  is approximately equal<sup>10</sup> to 11 kcal/mol), the temperatures being 100, 150, and 200 K (Fig. 1). Large temperature differences (approximately  $T_\gamma \pm 50 \text{ K}$ ) were chosen in order to stress the possible changes of the distribution  $E(U)$  with temperature.

The  $K_1$  and  $K_2$  values, determined in an earlier work<sup>10</sup>, lead to a conclusion that the distribution of activation energies  $E(U)$ , corresponding to the low-temperature dispersion of poly(2-hydroxyethyl methacrylate), either does not virtually change with temperature (Fig. 1b), or becomes narrower with increasing temperature (Fig. 1a). This result is consistent with the findings acquired to date<sup>3,13</sup>, that an increase in the internal mobility with temperature has a trend of depressing the differences between the conditions of motions of the individual kinetic units. On the contrary, a simplifying assumption that  $Q$  is temperature-independent is not suitable in the case of the distribution  $G(\tau)$  resulting from the distribution  $E(U)$ , since it would mean, as a consequence, that the distribution  $G(\tau)$  would considerably (and in a defined manner) be extended with temperature, which, however, is at variance with the experimental results.

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