LETTERS TO THE EDITORS

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A Dielectric-Constant Method for Following the Non-Stationary State of Radical Reactions

MUCH of the recent development in the kinetics of chemical reactions has been concerned with the absolute evaluation of rate constants for the elementary reactions comprising a complex process. This has been carried out mainly indirectly in photo-reactions, using intermittent radiation to determine the life of the radical or chain concerned in the rate-controlling step. It would, however, be much more desirable in such reactions to be able to determine these life-times directly, by delineating the rise in concentration of a radical following the commencement of irradiation and the corresponding decay when irradiation is stopped. This can be done in principle, given a method of detecting reaction which is both highly sensitive and also very rapid in response, since life-times may be as short as 10^{-3} sec. These stringent requirements have now been met in the case of the liquid-phase polymerization of vinyl compounds by the construction of an instrument for following the change in dielectric constant which accompanies the reaction. This instrument has a sensitivity of 1 part in 10^8 of dielectric constant and a response time of 10^{-4} sec. ; the frequency of operation is 50 Mc./s. We are indebted for the design of the instrument to Dr. C. M. Burrell, of the Radar Research and Development Establishment, and to the Ministry of Supply for invaluable help in its construction.

The polymerization, which is exothermic, is carried out adiabatically, and the amount of reaction is determined from the resultant fall in dielectric constant ; a correction is applied for the second-order increase in dielectric constant due to the accumulation of polymer. The sensitivity to polymer formation is of the order of 1 part in 10^7. A convenient illustration of the method is provided by the polymerization of pure vinyl acetate photosensitized by α-azo-*bis*-*iso*-butyronitrile $(NC.(CH_3)_2C.N.=N.C(CH_3)_2CN)$; the
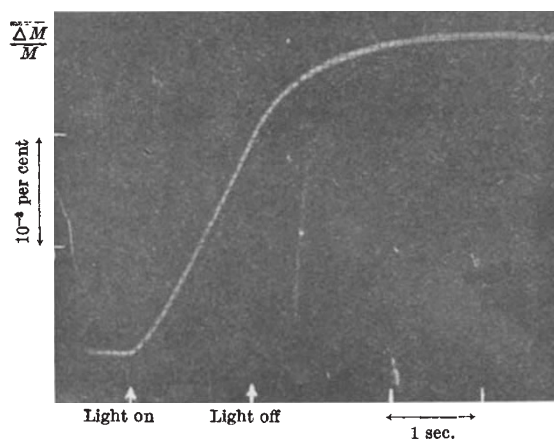
Fig. 1. Amount of polymer formed as a function of time, with continuous radiation
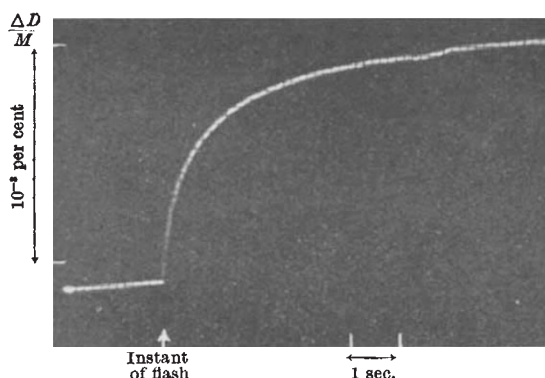
Fig. 2. Amount of polymer formed as a function of time, with instantaneous radiation

method has also been used for styrene, methyl acrylate, etc. Two techniques are used to evaluate the life-times of the radicals. In the first, the light is switched on and the approach to the stationary state is delineated ; when this state has been attained, the light is switched off and the decay of the reaction is also delineated. An oscilloscope trace of this sequence of events is shown in Fig. 1. It can be shown[1] that the life-time (τ) of the kinetic chain in the steady state is given by $t/\ln 2$, where t is the intercept on the time axis of the linear portion of this curve. Similarly, τ can be evaluated from the decay of reaction when the light is cut off.

In the second method, a brief flash of intense radiation from a 'Sieflash' tube is admitted to the system so that decomposition of a fraction of the sensitizer is complete before polymerization starts. The subsequent growth of polymer radicals is then observed directly on the oscilloscope. The average life of the radicals is again determined from the shape of this curve. A typical trace is shown in Fig. 2.

	Rate (%/hr.)	τ exp. (sec.)	τ calc. (sec.)
Continuous illumination	5·8	0·29	0·09
	2·0	0·73	0·26
Flash illumination	5·8	0·2	0·09
,, ,,	2·5	0·4	0·20

The results of a series of experiments are given in the accompanying table. The rates of polymerization are calculated on the basis that the heat of polymerization of vinyl acetate is 17 k.cal. per mole, and may require to be revised later. Alongside the experimental life-times are given the life-times for the rates concerned derived from the values of the growth and termination coefficients given by the method of intermittent illumination[2]. It will be seen that the results are in reasonably good agreement, having regard to the difference in the techniques employed.

A full description of the apparatus and results will be published later.

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[1] Symposium on Combustion and Explosion, Wisconsin (1947).
[2] Burnett, G. M., Valentine, L., and Melville, H. W., *Trans. Farad. Soc.*, **45**, 960 (1949).