

## IODINE INITIATED POLYMERIZATION OF VINYL MONOMERS

(A Review of the Field, 1866-1977)

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**Abstract.** A review of iodine initiated polymerization is presented here in order to outline the many different ideas which have been published about the kinetics and mechanism of these reactions.

The use of iodine to initiate vinyl polymerization is one of the earliest to be reported. Berthelet<sup>1,2</sup> first recorded the iodine initiated polymerization of styrene. Later Wislicenus<sup>3</sup> attempted preparation of the iodine addition product of vinyl ethyl ether. On addition of iodine to vinyl ether a violent reaction was observed and a low molecular weight polymer was obtained. It was suggested that at least one part of the catalyst to 200 parts of ether was necessary to bring about complete polymerization. The author failed to distil any appreciable portion of vinyl ether under high vacuum after polymerization. He thus anticipated the structure of polymeric bodies and suggested that iodine combined to give a mixture of various polymeric homologous compounds. It is significant that Wislicenus<sup>3</sup> postulated that a diiodide may be formed at an intermediate stage in the formation of the true polymer.

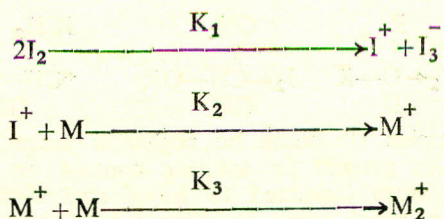
The resinification of coumarone<sup>4</sup> with iodine at temperatures above room temperature has been reported but no change was observed with the same system at room temperature. Dimerization of 1, 1 diphenyl ethylene<sup>5</sup> in warm acetic acid in the presence of iodine yielding 1, 1, 3, 3 tetraphenyl but-1-ene-3 has been observed. Stobbe<sup>6</sup> observed the polymerization of cinnamylidene benzyl cyanide in chloroform and in a benzene in the presence of iodine. He also reported the solid state polymerization of *p*-vinylanisole. The dimerization of cyclopentadienes has been reported by Staudinger and Bruson.<sup>8</sup>

Chalmers<sup>9</sup> tried to polymerize a number of vinyl ethers with low iodine concentration in the presence of iodine. It was observed that the reactivity of the monomer was a function of its structure, Chalmer's view was that an iodine atom, formed by thermal dissociation, added to the double bond of vinyl ether to give a free radical which triggered off a chain polymerization reaction. It was calculated

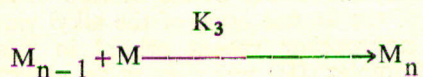
that one double bond per "mer" was present in the polymer. Again, an unsuccessful attempt was made to distil the vinyl-ethyl ether from the reaction mixture.

Later the polymerization of octadecyl vinyl ether with iodine was carried out producing paraffin-like solid polymers.<sup>10</sup>

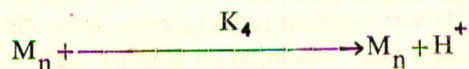
The first systematic kinetic studies on iodine-initiated polymerization were carried out by Eley and his associates.<sup>11-16</sup> They suggested the first detailed reaction mechanism for the iodine initiated polymerization of alkyl-vinyl ethers based on these kinetic studies. The effect of dielectric constant of the medium was also investigated and an ion-active intermediate was proposed; the suggested mechanism is outlined below:



Propagation:



Termination:



Thus for the above mechanism:

$$-\frac{d(M)}{dt} = K_3 (I^+ M_n) (M) \dots (1)$$

By making a stationary state assumption for  $(I^+)$  and  $(M_n^+)$  where  $(X)$  designates the concentration of the species, an overall rate expression was obtained for the loss of the monomer as follows:

$$K_1 (I_2)^2 - K_2 (I^+) (M) = 0 \quad \dots(2)$$

$$\text{or} \quad (I^+) = \frac{K_1 (I_2)^2}{K_2 (M)} \quad \dots(3)$$

$$\text{Again,} \quad K_2 (I^+) (M) - K_4 (M^+) = 0 \quad \dots(4)$$

$$\text{where} \quad (M^+) = \frac{K_2}{K_4} (I^+) (M) \quad \dots(5)$$

Substituting these values in Eq. 1, we have :

$$(M^+) = \frac{K_1}{K_4} K_3 (I_2)^2 \quad \dots(6)$$

$$\frac{-d(M)}{dt} = K_3 (M^+) (M) \quad \dots(7)$$

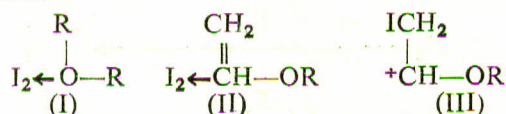
$$\frac{-d(M)}{dt} = \frac{K_1}{K_4} K_3 (I_2)^2 (M) \quad \dots(8)$$

$$\text{By assuming DP} = \frac{\text{Rate of propagation steps}}{\text{Rate of all termination steps}}$$

$$\overline{DP} = \frac{K_3 (M^+) (M)}{K_4 (M) + K_3 (M^+) (M)} \quad \dots(9)$$

where  $\overline{DP}$  is the degree of polymerization.

In the polymerization of octyl vinyl ether it was reported that the reaction velocity reached a maximum value for a given initial concentration of monomer. Therefore, several different complexes between alkyl vinyl ether and molecular iodine were proposed.



Complex (I) could be neglected since all the molecules present in solution contain an ethereal oxygen atom (assumed to be of equivalent donor character which could coordinate to form an iodine complex). Complex (II) was envisaged as a charge transfer complex formed by the overlap of the filled  $\pi$ -orbital of the double bond of the alkyl vinyl ether with an appropriate vacant orbital in molecular iodine. Complex (III) was seen as an adduct of the iodonium ion ( $I^+$ ) from an initiation pre-equilibrium with the double bond of ether. The iodine in complex (II) was assumed to be inactive as an initiator.

These new assumptions modify the initiation process and give rise to the overall rate expression down below :

$$\frac{d(M)}{dt} = \frac{K_p (I_2)^2 (\text{initial})^2 (M) \text{ initial}}{K_t (1 + K_c (M) \text{ initial})^2} \quad \dots(10)$$

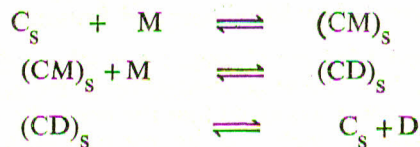
A re-investigation of the evidence for complex formation was carried out by the same group of workers and it was suggested that this occurred through the olefinic group rather than the ether oxygen because anisole complex could be formed.



So the complex formation was not inhibited by the presence of electron attracting side group on the vinyl ether. True velocity constants for the polymerization of different vinyl alkyl ethers were reported later in 1964 and 1968 when the same author used uv and ir techniques for the elucidation of the kinetics of *n*-butylvinyl ether and it was proposed that  $\pi$  complex (II) dissociates to liberate more iodine as it is taken up in initiating polymerization. It was assumed that the concentration of ion-pairs which constitutes the active intermediate remained constant. An increase of rate constant with increase of polarity of the solvent was reported. The existence of  $I_4$  was suggested in the polymerizable solution. Absence of  $\bar{I}_3$  during polymerizations and increase in the concentration of free ions at the end of polymerization was reported.

Bartlet and Kwart<sup>17</sup> carried out the polymerization of vinyl acetate in the presence of iodine and reported a remarkable dual effect. Small concentrations of iodine in vinyl acetate at moderate concentrations of iodine undergo spontaneous heating giving iodine fumes and a polymeric residue.

The authors suggested that the polymerization brought about by concentrated solution of iodine has a polar mechanism and not an atomic one. The order of reaction with respect to iodine was greater than one. The concept of an ionic mechanism was thought to be proved in the related case of styrene polymerization.<sup>18</sup> The kinetics of dimerization of 1:1 diphenyl ethylene in 2-nitropropane was elucidated by Evans *et al.*,<sup>19, 20</sup> using dilatometric techniques. The effect of reagent concentration on the reaction rate and the forward and reverse activation energies were calculated. A mechanism of dimerization was proposed as follows :

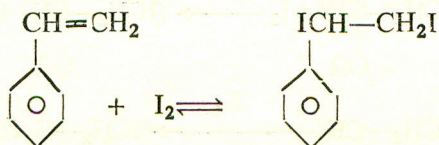


M = monomer.

D = dimer.

Cs = solvated catalyst.

Styrene diiodide formation was reported by Trifan and Bartlett<sup>21</sup> and the kinetics and mechanism of its formation were formulated in the initial stages of polymerization.



At low temperatures<sup>22</sup> the presence of radical and non-radical propagating centres was suggested during polymerization. The former reaction was inhibited by effective radical capturing reagents while the latter was not inhibited.

The kinetics of the uninhibited reaction was followed by spectrophotometer and indicated an overall first-order dependence of the rate on iodine concentration and a 3/2 order dependence on styrene concentration. The authors prepared the colourless crystals of styrene diiodide at low temperature which, however, proved very unstable at room temperature. A solution of iodine in styrene were concentrated to more than 20% and brought about an exothermic polymerization at room temperature. This was shown to proceed through a cationic mechanism. Cryoscopic results showed that 39% of the polymer chain were terminated by the combination of the polystyrene cation with the iodide ion and 61% by loss of a portion to produce a terminal double bond. According to these authors, hydrogen iodine must accompany every polymer molecule which ends in a double bond rather than a second iodine being added in the anionic form.

In an extensive series of publications Higashimura, *et al.*<sup>23-27</sup> tried to elucidate the mechanism and kinetics of the iodine initiated polymerization of alkyl vinyl ethers and styrene derivatives. Uv-spectroscopy was used to study the  $\pi$ -complex between iodine and alkyl vinyl ethers. The concentration of the propagating species were determined spectrophotometrically and iodometrically. The initial rate of polymerization and the mechanism of iodine initiated polymerization of methoxy styrene with different solvents were determined at 30° and can be summarized as follows :

Initial rates:	$(R_1=(M_2)(I_2)^2)$	Solvents :
	$(R_1=(M_1)(I_2)^2)$	ethylene dichloride and carbon tetrachloride
Initiation mechanism:	$(M_1+I_2 \rightleftharpoons IM^+ I^-)$	ethylene dichloride
	$(M_1+2I_2 \rightleftharpoons IM^+ I_3^-)$	carbon tetrachloride

The change in kinetic order was explained in terms of ion-pair solvation stabilization of the system. A method was suggested for the determination of the propagation rate content and it was assumed that no iodine was incorporated into the polymer on

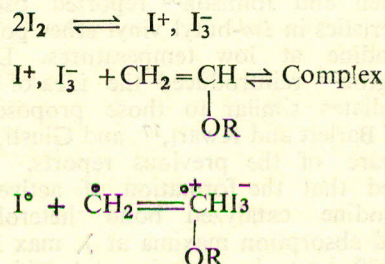
termination. The authors also determined the pre-exponential factor  $A_p$  and the activation energy ( $\Delta E_p$ ) of the propagation constant in the cationic polymerization of styrene initiated by iodine in ethylene chloride and suggested that the propagation reaction is fundamentally affected by the counter ion and ion-pair propagation was suggested. solvent effect on the cationic polymerization of the Styrene derivative was studied and it was reported that the copolymerization of the monomer with less solvating power increased as the polarity of the medium increased. They suggested that the process of dissociation of the gegenanion by the attacking monomer is predominantly rate determining in the propagation reaction.

The effect of pressure on the rate of polymerization of *isoamyl* vinyl ether with iodine has been reported.<sup>28</sup> These authors examined the effect both in diethyl ether and in the undiluted monomer up to 10,000 bar and suggested that in the presence of a large excess of monomer iodine ions can form a complex with the monomer in the same way as in the presence of iodine.

The solid state polymerization of trioxane with iodine by simultaneous sublimation of monomer and catalyst has been studied.<sup>29</sup> These authors confirmed the presence of free radical by esr measurement.

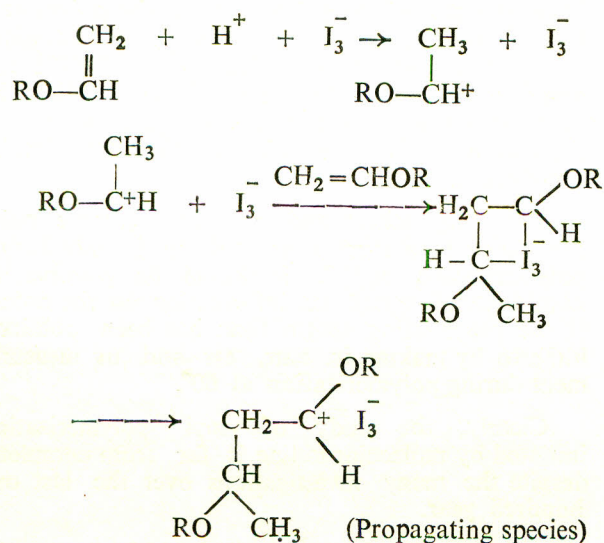
The interaction between polymer and iodine was studied by X-ray diffraction. The polymerization was considered to occur by a radical mechanism. In order to investigate the propagating species in the *p*-methoxy styrene iodine system the electric field effect was studied by Sakurada *et al.*<sup>30</sup> They confirmed that the field effect was neither due to Joule heat nor was it related to polymerization initiation by ionic species nor radicals produced electrically. The dissociation of ion pairs at the growing chain ends were held responsible for the observed effect.

A free radical produced by the interaction between iodine and the double bond of an alkyl vinyl ether was reported by Okamura's group<sup>31</sup> using electron spin resonance methods and has been explained by the following series of reactions :

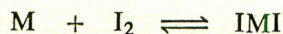


Giusti and his colleagues<sup>32-34</sup> observed the pseudo-cationic behaviour and non-ionic propagation was proposed in the iodine initiated polymerization of styrene and acenaphthylene. The authors suggested





Several recently reported mechanisms for iodine initiated polymerization propose that hydroiodic acid and hydrogen triiodide are liberated in the initial stages of the reaction, giving rise to a molecule with a double bond. Iodination reactions are probably reversible processes, but an excess of olefin will keep the equilibrium towards the right hand side of the equation.

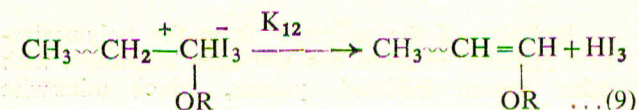
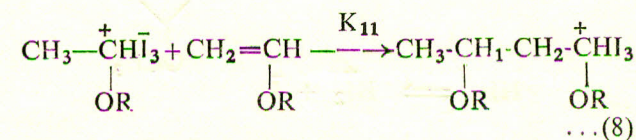
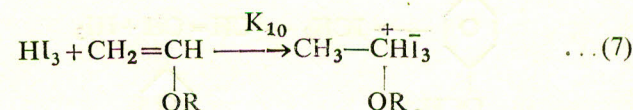
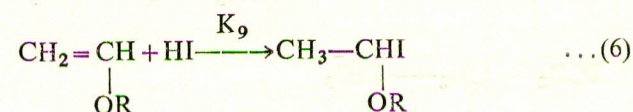
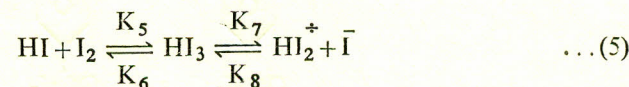
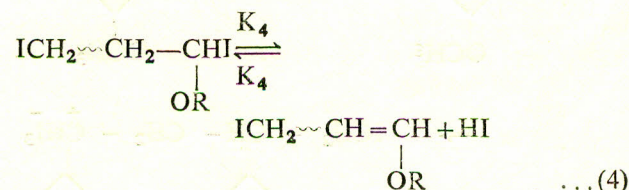
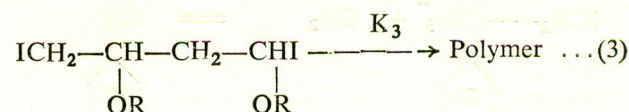
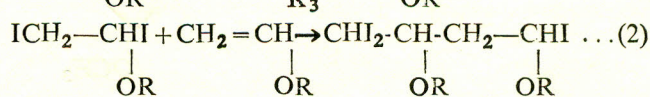
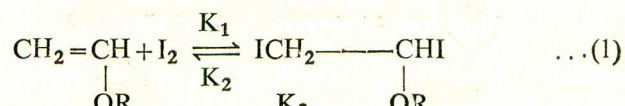


The liberation of these acids (HI, HI<sub>3</sub>) can, however, take place either in the presence of moisture or at the end of polymerization when termination is due to proton expulsion.

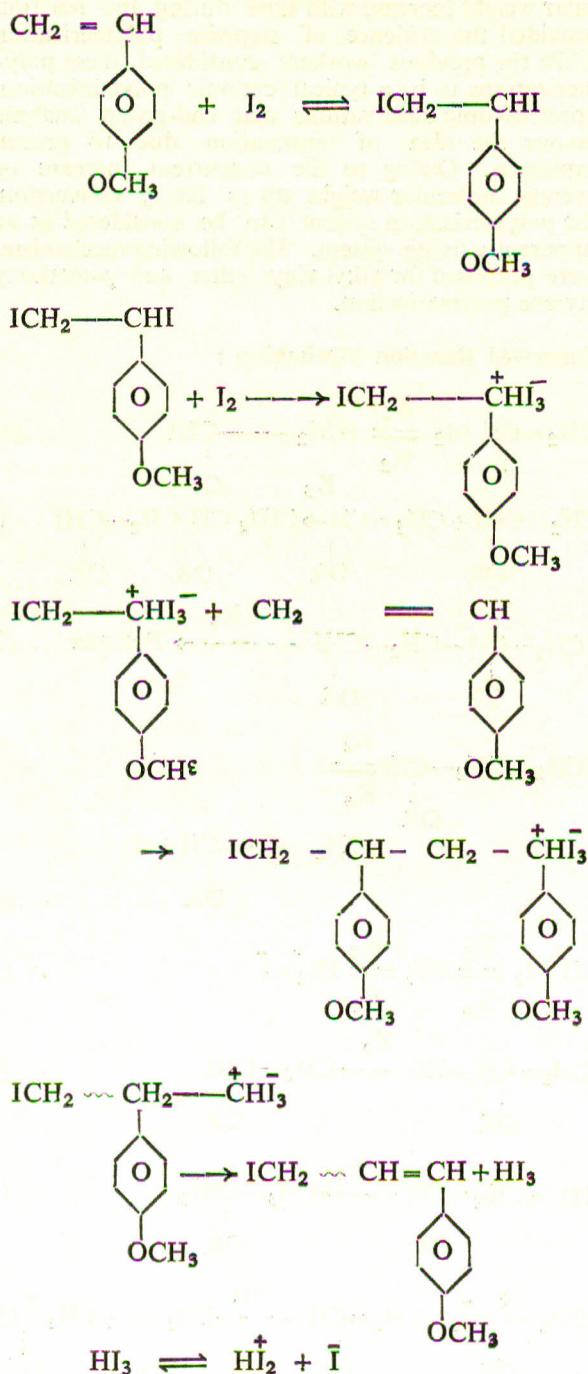
Janjua and Johnson<sup>40, 41</sup> observed the pseudo-cationic behaviour in the iodine initiated polymerization of alkyl vinyl ether, and *p*-methoxy styrene but a similar phenomenon was not observed in *N*-vinyl-carbazole-iodine polymerization at low temperature (-60°). Experimental evidence shows that spectroscopically it is very difficult to distinguish charge transfer complexes diiodide and a monoiodide chromophores. In most of the previous publications spectroscopic evidences were quoted for the determination of mode of initiation. Our experiments proved that the spectroscopic evidences were not reliable. Therefore, the authors concentrated on the first-adducts analysis, influence of additives (H<sub>2</sub>O, alcohol, HgO, DPPH) and kinetic studies for the elucidation of the mechanism of the reaction. Conductometric measurements and electron spin resonance results of the reactions were carried out in the presence of DPPH, and evidence for the presence of free radical in the system was observed. It is suggested that the initiation takes place through radical chain mechanism with the formation of a diiodide. The idea of diiodide formation was supported by iodinated reactions carried out in

non-polymerizable media. The analysis of these iodinated compounds favoured the idea of diiodide formation in the initial stages of reaction. Molecular weight increase with time during the reaction provided the evidence of stepwise polymerization while the previous workers considered these polymerizations to be a typical cationic polymerization. Spectroscopic observations and end-group analysis favour the idea of termination due to proton expulsion. Owing to the concurrent increase of average molecular weight up to 100% conversion, the polymerization system can be considered as an apparently living system. The following mechanisms were proposed for alkyl vinyl ether and *p*-methoxy styrene polymerization.

#### Suggested Reaction Mechanism :



**Suggested Mechanism for Iodine Initiated  
Polymerization of *p*-Methoxy Styrene.**



**Suggestions for Further Work**

Isolation of the polymer from the polymerization reaction mixture has not been attempted with other iodine initiated systems, which otherwise

have been studied extensively, viz., the polymerization of styrene and acenaphthylene. In addition, for these systems also the influence of DPPH and other radical scavengers could indicate whether the observations mentioned in this work are specific to the systems studied or whether they are of wider significance.

The vinyl ethers and *p*-methoxy styrene polymerization lend themselves to detailed study during polymerization at 60°. It should be possible to obtain more significant information on the nature of the propagating centre than has been obtained hitherto by making ir, nmr, esr and uv measurement during polymerization at 60°.

Clearly, the study of vinyl polymerization initiated by molecular iodine is far from complete, despite the many investigations over the last one hundred year.

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