Polymerization of Methacrylonitrile Initiated by Ascaridole and Dihydroascaridole[1]

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The decomposition of ascaridole (1,4-epidioxy-2-*p*-menthene) and dihydroascaridole (1,4-epidioxy-*p*-menthane) by the action of heat,[3] light[4] and metallic ions[3a,5] has been studied by several workers. The recent work of Tobolsky and Russell[4] has demonstrated that the primary diradical produced by the photolysis of ascaridole in methyl methacrylate at 60° rapidly reacts to produce monoradical initiation of polymerization. The present investigations support the results of these workers and enable a more detailed consideration of the decomposition reaction of dihydroascaridole.

Experimental

Reagents.—Methacrylonitrile (Shell Development Co.) was vacuum distilled from inhibitor under nitrogen: b.p. 37.5° (100 mm.); $n^{20}D$ 1.4007.

Tetralin was purified by sulfuric acid washing followed by fractional distillation. The product gave no response to iodometric peroxide tests.

Ascaridole (Burroughs, Wellcome Co.) was used as obtained or prepared by distillation of chenopodium oil (Amend Drug and Chemical Co.). An infrared absorption spectrum did not differ significantly from that reported by Szmant and Halpern.[6]

Dihydroascaridole was prepared from ascaridole according to the method of Paget.[5]

Di-*t*-butyl peroxide 97–98% pure (Shell Development Co.) was used as obtained.

Procedures.—Polymerization of methacrylonitrile at 115° with the various initiators was performed in conventional manner. Viscosity measurements were performed with an Ubbelohde dilution viscometer having a flow time of 120 seconds for acetone at 20°. Using a previously established[7] relationship between limiting viscosity number $[\eta]$ and number average degree of polymerization, $\bar{P}_n$, for unfractionated polymethacrylonitrile terminated by disproportionation (*i.e.*, transfer), equation 1 was calculated by the method of Baysal and Tobolsky[8] for polymer chains initiated by a monoradical source and terminated by recombination.

$$\bar{P}_n = 1.28[\eta]^{1.31} \quad (1)$$

Peroxide estimations of dihydroascaridole in various solvents were performed by the hydriodic acid method of Vaughan, *et al.*[9] In runs employing methacrylonitrile solvent, the polymer formed during decomposition obscured the end-point of the thiosulfate titration, requiring separation of polymer prior to titration. This was achieved by adding known quantities of solution dropwise to a measured excess of glacial acetic acid, filtering the precipitate, and titrating an aliquot of the filtrate.

Results and Discussion

Rate and molecular weight measurements have been made on the polymerization of methacrylonitrile at 115° initiated thermally and by ascaridole, dihydroascaridole and di-*t*-butyl peroxide. A plot of $1/\bar{P}_n$ *versus* rate of polymerization (R_p) is shown in Fig. 1. It is seen that all experimental values lie on a common straight line. In accordance with the kinetic derivations of Tobolsky and co-workers,[10] the linearity of the plot indicates that no significant transfer reaction occurs between growing polymer radicals and the peroxide initiators. In addition, the magnitude of the intercept on the ordinate axis is 0.5×10^{-4}, signifying that the sum of the transfer constants for the reaction of growing radicals with monomer and solvent is small. Since the polymerization data obtained with ascaridole and dihydroascaridole lie on the same linear plot as those obtained with di-*t*-butyl peroxide, a known monoradical initiator, it is concluded that the former two peroxides also initiate *via* monoradicals.

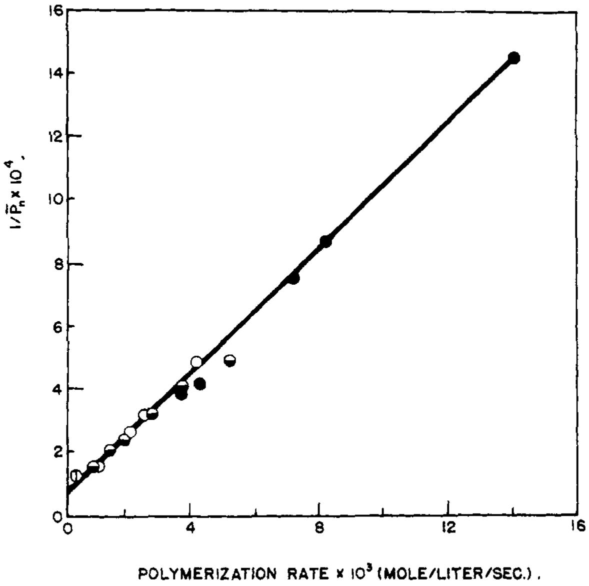

Fig. 1.—Polymerization of methacrylonitrile at 115° initiated by various catalysts: ●, di-*t*-butyl peroxide; ◒, ascaridole; ○, dihydroascaridole; ⦶, thermal. Methacrylonitrile concentration = 7.93 *M* in dimethylformamide.

The rate of initiation of polymer chains (R_i) can be obtained[10a] from equation 2 (assuming no disproportionation)

$$R_i = \frac{2A'}{[M]^2} R_p^2 \quad (2)$$

where A' is calculated from the slope of the line in Fig. 1 to be 6.76 l. sec. mole^{-1}, and [M] is the monomer concentration. The rate of initiation may also be defined by the relation

$$R_i = 2fk_d\,[\text{Cat}] \quad (3)$$

where k_d[Cat] is the rate of decomposition of the catalyst and f, the catalyst efficiency, is the fraction of primary radicals which are effective in starting chains. The specific rate constant k_d has been determined for dihydroascaridole at 115° in three widely different solvents and the results obtained are as follows: 0.90×10^{-6} sec.$^{-1}$ in tetralin, 0.72 $\times 10^{-6}$ in chlorobenzene and 0.92×10^{-6} in a 2:1

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(3) (a) E. K. Nelson, This Journal, **33**, 1404 (1911); (b) O. Wallach, *Ann.*, **392**, 52 (1912); (c) F. Richter and W. Priesting, *Ber.*, **64**, 878 (1931); (d) H. Thomas and W. Dobke, *Arch. Pharm.*, **268**, 128 (1931); (e) C. G. Moore, *J. Chem. Soc.*, 234 (1951).

(4) K. E. Russell and A. V. Tobolsky, This Journal, **76**, 395 (1954).

(5) H. Paget, *ibid.*, 829 (1938).

(6) H. H. Szmant and A. Halpern, This Journal, **71**, 1133 (1949).

(7) N. Fuhrman and R. B. Mesrobian, *ibid.*, **76**, 3281 (1954).

(8) B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **9**, 171 (1952).

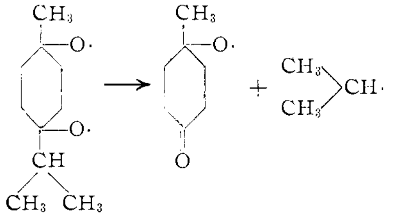
(9) F. H. Dickey, J. H. Raley, F. F. Rust, R. S. Tresede and W. F. Vaughan, *Ind. Eng. Chem.*, **41**, 1673 (1949).

(10) (a) D. H. Johnson and A. V. Tobolsky, *ibid.*, **74**, 938 (1952); (b) B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).

volume ratio of methacrylonitrile to dimethylformamide. The rate constant in each solvent was evaluated from four or more experimental values in the range of 4–19% decomposition at an initial concentration of peroxide of 0.025 mole/l. which is comparable to the quantities employed in the polymerization measurements presented in Fig. 1.

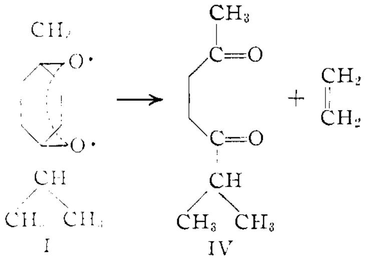
The average value for f calculated from equations 2 and 3 is 1.1 assuming no disproportionation and employing a value of 0.92×10^{-6} sec.$^{-1}$ for k_d. If termination of growing chains occurs exclusively by disproportionation, f will have the value 0.55. In either event it is apparent that the majority of the radicals derived by the decomposition of dihydroascaridole initiate polymer chains as monoradicals. Additionally, the observation that k_d does not vary appreciably for decompositions run in three widely different solvents, demonstrates that the recombination of primary diradicals to reform dihydroascaridole is not effected to any great extent by the solvent medium.

A convenient mechanism to describe the transformation of the primary diradical (I) into two monoradicals (II and III), is that denoted in equation 4



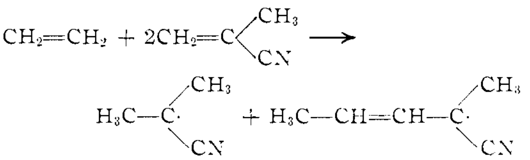
(4)

On the other hand, Moore[3c] has identified a diketone IV to be one of the major products (43 mole %) obtained when dihydroascaridole is thermally decomposed at 240°. Other decomposition products were an unidentified gas (105 mole % estimated as ethylene) and a viscous, polymeric residue. The mechanism suggested by Moore to describe the formation of the diketone is



I IV (5)

This mechanism specifies that the primary diradicals dismute to non-radical structures which might not be expected to initiate vinyl polymerization. An approximate calculation of the heat changes in steps (4) and (5) indicates that whereas (4) is exothermic by 19 kcal./mole, (5) is considerably more exothermic, *viz.*, 102 kcal./mole. Although a reaction does not always follow the energetically more favorable path, since it is known that step (5) predominates at 240°, it can be assumed that (5) is the preferred path at 115° as well. The ethylene molecule formed by step (5) will undoubtedly contain energy in excess of the ground state and accordingly one can picture the reaction of an excited ethylene molecule and methacrylonitrile to involve the transfer of a hydrogen atom to produce two monoradicals analogous to the mechanism of styrene thermal initiation suggested by Mayo.[11]



$$CH_2{=}CH_2 + 2CH_2{=}C\begin{smallmatrix}\diagup CH_3\\ \diagdown CN\end{smallmatrix} \longrightarrow H_3C{-}\overset{CH_3}{\underset{CN}{C}}\cdot + H_3C{-}CH{=}CH{-}\overset{CH_3}{\underset{CN}{C}}\cdot \qquad (6)$$

In contrast with initiation by structure II obtained in equation 4, the polymerization of methacrylonitrile initiated by an excited ethylene molecule should produce polymer void of carbonyl end groups. It is significant to note that the infrared spectra of several specimens of polymethacrylonitrile ($\bar{P}_n$ ranging from 3520 to 721) prepared in bulk with dihydroascaridole initiator and repeatedly washed with monomer to remove catalyst fragments exhibited no absorption between 5.75–6.0 μ which is a region of strong absorption by carbonyl groups.[12]

It is perhaps more plausible to assume that the primary biradical I does not dissociate into ethylene but rather undergoes a stepwise decomposition to IV and an isopropyl and a methyl radical, a sequence which would also produce polymer void of carbonyl groups. Differentiation between this process and reaction (5) cannot be made from the present work but should be available from structure determination of the gaseous products of dihydroascaridole decomposition in a solvent such as tetralin.

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[11] F. R. Mayo, THIS JOURNAL, **75**, 6133 (1953).

[12] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand, Inc., New York, N. Y., 1949.