442. *The Kinetics of Catalytic Polymerizations. Part V.* The Molecular-weight Distribution of Poly-(α-methylstyrene) prepared by the Aluminium Chloride-catalyzed Polymerization.*

By D. O. Jordan and A. R. Mathieson.

The molecular-weight distribution data obtained by Hersberger, Reid, and Heiligmann (*Ind. Eng. Chem.*, 1945, **37**, 1073) for α-methylstyrene have been interpreted by employing the distribution functions derived in Part IV. The information obtained when taken in conjunction with the kinetics of the reaction given in Part III (*J.*, 1952, 2354) indicates that this reaction over the temperature range −130° to 0° is terminated by monomer deactivation and solvent transfer.

Polystyrene and poly-(α-methylstyrene) prepared at room temperature by aluminium chloride catalysis in carbon tetrachloride solution (Parts I and III, *J.*, 1952, 611, 2354) are of too low a molecular weight to permit accurate fractionation. Hersberger, Reid, and Heiligmann (*Ind. Eng. Chem.*, 1945, **37**, 1073), however, have fractionated two samples of poly-(α-methylstyrene) prepared by the aluminium chloride-catalyzed polymerization in ethyl chloride solution, one of relatively high molecular weight (*ca.* 10^5), prepared at −130°, and the other of lower molecular weight (*ca.* 10^4), prepared at −50°. The data obtained permit the application of the theoretical distribution functions developed in Part IV,* and thereby the production of information on the reaction mechanism at low temperatures. The mechanism at room temperature has already been discussed in Part III (*loc. cit.*).

The two polymers have very different distribution curves, that of the high molecular weight polymer having a form indicating predominantly monomer termination or monomer transfer, whereas that of the low molecular weight polymer has a form indicating predominantly spontaneous or solvent termination, or solvent transfer † [see Part IV, Figs. 1 and 2, curves (*a*) and (*b*)]. Hersberger, Reid, and Heiligmann calculated molecular weights from intrinsic viscosities by using Kemp and Peters's equation (*Ind. Eng. Chem.*, 1942, **34**, 1097) which relates to polystyrene. Consequently it has been thought advisable to recalculate the molecular weights (M) by using the equation obtained in Part III (*loc. cit.*), *viz.*:

$$[\eta] = 0{\cdot}0115 + 1{\cdot}93 \times 10^{-5}M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $[\eta] = \lim_{c \to 0} \eta_{sp}/c$ and c is the concentration of the solution in g./100 c.c. The use of either equation, however, involves a large extrapolation for the high polymer, since each was established for low molecular weight polymers. This recalculation of the molecular weights does not involve any change in the shape of the distribution curves, since both equation (1) and Kemp and Peters's equation (*loc. cit.*) have $[\eta] \propto M$.

The symbols employed in this paper are identical with those used in Part IV.

The Distribution Curve for the High Polymer.—The experimental data are shown in Fig. 1, and the shape of the experimental integral (Fig. 1, curve 1) and differential (Fig. 2, curve 5) distribution curves is such as to indicate the predominance of monomer termination or monomer transfer. We have observed monomer termination in this system at 0° (Part III, *loc. cit.*) and have therefore based our calculations on the occurrence of this termination reaction.

For a reaction scheme involving only monomer termination, $k_{tm}/k_p = \lambda_m = 1/n$ where n is the number-average chain length of the polymer. The value of λ_m for the high polymer is found to be 0·000628. By substituting this value into the equation (Part IV) for the weight fraction (w_r)

$$w_r = r\lambda_m{}^2/(1 + \lambda_m)^{r+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

---

* Part IV, preceding paper.

† Hersberger, Reid, and Heiligmann incorrectly plotted the differential distribution curve for the high polymer from the data given elsewhere in their paper. This curve has been reproduced by Plesch (*Research*, 1949, **2**, 267). The correct curve is given in Fig. 2.

we obtain the integral and differential distribution curves shown in Fig. 1 (curve 2) and Fig. 2 (curve 6), respectively. Whilst the theoretical curves are of the correct shape, they are by no means coincident with the experimental curves. For a reaction involving both monomer termination and monomer transfer the appropriate equation is (Part IV)

$$w_r = r\lambda_m^2(1 + 1/\phi_{m_3})/(1 + \lambda_m)(1 + \lambda_m + \lambda_m/\phi_{m_3})^r \quad . \quad . \quad . \quad . \quad (3)$$

FIG. 1. *Integral distribution curves for the high polymer.*

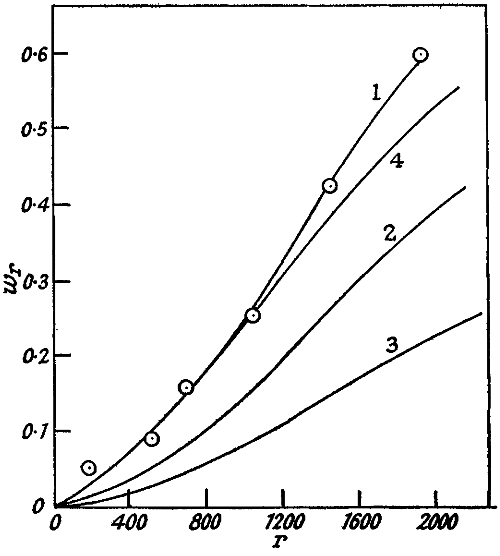


FIG. 2. *Differential distribution curves for the high polymer.*

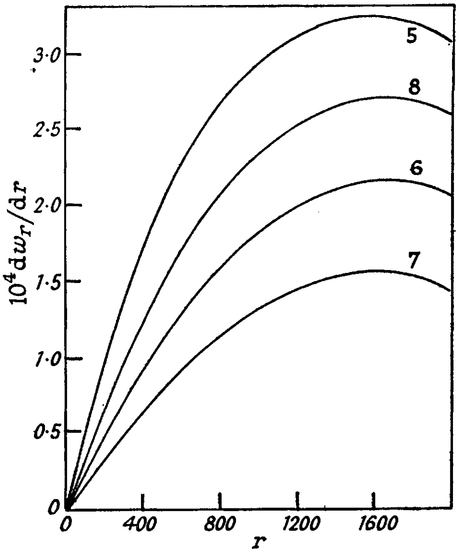


FIG. 3. *Integral distribution curves for the low polymer.*

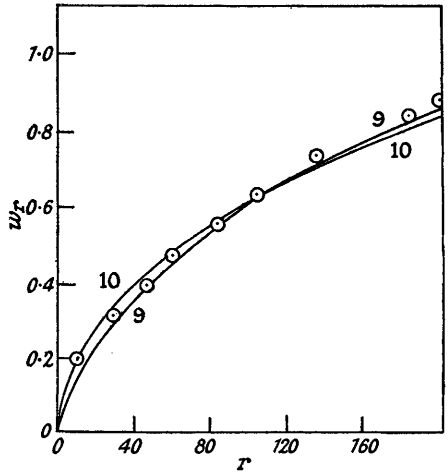
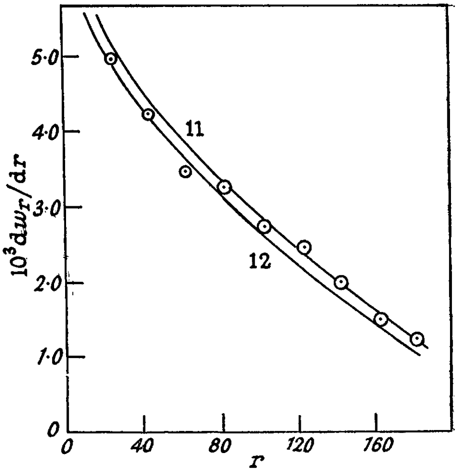


FIG. 4. *Differential distribution curves for the low polymer.*



In order to apply this equation we shall consider the case where $V_{tr} = V_{tm}$, *i.e.*, $\phi_{m_3} = 1$ and $\lambda_m = 1/2n$. Curves 3 (Fig. 1) and 7 (Fig. 2) were obtained, and it is apparent that the introduction of monomer transfer has produced a shift in the position of the theoretical distribution curves in the wrong direction. This will be true whatever value of the ratio V_{tr}/V_{tm} is employed. Easily the best correspondence between a theoretical and the experimental distribution curve is that obtained with theoretical curves (curve 4, Fig. 1 and curve 8, Fig. 2) calculated from the equation (Part IV)

$$w_r = 0{\cdot}7r\lambda_{\text{m}}^2/(1 + \lambda_{\text{m}})^{r+1} + 0{\cdot}3[\lambda_{\text{st}}/M(1 + \lambda_{\text{st}}/M)^r]_M^{M_0} \quad . \quad . \quad . \quad (4)$$

which describes a reaction scheme involving 70% monomer termination and 30% solvent transfer or termination.

The Distribution Curve for the Low Polymer.—The experimental data are given in Fig. 3; the shape of the experimental integral (Fig. 3) and differential (Fig. 4) distribution curves are such as to indicate the prevalence of spontaneous or solvent termination or solvent transfer. The experimental results also show that at $-50°$ the reaction ceased in certain cases before all the monomer was consumed. The average value of the ratio (monomer consumed) : (catalyst concentration) was 330 and the corresponding value of the chain length calculated by equation (1) was 84, which means that one catalyst molecule can initiate on average $330/84 \approx 4$ polymer chains. This evidence indicates clearly that some form of transfer or of catalyst regeneration is taking place. In view of the conclusions drawn from the shape of the distribution curves we are restricted in our choice of such mechanisms to spontaneous or solvent termination with release of active catalyst, or to solvent transfer associated with monomer termination such that $V_{\text{st}}/V_{\text{t}} = 4$, this ratio being sufficiently large to give a distribution curve of the required form. Calculations have been made for both these systems, and curves 9 (Fig. 3) and 11 (Fig. 4) have been obtained by the use of the equations (Part IV)

$$w_r = [\lambda/M(1 + \lambda/M)^r]_M^{M_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

for spontaneous termination,

$$w_r = [\lambda_{\text{ts}}/M(1 + \lambda_{\text{ts}}/M)^r]_M^{M_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

for solvent termination, and

$$w_r = [\lambda_{\text{m}}/\phi_{\text{m}_2}M(1 + \lambda_{\text{m}} + \lambda_{\text{m}}/\phi_{\text{m}_2}M)^r]_M^{M_0} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

for solvent transfer and monomer termination. The values of λ, λ_{ts}, ϕ_{m_2}, and λ_{m} have been calculated as follows: the relations $\lambda/M = \lambda_{\text{ts}}/M = 1/n$, and the experimental data, give $M_0 = 2{\cdot}3$ moles/l. and $n = 84$, hence $\lambda = \lambda_{\text{ts}} = 0{\cdot}0274$ mole/l.

$V_{\text{st}} = 4V_{\text{tm}}$ and $1/\phi_{\text{m}_2} = 4M$, and hence $\phi_{\text{m}_2} = 0{\cdot}1087$ l. mole^{-1}; also $n = V_{\text{p}}/(V_{\text{tm}} + V_{\text{st}})$ and $1/n = k_{\text{tm}}/k_{\text{p}} + k_{\text{st}}S/k_{\text{p}}M = \lambda_{\text{m}} + \lambda_{\text{m}}/\phi_{\text{m}_2}M$, hence $\lambda_{\text{m}} = 0{\cdot}00238$.

Slightly better agreement with the experimental data is obtained by using the more exact form of equation (7), *viz.* (Part IV):

$$w_r = Ar\lambda_{\text{m}}^2/(1 + \lambda_{\text{m}})^{r+1} + B[\lambda_{\text{st}}/M(1 + \lambda_{\text{st}}/M)^r]_M^{M_0} \quad . \quad . \quad . \quad . \quad (8)$$

with the values of A and B (0·2 and 0·8, respectively) being determined by the experimental condition that $V_{\text{st}}/V_{\text{tm}} = 4$ and $A + B = 1$, in contrast to the case of the high polymer where the values of A and B were arbitrarily chosen to obtain the most satisfactory theoretical curve. The curves so obtained are given in Fig. 3, curve 10, and Fig. 4, curve 12.

Discussion.—The conclusions concerning chain termination to be drawn from the distribution curves at $-130°$ and $-50°$, and from the kinetic analysis at 0° (Part III, *loc. cit.*), are summarized in the table. It is evident that the one scheme common to the reaction at all three temperatures is monomer termination plus solvent transfer, and so this mechanism is to be preferred. That the same mechanism should be operative over the whole temperature range is to some extent indicated by the fact that the variation of

Permitted termination mechanisms for the aluminium chloride-catalyzed polymerization of α-methylstyrene in ethyl chloride solution.

Temperature	Permitted termination mechanisms
−130°	Monomer termination (70%) + solvent termination or transfer or spontaneous termination (30%)
− 50°	Either (1) monomer termination (20%) + solvent termination or transfer or spontaneous termination (80%)
	Or (2) solvent termination or transfer or spontaneous termination (100%)
0°	Monomer termination + solvent transfer

molecular weight with temperature obeys the same law over this temperature range (Part II, *J.*, 1952, 621). This mechanism is the same as that established kinetically for the same polymerization in carbon tetrachloride solution (Part III, *loc. cit.*) and is closely similar to that established for the aluminium chloride-catalyzed polymerization of styrene in carbon tetrachloride (Part II, *loc. cit.*).

The decrease in molecular weight with increase of temperature (Part II, *loc. cit.*) is explained by the increase in the ratio of transfer to termination. At 0° this ratio is very probably not dissimilar to that at —50° since the molecular weights of the polymers obtained are comparable.

THE UNIVERSITY, NOTTINGHAM.

[*Received, February* 18*th*, 1952.]