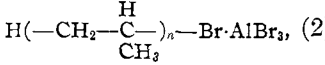
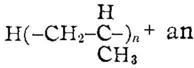
Mechanism of the Polymerization of Propylene with Aluminum Bromide-Hydrogen Bromide Catalyst[1]

BY FRANK R. MAYO AND CHEVES WALLING

The recent excellent experimental work of Fontana and Kidder[2] on the kinetics of the polymerization of propylene by aluminum bromide-hydrogen bromide at about −80° showed that, after the steady rate is obtained, the rate of polymerization is consistent with the equation

$$\frac{-\mathrm{d}[\mathrm{m}]}{\mathrm{d}t} = \frac{kKc[\mathrm{m}]}{1 + K[\mathrm{m}]}$$

where [m] is the monomer concentration, c is the total concentration of catalyst in all forms, K is the equilibrium constant for the reversible formation of a postulated complex formed from a catalyst–monomer complex plus additional monomer, and k is the rate constant for chain lengthening, considered to be rearrangement of the catalyst–polymer–monomer complex into a stable form.

The object of this communication is to present an alternative interpretation of their data. Our scheme assumes (1) that essentially all of the catalyst (or promoter) is bound to the polymer as an un-ionized complex such as  $\mathrm{H(—CH_2—\overset{H}{\underset{CH_3}{C}}—)_n—Br{\cdot}AlBr_3}$, (2) that the first rate determining step in the propagation reaction is the dissociation of this complex into  $\mathrm{H(–CH_2–\overset{H}{\underset{CH_3}{C}}–)_n^+}$ and $\mathrm{AlBr_4^-}$, (3) that actual chain propagation involves addition of the carbonium ion and anion to the propylene before recombination of the original ions occurs. Since, in a solvent of low dielectric constant, the dissociated complex will exist as an *ion pair* surrounded by a cage of solvent and propylene molecules, recombination will be kinetically first order, and the situation parallels that suggested by Matheson[3] for peroxide-initiated polymerizations. Thus, the fraction of the dissociations in which the carbonium ion will add a propylene unit before recombining with the negative ion will be $K'[\mathrm{m}]/(1 + K'[\mathrm{m}])$ where K' is the ratio of the rate constant for the reaction of the ion pair with propylene divided by the rate constant for recombination of the ion pair. The over-all rate of polymerization is then

$$\frac{-\mathrm{d}[\mathrm{m}]}{\mathrm{d}t} = \frac{k'K'c\ [\mathrm{m}]}{1 + k'\ [\mathrm{m}]}$$

where k' is the rate of dissociation of the catalyst-polymer complex, c.

The form of the equation shows that an appreciable fraction of the dissociations are accompanied by growth, and also that only one growth step occurs at a time. These requirements are easily met if both ions simultaneously add to the propylene. Experiments with scale models indicate the probability of this course; they also show that the two mechanisms here considered differ only in details. When this interpretation is applied to isobutylene[4], styrene[5] and vinyl ethers[6] the integral orders of these polymerizations with respect to monomer suggest that the fraction of ionizations resulting in chain growth is lower, a result to be expected if the respective complexes ionize more readily but give less reactive carbonium ions.

Our proposed interpretation provides a mechanism for carbonium ion polymerizations in solvents of low dielectric constant similar to that proposed for the polymerization of alkenes by sulfuric acid, the solvolyses of alkyl halides, and the Friedel–Crafts reaction. Further, it accounts more readily than the mechanism of Fontana and Kidder for observations[5,6] that the rates of carbonium ion polymerizations increase very rapidly with the dielectric constant of the solvent. However, our interpretation is inconsistent with one conclusion of Fontana and Kidder, that ΔH for reversible addition of monomer to complex is 8.9 kcal./mole and that K decreases with increasing temperature. In our scheme, this corresponds to the anomaly that the activation energy for simple recombination of two ions is 8.9 kcal./mole *larger* than for addition of propylene to a carbonium ion. Since, in the experiments cited, an appreciable but unknown proportion of catalyst precipitated in an inactive form from each reaction mixture, we suggest that experiments at different temperatures have not yielded correct temperature coefficients, a point which is a critical test of our proposal.

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(1) Contribution No. 95 from the General Laboratories of the United States Rubber Company.

(2) Fontana and Kidder, THIS JOURNAL, **70**, 3745 (1948).

(3) Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

(4) Evans and Meadows, *J. Polymer Sci.*, **4**, 359 (1949).

(5) Pepper, *Trans. Faraday Soc.* **45**, 397, 404 (1949).

(6) Eley and Richards, *ibid.*, 425.

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Investigation of Possible Interactions between Thallium(I) and Thallium(III) in Solution and in the Crystalline Thallium Sesqui-halides

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The discovery[1] that the rate of radioactive exchange between Tl(I) and Tl(III) in aqueous solutions is slow has prompted us to: (1) examine, by a radiochemical method, whether or not the substances $\mathrm{Tl_2Cl_3}$ and $\mathrm{Tl_2Br_3}$ contain non-equivalent Tl(I) and Tl(III) ions; (2) look for non-additive light absorption[2] in some aqueous solutions containing Tl(I) and Tl(III). Problems (1) and (2) are related because the $\mathrm{Tl_2X_3}$ compounds are more colored than the corresponding TlX or $\mathrm{TlX_3}$ compounds.[3]

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(1) Harbottle and Dodson, THIS JOURNAL, **70**, 880 (1948); Prestwood and Wahl, *ibid.*, **71**, 3137 (1949); see also pp. 226, 205 of "Isotopic Exchange Reactions and Chemical Kinetics," Brookhaven National Laboratory, Patchogue, New York, Dec., 1948.

(2) Whitney and Davidson, THIS JOURNAL, **69**, 2076 (1947).

(3) Benrath, *Z. anorg. Chem.*, **93**, 161 (1915); **136**, 358 (1924).