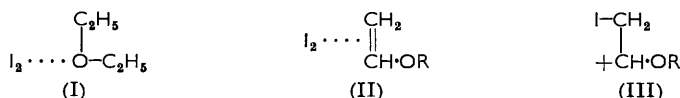**410.** *The Kinetics of Ionic Polymerisation. Part VIII.* The Ultraviolet Absorption of the Polymerising Iodine–n-Butyl Vinyl Ether System.*

By D. D. ELEY and ANNE SEABROOKE.

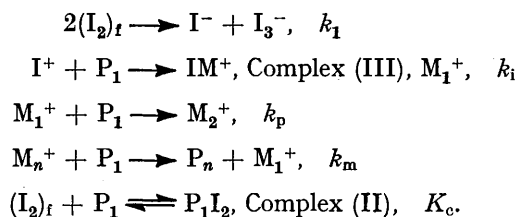A solution of n-butyl vinyl ether (nBVE) and iodine in diethyl ether shows a definite absorption at 2950 Å, due in part to a π-complex, nBVE $\cdots$ I$_2$, and in part possibly to carbonium and tri-iodide ions. The initial rate of decrease of optical density at 2950 Å with time obeys kinetics similar to those for the rate of polymerisation. It is supposed that the π-complex dissociates to liberate more iodine as this is taken up in initiating polymerisation. Irradiation with visible light has no effect in the initial absorption at 2950 Å or on its rate of change, but does lead to a change in the absorption spectrum of the final polymerised system, owing to photoactivated addition of iodine to the double bonds of the dead polymer.

EARLIER kinetic studies of the system n-butyl vinyl ether (nBVE)–iodine–diethyl ether assumed the presence of three complexes, (I)—(III).[1] Iodine in a complex with ether

$$
\begin{array}{ccc}
\underset{\text{(I)}}{\text{I}_2\cdots\text{O}-\text{C}_2\text{H}_5} & \underset{\text{(II)}}{\text{I}_2\cdots\overset{\text{CH}_2}{\underset{\text{CH}\cdot\text{OR}}{\|}}} & \underset{\text{(III)}}{\overset{\text{I}-\text{CH}_2}{\underset{+\text{CH}\cdot\text{OR}}{|}}}
\end{array}
$$

groups, as in (I) or in n-butyl vinyl ether, is denoted as "free iodine" $(\text{I}_2)_\text{f}$. Iodine in the π-complex (II) is regarded as catalytically unreactive, leading to a maximum in the graph of polymerisation rate against monomer concentration.

The kinetic analysis is based on the following steps:

$$2(\text{I}_2)_f \longrightarrow \text{I}^- + \text{I}_3^-, \quad k_1$$

$$\text{I}^+ + \text{P}_1 \longrightarrow \text{IM}^+, \text{Complex (III)}, \text{M}_1^+, \quad k_i$$

$$\text{M}_1^+ + \text{P}_1 \longrightarrow \text{M}_2^+, \quad k_p$$

$$\text{M}_n^+ + \text{P}_1 \longrightarrow \text{P}_n + \text{M}_1^+, \quad k_m$$

$$(\text{I}_2)_f + \text{P}_1 \rightleftharpoons \text{P}_1\text{I}_2, \text{Complex (II)}, \quad K_c.$$

Assuming stationary concentrations of I^+ and M_n^+, the rate and average degree of polymerisation of product are:

$$\frac{-\text{d}[\text{P}_1]}{\text{d}t} = \frac{k_1 k_p [\text{P}_1][\text{I}_2]^2}{k_t (1 + K_c[\text{P}_1])^2}, \quad \overline{\text{D.P.}} = \frac{k_p[\text{P}_1]}{k_t + k_m[\text{P}_1]},$$

where $[\text{P}_1]$ is the initial monomer concentration; $[\text{I}_2]$ is the total iodine concentration.

In the present ultraviolet spectroscopic study of the polymerising system we are concerned with possible absorption bands of the complexes (I) and (II), the carbonium ion (III), the species I^+ and I_3^+, and the monomer. Iodine in diethyl ether shows a visible band with $\lambda_\text{max.}$ 4650 Å (ε 870), and an ultraviolet band with $\lambda_\text{max.}$ 2480 Å (ε 2450).[2] The visible band is the 5200 Å band of iodine vapour shifted by the donor action of the solvent, and is responsible for the brown colour of the solution.[3] The ultraviolet band is the charge-transfer band, and a similar band may be predicted for complex (II).[4] If we assume an ionisation potential of 9 ev for vinyl alkyl ether, the relation of McConnell, Ham, and

* Part VII, Coombes and Eley, *J.*, 1957, 3700.

[1] Eley and Saunders, *J.*, 1952, 4167; 1954, 1672.

[2] Kortum and Friedheim, *Z. Naturforsch.*, 1947, **2a**, 20.

[3] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600.

[4] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1952, **74**, 458,

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Platt[5] places $\lambda_{max.}$ for the complex (II) at 2980 Å. In addition, there are reasons for expecting a constant absorption around 3000 Å for the complex (III) and I_3^-, which will maintain a constant concentration for a stationary-state polymerisation. When these experiments were carried out[6] it was thought that the concentration of carbonium ions was negligible, but recent studies by Okamura, Higashimura, and their co-workers[7] indicate that it is comparable with the concentrations of the complexes (I) and (II) in the polymerising mixture. The same group[8] found a band with a maximum at 2750 Å, and derived an equilibrium constant of 5·2 l. mole^{-1} for the n-butyl ether–iodine complex in iso-octane, which supports the general approach adopted here.

Experimental

Optical densities were measured in 2-mm. stoppered cells, using a Unicam S.P. 500 spectrophotometer. Equal volumes of vinyl ether and iodine solutions in diethyl ether were added to the cell by means of an Agla micropipette. Diethyl ether was placed in the comparison cell.

Materials.—Diethyl ether was B.D.H. spectroscopic grade.

Iodine was B.D.H. AnalaR grade mixed with potassium iodide and sublimed *in vacuo* through a sintered glass disc; it was free from tri-iodide ion, as shown by spectroscopy. Vinyl ether monomers (B.D.H.) were purified by the method of Schildknecht.[9] They were washed five times with an equal volume of water, made slightly alkaline with potassium hydroxide, and dried overnight over solid potassium hydroxide. After decantation they were dried over sodium, and then distilled from sodium through a 4-ft. column packed with Fenske helices. The middle fraction was stirred *in vacuo* over sodium, and further distilled *in vacuo* for use as required.
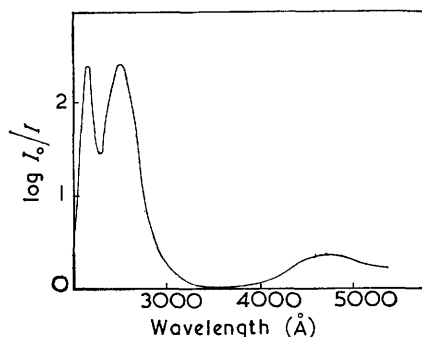

Fig. 1.   The absorption spectrum of iodine (2·11 × 10^{-3}M) in diethyl ether.

Results

Iodine in Diethyl Ether.—The spectrum in Fig. 1 shows a strong band at 2160 Å which does not obey Beer's Law and may be due to light-scattering effects. The other two bands have $\lambda_{max.}$ 2480 Å (ε 5220) and 4660 Å (ε 911). The ultraviolet band makes an appreciable contribution to the optical density at 2950 Å. Therefore, a calibration was established for different concentrations of iodine in diethyl ether, which allows a calculation of the 2950 Å contribution from the measured optical density at 4660 Å: (log I_0/I) at 2950 Å = 1·45(log I_0/I)at 4660 Å.

Iodine and Vinyl Ether in Diethyl Ether.—When a molar solution of n-butyl vinyl ether in diethyl ether is added to a millimolar solution of iodine in diethyl ether, the brown colour disappears; it reappears (if the solution is kept in the dark) at the end of the polymerisation. It is a reasonable assumption that the iodine is largely transferred to form complexes of type (II) with the monomer, and that it is held as such until the monomer has been largely used up in forming polymer. To establish the ultraviolet spectrum of the polymerising mixture, equal volumes of vinyl ether and iodine solutions were mixed in the spectrometer cell, and left in

[5] McConnell, Ham, and Platt, *J. Chem. Phys.*, 1955, **21**, 66.
[6] Seabrooke, Thesis, Nottingham, 1958.
[7] Okamura, Kanoh, and Higashimura, *Makromol. Chem.*, 1961, **47**, 19.
[8] Higashimura, Kanoh, Yonezawa, Fukui, and Okamura, *J. Chem. Soc. Japan*, 1960, **81**, 550.
[9] Schildknecht, " Monomers," ed. Blout and Mark, Interscience, New York, 1951.

the dark until optical density at 4660 Å had decreased to 0·10. This change took 10—15 min., and corresponds to the disappearance of the brown colour, mentioned above, with the formation of the complex (II). The spectrum (Fig. 2) was then taken. The excess absorption at 2950 Å, denoted as a–b, arises from products of interaction of the vinyl ether and the iodine, including the complex (II). If this mixture was kept in the dark until polymerisation was complete, the 2950 Å absorption disappeared, and bands at 4660 and 2480 Å characteristic of " free iodine " (which includes complex I in this context), reappeared. A number of other
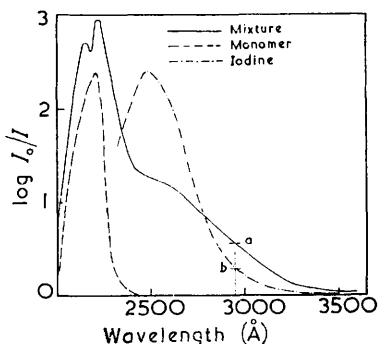
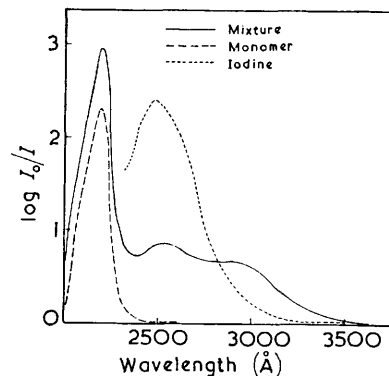FIG. 2. The spectrum of a polymerising solution of 2·11 × 10^{-3}M-iodine in 0·385M-n-butyl vinyl ether.

FIG. 3. The spectrum of a polymerising solution of 2·11 × 10^{-3}M-iodine in 0·392M-2-chloroethyl vinyl ether.

vinyl ethers gave a similar excess absorption at 2950 Å, but 2-chloroethyl vinyl ether–iodine gave an additional feature (Fig. 3). While the excess absorption at 2950 Å is present, denoting definite interaction of vinyl ether and iodine, there also remains a definite peak around 2500 Å which corresponds to a marked concentration of " free iodine." This agrees with expectation, since the earlier kinetic evidence pointed to negligible or very weak formation of the complex (II) for this monomer.
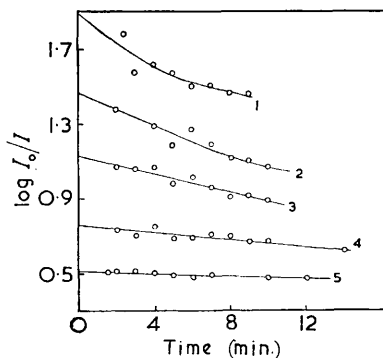

FIG. 4. Change of " corrected optical density (2950 Å) " with time, at room temperature and [nBVE] = 0·772M.

Curve 1, [I_2] = 5·72 × 10^{-3}M; 2, 4·07 × 10^{-3}M; 3, 3·15 × 10^{-3}M; 4, 2·17 × 10^{-3}M; 5, 1·36 × 10^{-3}M.

Kinetics of the Disappearance of the 2950 Å *Absorption.*—A series of kinetic runs were made with different initial concentrations of iodine and vinyl ether in diethyl ether. For each run optical density values were taken at a series of times at 2950 and 4660 Å. The second reading allowed the optical density (O.D.) 2950 Å to be corrected for the presence of " free iodine " [complex (I)], *i.e.,* corrected O.D. (2950 Å) = O.D. (2950 Å) — 1·45 × O.D. (4660 Å). The " corrected O.D. (2950 Å) " reading decreased with time at room temperature during the first 10 min., as shown in Fig. 4. During this time it is known from earlier work [1] that the percentage polymerisation varies from about 5 for curve 5 to 40% for curve 1, with the higher catalyst concentration. Stationary reaction velocities were observed over the first 24% of polymerisation. The initial rate of change of " corrected O.D. (2950 Å) " with time as a function of catalyst and monomer concentrations is shown in Figs. 5a and 5b.

Nature of the 2950 Å *Absorption.*—The excess absorption at 2950 Å corresponds to that predicted for the complex (II), but it is also necessary to consider how far the complex (III) (carbonium ion) and I_3^- may give overlapping spectra.

Carbonium Ions (With G. BLAKE).—We may expect the ion $(MeCH \cdot OR)^+$ to have a spectrum similar to that of $(CH_2I \cdot CH \cdot OR)^+$ [complex (III)]. Rosenbaum and Symons [10] generated carbonium ions by using $10^{-3}M$-solutions of olefins in sulphuric–acetic acid mixtures, and found a band with $\lambda_{max.}$ 2970 Å (ε 2100). Under these conditions n-butyl vinyl ether showed a band
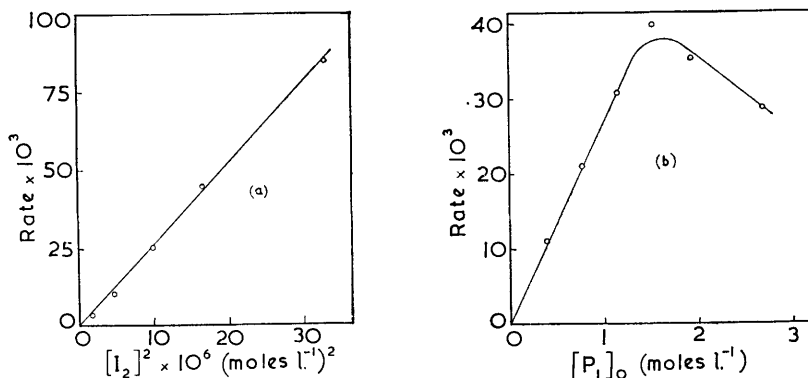

FIG. 5. Initial rate of change of " corrected optical density (2950 Å) " with (a) iodine concentration, and (b) monomer concentration.
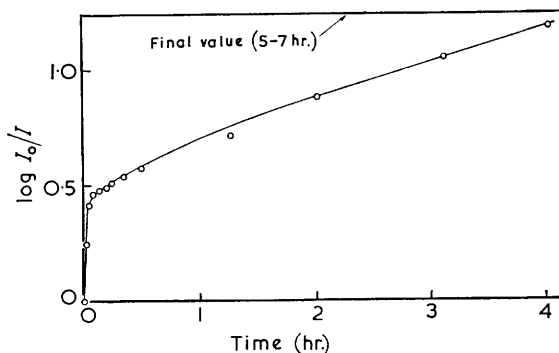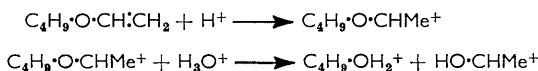

FIG. 6. The growth of absorbance at 2850 Å with time for $10^{-3}M$-n-butyl vinyl ether in glacial acetic acid–conc. sulphuric acid (1 : 10) at room temperature.

at 2850 Å which increased with time (Fig. 6). It seems most likely that chemical decomposition occurs, with the generation of two or more carbonium ions:

$$C_4H_9 \cdot O \cdot CH{:}CH_2 + H^+ \longrightarrow C_4H_9 \cdot O \cdot CHMe^+$$

$$C_4H_9 \cdot O \cdot CHMe^+ + H_3O^+ \longrightarrow C_4H_9 \cdot OH_2^+ + HO \cdot CHMe^+$$

This reaction requires the presence of a small amount of water for the hydrolysis. We may assume, therefore, that the carbonium ion (III) in the polymerisation will possess optical absorption in the region of 2970 Å. Di-n-butyl ether showed no absorption band in sulphuric–acetic acid mixture.

Tri-iodide Ions.—It is difficult to predict bands for the I_3^- ion; in hydroxylic solvents and pyridine it shows $\lambda_{max.}$ 3650 Å ($\varepsilon \sim 25{,}000$) and 2900 Å ($\varepsilon \sim 40{,}000$).[11] We might, therefore, take the 3650 Å band as an indicator, in vinyl ether–iodine mixtures, of the presence of I_3^-.

Only a fraction of the total added iodine concentration of about $10^{-3}M$ will be in the form of

[10] Rosenbaum and Symons, *Mol. Phys.*, 1960, **3**, 205.
[11] Reid and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 3874.

I_3^-. The data of Okamura, Kanoh, and Higashimura [12] allow us to estimate a concentration of active species, M_n^+, as about $10^{-4}M$, which we may equate to the concentration of I_3^- to a first approximation. For a path-length of $0\cdot2$ cm., as used here, we therefore expect an optical density at 3650 Å due to I_3^- of only $0\cdot05$, which is not very different from the measured value of $0\cdot03$, near the limit of the instrument's range (Figs. 2 and 3).

The I^+ Ion (With G. BLAKE).—According to Symons,[13] I^+ is blue in concentrated oleum, with a maximum at 6500 Å. No trace of this band was observable in the polymerising mixture n-butyl vinyl ether–iodine–diethyl ether; this agrees with the expected very small concentration of I^+.

Effect of Light.—In earlier analytical studies on the final polymer it was concluded that, while each molecule possessed a terminal double bond, a certain rather variable percentage of these was subsequently converted into di-iodide.[14] It has now been found that if the polymerisation is carried out in the dark at least half the total iodine originally added reappears when polymerisation is complete. Spectrophotometric work makes this clear, since in a mixture of n-butyl vinyl ether ($0\cdot26M$) and iodine ($2\cdot46 \times 10^{-3}$) in diethyl ether the peak at 2500 Å, characteristic of iodine in ether, considerably increases, from its value one minute after mixing, towards the end of the polymerisation. The same mixture continuously irradiated by a 60 w tungsten lamp showed a strong decrease in the 2500 Å band, corresponding to loss of molecular iodine, presumably by addition to terminal double bonds. However, irradiation had no effect on the initial rate of decrease of the 2950 Å absorption.

DISCUSSION

These experiments have established a definite optical absorption at 2950 Å arising from the interaction of vinyl ether and iodine during polymerisation in diethyl ether. A part of this must be associated with the complex (II), but a part may be due to the two components of the ion-pair, complex (III) and I_3^-. Since the kinetic studies made here and in earlier Papers refer to the stationary state, we may assume that the concentration of ion-pairs, which constitute the active intermediate, remains constant. Therefore, the decrease in optical density at 2950 Å which occurs during the first ten minutes or so may be associated with a decrease in concentration of the complex (II).

The initial rate of decrease of the 2950 Å absorption depends on $[P_1][I_2]^2$ at low monomer concentrations $[P_1]$, and passes through a maximum velocity at $[P_1]_m = 1\cdot5M$. This is the same behaviour as that found by Eley and Saunders,[1] for the initial rate of polymerisation, as expressed in the kinetic equations in the introduction, where the velocity maximum was at $[P_1]_m = 1\cdot8M$. This kinetic dependence will be expected if the " free iodine," $(I_2)_f$, which initiates polymer chains, is provided by dissociation of the complex (II), PI_2. Thus,

$$-d[PI]_2/dt = -K_c[P_1](d[I_2]_f/dt).$$

The kinetic scheme of Eley and Richards [14] gives, for the stationary state,

$$-d[I_2]_f/dt = k_1[I_2]_f^2 = k_1[I_2]^2/(1 + K_c[P_1])^2 \qquad \cdot$$

where $[I_2]$ is the total concentration of iodine, including that bound as complex (II).

$$\frac{-d(\log_{10} I_0/I) \text{ at } 2950 \text{ Å}}{dt} = -(\varepsilon_c l K_c k_1)\frac{[P_1][I_2]^2}{(1 + K_c[P_1])^2}$$

This is the correct form for the observed equation but the constant in brackets cannot be estimated until values of ε_c, K_c, and k_1 are known. The values of Higashimura *et al.*[8] of $\varepsilon_c = 15,000$, $K_c = 5\cdot2$ l. mole^{-1} for nBVE–I_2 in iso-octane will not necessarily apply to diethyl ether as solvent. Eley and Saunders [1] obtained $K_c = 0\cdot4$ l. mole^{-1} from the rate

[12] Okamura, Kanoh, and Higashimura, *Makromol. Chem.*, 1961, **47**, 35.
[13] Symons, *J.*, 1957, 387, 2186.
[14] Eley and Richards, *Trans. Faraday Soc.*, 1949, **45**, 425.

of polymerisation in diethyl ether, and the difference may well arise from the difference in solvents, rather than difference in method. Unlike diethyl ether, iso-octane will not form a complex and, therefore, will not compete with the vinyl ether for the iodine. Given ε_c and K_c values for the reacting system it should be possible to calculate k_1 and hence k_p/k_t. Attempts to apply Benesi–Hildebrand plots to the initial 2950 Å absorption values have failed so far to give the appropriate straight line. This may be due to overlapping spectra, or failure to observe the band maximum.

Earlier variability in double-bond content of the polymer is to be explained by photo-activated addition of iodine to the polymer. In view of the known effects of light on this reaction,[4] this result is not unexpected. The relative slowness of photoactivated addition of iodine to the monomer probably explains the absence of any effect of light on the initial rate of decrease of the 2950 Å absorption.

THE UNIVERSITY, NOTTINGHAM.