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Thermal Polymerisation and Oligomerisation of Monomers

V.A.Kurbatov

Two competing types of thermal reactions of monomers of different classes, namely oligomerisation and polymerisation, are examined. The characteristics of the formation of the initiating radicals and of low-molecular-weight products (dimers and trimers) and of the inhibition of the thermal polymerisation by radical acceptors have been subjected to kinetic analysis. The mechanisms of the principal pathways in this process and the relations between them are discussed.
The bibliography includes 136 references.

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I. INTRODUCTION

Thermal polymerisation† is the principal type of reactions of monomers; it proceeds exclusively under the influence of heat in the range of relatively low temperatures where the reactions involving the decomposition of the carbon skeleton of the molecule hardly occur. Its products are polymer and low-molecular-weight compounds—oligomers (dimers and trimers) having both linear and cyclic structures.

The importance of this study of thermopolymerisation is determined by practical and theoretical factors. Firstly, thermopolymerisation is an inseparable component of the overall polymerisation process occurring in the industrial isolation of monomers, which leads to the formation of polymer deposits and the breakdown of equipment. Secondly it is one of the methods of synthesis of polymers, for example styrene polymers. For this reason, the knowledge of the detailed features of the mechanism of the thermal reactions of monomers permits a more deliberate and better founded purposeful regulation of this reaction depending on the character of the problems undertaken. The mechanism of the generation of initiating radicals and oligomers, especially six-membered oligomers, is of theoretical interest. As regards the latter, two mechanisms of their formation have been discussed in the literature during a number of years: the synchronous and two-centre (biradical) mechanism.

The aim of the review was therefore to survey and analyse the literature data on the thermal reactions of various representatives of vinyl and acetylenic monomers, to discover the general features of these processes, and to attempt to formulate on this basis a single mechanism of the phenomenon under consideration. The need for the present review arose because, despite the fairly long history of the research into monomer reactions of this type, scarcely any attempts have been made to survey the available literature data which have accumulated during the last 20–30 years. In view of the fact that the cyclo-addition reactions constitute an independent branch of organic chemistry, as regards the latter we shall confine ourselves to conclusions which have a direct bearing on the topic of the present review.

† Henceforth we shall also use the term "thermopolymerisation", since it has become a traditional designation of this phenomenon.

II. MONOMERS OF THE VINYL-AROMATIC SERIES

1. Styrene and Its Derivatives

In the early studies, only the formation of the polymer was investigated. Reactions of both first and second order with respect to the monomer have been reported. The first exact reaction order, amounting to 2.5, was established by Flory[1] and then by Mayo and co-workers[2–5] and an expression has also been found for the rate of initiation:[2]

$$w_i \text{ (mol litre}^{-1}\text{s}^{-1}) = 1.32\times10^6 \exp(-121/RT)\,[\text{M}]^3$$

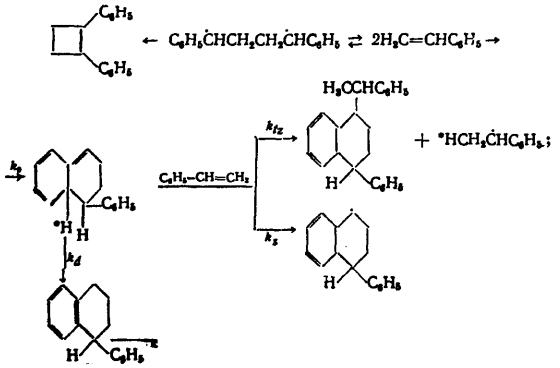
(here and henceforth M represents the monomer), which agrees well with the equation which we obtained on the basis of Flory's results.[1]

The reaction order obtained has been interpreted in different ways. Thus it has been assumed that the polymerisation is initiated by the radicals formed as a result of a trimolecular reaction of styrene, via a trimeric biradical, or by monoradicals arising from the latter (see Bagdasar'yan,[6] pp.9, 59). However, it has been shown[6,7] that biradicals cannot ensure the propagation of the chain process. This has also been confirmed by the polydispersity of the polymer, amounting to 1.8–2.0,[8] which is characteristic of monoradical initiation. Finally, special generation of the biradicals $C_6H_5\dot{C}HCH_2.\,.CH_2\dot{C}HC_6H_5$ by the decomposition of the corresponding tetrahydropyridazine only slightly increased the rate of polymerisation of styrene.[9] The trimolecular reaction is regarded as unlikely because of the lack of a kinetic isotope effect in the polymerisation of ββ'-dideuteriostyrene.[10]

A qualitatively new stage in the development of a theory of thermopolymerisation was represented by Mayo's studies,[2,11] in which, together with the polymer, low-molecular-weight products L were detected, the rate of formation of which obeys a second order equation with respect to the monomer:

$$w_L \text{ (mol litre}^{-1}\text{s}^{-1}) = 1.8\times10^5 \exp(-95/RT)\,[\text{M}]^2.$$

Among the low-molecular-weight products, *cis*- and *trans*-diphenylcyclobutanes (DPCB), 1-phenyltetralin (PT), and 1-phenyl(phenylethyl)tetralin (PPET) were identified.[11-13] On this basis, Mayo proposed a new thermopolymerisation mechanism, according to which the primary product, 1-phenyl-1,2,3,9-tetrahydronaphthalene (PTHN), arising from a bimolecular reaction of styrene of the type of the Diels–Alder condensation, is responsible for the formation of the initiating radicals and oligomers. The set of reactions occurring under these conditions is described by the scheme



The expressions for the rates of initiation (w_i) and trimerisation (w_{tr}) arising from this scheme, i.e.

$$w_i = \frac{k_0 k_s [M]^3}{k_d + (k_s + k_{tr})[M]}; \quad w_{tr} = \frac{k_0 k_{tr} [M]^3}{k_d + (k_s + k_{tr})[M]}$$

are consistent with the experimental relations. The DPCB formation reaction is of second order with respect to styrene and is characterised by an activation energy of 104 kJ mol^{-1}.[12] It has been suggested that the high reactivity of PTHN is due to the lability of the hydrogen atom H*.[11,12]

The main evidence for this mechanism is believed to be the presence of the kinetic isotope effect in the initiation stage of the thermopolymerisation of *o*-dideuteriostyrenes,[14,15] the direct identification of PTHN by UV spectroscopy,[16-18] the absence among the reaction products of biradicals generated from diphenyltetrahydropyridazine and phenyltetralin,[19] and the manifestation of an initiating capacity by certain PTHN analogues.[20,21] An additional argument is provided by the ability of styrene dimers to regulate the molecular weight of the polymer;[8,22-24] it has been suggested that this role is played by PTHN.[25,26] Indeed the molecular weight of polystyrene and the concentration of PTHN exhibit an antiparallel time variation,[16,17] while compounds modelling PTHN are capable of playing the role of a chain transferring agent.[20,21]

Among the styrene derivatives, compounds substituted both in the aromatic ring and in the α- and β-positions in the side chain were investigated in the thermopolymerisation reaction. We shall consider initially derivatives of the first type. Data for the polymerisation of methylstyrenes have been published in a number of communications.[27-29] The activation energies for the overall process are 70, 80, and 70 kJ mol^{-1} for *o*-methylstyrene, *m*-methylstyrene, and vinylxylene respectively. Vinylmesitylene does not polymerise even in the presence of initiators. The thermopolymerisation of *p*-methoxystyrene has been investigated.[30] If it is supposed that the overall reaction order is also 2.5, it is possible to obtain an expression for the rate of initiation:

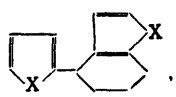
$$w_i \text{ (mol litre}^{-1}\text{s}^{-1}) = 4.6\times10^7 \exp(-125/RT)\ [M]^3.$$

The rate constant for the initiation of the polymerisation of *o*-chlorostyrene is described by an expression with the following parameters: $E_i = 125$ kJ mol^{-1} and $A_i = 3.47 \times 10^{10}$ litre^2 mol^2 s^{-1}.[31] For pentafluorostyrene, $E_i = 84$–92 kJ mol^{-1}.[32] Fairly numerous data are also available for other halogeno- and alkyl-halogeno-styrenes,[33-37] but the lack of information about the polymerisation rate constants precludes the calculation of the rate of initiation. Nevertheless, one may conclude that the variation within wide limits of the activation energies (by 37 kJ mol^{-1}) and pre-exponential factors for the rate constants (by 5 orders of magnitude) for the thermopolymerisation reactions of various styrenes is in the main a result of the variation of the corresponding parameters of the initiation stages.

The thermopolymerisation of styrenes containing substituents in the side chain has been little studied. It has been shown that α-methylstyrene polymerises only at high pressures.[38] Together with the polymer, a linear unsaturated α-methylstyrene dimer has been detected.[39] Only perfluorocyclobutane is formed from αββ′-trifluorostyrene,[40] while α-bromostyryl-1-phenylnaphthalene[41] and various chloro- and fluoro-styrenes are capable only of slow dimerisation.[42]

2. Other Vinyl-aromatic Monomers

The polymerisation of vinylthiophen (VT) and vinylfuran (VF) has been investigated.[44,45] Together with the polymer, a dimer having the structure



where X = O or S, is formed. Its yield is comparable to that of the polymer. The initiation process is characterised by third order with respect to the monomer, the activation energies being 117 and 125 kJ mol^{-1} for VT and VF respectively. The pre-exponential factors in the expressions for the VT and VF polymerisation rate constants were similar, amounting to 9×10^2 litre$^{3/2}$ mol$^{-3/2}$ s^{-1}. The data obtained are consistent with a polymerisation mechanism identical with that proposed by Mayo.

Analysis showed that the observed polymerisation rate constant is almost independent of the monomer concentration and the stage involving the conversion of the intermediate into trimers does not therefore exist. This is confirmed by the observation of only the dimer in the low-molecular-weight fraction,[45] from the yield of which it is possible to estimate approximately the dimerisation rate constant. At 130 °C the latter is approximately 1.6×10^{-6} litre mol^{-1}, i.e. is comparable to the rate constant for the oligomerisation of styrene.

The thermopolymerisation of vinylpyridines (VP) has been investigated in a number of studies.[32,46-48] Expressions describing the rate of initiation have been found for 4-VP and 2-methyl-5-VP:[46,48]

$$w_i \text{ (mol litre}^{-1}\text{s}^{-1}) = 9.7\times10^{11} \exp(-133/RT)\ [M];$$
$$w_i \text{ (mol litre}^{-1}\text{s}^{-1}) = 2.38\times10^{9} \exp(-88/RT)\ [M]^3.$$

The first order observed in the case of 4-VP is open to definite doubt. The surface of the glass probably exerts an influence in this instance, as noted by Onyon.[47] The overall rate constant is independent of the monomer concentration. An initiation activation energy similar to that found for 4-VP has been obtained also for 2-VP.[32] Aminov and co-workers[46,48] give preference to a biradical mechanism, although one cannot rule out the possibility of the formation of an intermediate similar to PTHN.

The thermopolymerisation of vinylpyridinium salts in aqueous solution proceeds via a radical-chain mechanism and the rate of reaction is proportional to $[M]^{2.2}$.[49]

Although the polymerisation of indene has not been subjected to kinetic analysis, nevertheless it has been shown that the rate of this process is lower than the rate of polymerisation of styrene and the degree of polymerisation ranges from 2 to 10, amounting on average to 4–6.[50] The rates of reaction at different temperatures, obtained in different studies, fit satisfactorily on a single linear Arrhenius plot and the activation energy is 94 kJ mol^{-1}.[51–54] There are no literature data for the relative kinetic chain propagation rate constant $k_p/k_t^{0.5}$, where k_p and k_t are the kinetic chain propagation and termination rate constants respectively. We calculated it using the data[54] for the polymerisation of indene initiated by benzoyl peroxide. The required constant was found to be given by the following expression

$$k_p k_t^{0.5}\ (\text{litre}^{1/2}\text{mol}^{-1/2}\text{s}^{-1/2}) = 3.2\times10^5 \exp(-33.6/RT).$$

The dependence of the degree of polymerisation on the initiator concentration (indene peroxide)[55] shows that the molecular weight of the polymer is regulated by chain transfer via the monomer. The calculated transfer constant was found to be 0.1. This can explain the low-molecular-weight of the polymer. The exact concentration-based measurement of the order of the polymerisation reaction with respect to the monomer was not carried out, but, according to an approximate estimate, it should be greater than 2. If it is assumed to be 2.5, then the pre-exponential factor in the expression for the initiation rate constant is 3.8 litre^2 mol^{-2} s^{-1} and the activation energy is 120 kJ mol^{-1}.

According to the data of different workers, the activation energies for the overall polymerisation (numerals designated by an asterisk) and initiation processes involving naphthalene derivatives are respectively 73*,[56] 71*,[32] and 123 kJ mol^{-1} [32] for α-vinylnaphthalene, 129* and 159* kJ mol^{-1} for acenaphthalene,[32] 76* kJ mol^{-1} for β-vinylnaphthalene, and 87* kJ mol^{-1} [56] for 6-vinyltetrahydronaphthalene. Decahydronaphthalene does not polymerise at 100 °C in the course of three days.[56]

If the order of the initiation stage of the polymerisation of α-vinylnaphthalene (α-VN) with respect to the monomer is three, then the rate constant can be calculated from the data of Koton and Kiseleva:[56]

$$k_i\ (\text{litre}^2\text{mol}^{-2}\text{s}^{-1}) = 4\times10^9 \exp(-73.0/RT)$$

(the polymerisation constants taken from Lipatov et al.[57] were used in the calculation).

3. The Kinetics and Mechanism of the Inhibition of the Thermopolymerisation of Styrene by Alkyl Radical Acceptors

The characteristic features of the inhibition of thermopolymerisation exhibit a number of significant differences from the initiated reaction. The relation between the inhibitor concentration and the induction period is usually non-linear.[58–62] The kinetic orders of the acceptor consumption reaction can be both zero[60,63–67] and unity[64,67] and in the former case the rates of destruction of different acceptors can differ by a factor of several tens and can greatly exceed the rate of initiation in the absence of acceptors.[63–69] The products of the thermal and initiated reactions are frequently different.

Thus the high-molecular-weight product formed in the initiated thermopolymerisation of styrene in the presence of quinones is a styrene–quinone copolymer, while the product of the non-initiated process is a styrene homopolymer.[70] The formation of 2 : 1 or 2 : 2 adducts of the monomer and the inhibitor (benzoquinone, sulphur, picric acid),[71,72] in which the dimeric styrene fragment has a linear structure, is a characteristic feature.

Details kinetic analysis of the thermopolymerisation inhibition process has shown[72] that the above features are caused by the reactions of the intermediate arising as a result of a bimolecular reaction of styrene:

$$M + M \xrightarrow{k_s} Z,$$
$$Z \xrightarrow{k_d} D,$$
$$M + Z \xrightarrow{k_{tr}} T,$$
$$M + Z \xrightarrow{k_s} \dot{R},$$
$$n\,In + Z \xrightarrow{k_b} \text{products},$$
$$f\dot{R} + In \xrightarrow{k_{in}} \text{products},$$

where M, D, and T are the monomer, dimer, and trimer respectively, Z is the intermediate, In the inhibitor, n the stoichiometric coefficient, f the acceptance coefficient, and $\dot{R}$ the initiating radical. According to this scheme, the consumption of the inhibitor is defined by the expression

$$-\frac{d[In]}{dt} = k_0[M]^2 \frac{k_s[M]/f + nk_b[In]}{k_d + (k_{tr} + k_s)[M] + k_b[In]}.$$

Since $k_s[M]$ is fairly small, we obtain

$$-\frac{d[In]}{dt} \simeq \frac{nk_0k_b[M]^2[In]}{k_d + k_{tr}[M] + k_b[In]}.$$

Depending on the absolute values of the individual terms, two limiting cases can occur, where the inhibitor is consumed either in accordance with a zero order law at a rate $nk_0[M]^2$ and W_i/f or in accordance with a first-order law at a rate proportional to $nk_0k_b[M]^2/k_d + k_{tr}[M]$. This agrees with the experimental reaction orders (see above) and also shows that, depending on the conditions and the reaction time, the order may also assume intermediate values (between 0 and 1).

An equation relating the induction period τ to the inhibitor concentration was obtained in the same study:[72]

$$\tau = \frac{[In]_0}{nk_0[M]^2} + \frac{k_d + k_{tr}[M]}{nk_0k_b[M]^2} \ln\frac{nfk_0k_b[M]^2}{k_d + k_{tr}[M]w_i}[In]_0.$$

Depending on the initial inhibitor concentration, both a linear and a logarithmic relation between τ and $[In]_0$ can be obtained, which has been observed in practice. Furthermore, the above equation makes it possible to determine the reactivity of the intermediate towards the acceptor {the effective rate constant $k = nk_0k_b[M]^2/k_d + k_{tr}[M]$}, the rate of initiation, and the lower threshold of the rate constant for the reaction of the radicals, propagating the kinetic chains, with the inhibitor.

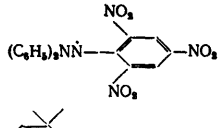
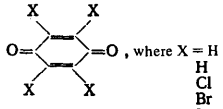
With the aid of this approach, we calculated the effective rate constants k for the interaction of the intermediate with various inhibitors (Table 1). A satisfactory agreement is observed between the values of k calculated from the induction period and from the consumption of the acceptor. A satisfactory agreement was also noted for the rate of initiation w_i and the inhibition rate constant k_{in} found in this way.[72] The constant k for different acceptors varies within the limits of one order of magnitude and has the maximum value for stable radicals. However, there are exceptions: Kolesch's radical# and tetramethyl-p-benzoquinone are consumed at a

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1,3-Bis(diphenylene)-2-phenylallyl (BDPA)—see Pryor et al.[64] (cf. Table 1) (Ed. of Translation).

rate close to the rate of initiation and the interaction with the intermediate does not accordingly occur. It is of interest that, on passing to pentafluorostyrene, such reaction with Kolesch's radical becomes possible (Table 1).

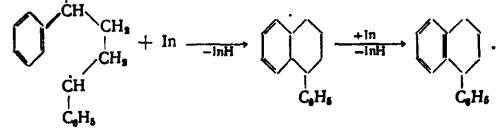
Table 1. The effective rate constants for the reactions of the intermediate with inhibitors.

Inhibitor	t, °C	10^4k, s^{-1}	Method of determination
Styrene (Ref.72)			
	75	1.67	from consumption of inhibitor
	80	1.67	from τ
Ditto	80	1—2	from consumption of inhibitor
$(C_6H_5OC_6H_4)_2N\dot{O}$	80	1.15	from τ
$(C_6H_5)_3\dot{C}$	100	0.71	from τ
 where X = H	70	0.11	from τ
H	90	1.00	from consumption of inhibitor
Cl	80	0.14	from consumption of inhibitor
Br	80	0.17	from τ
I	80	0.36	from τ
Pentafluorostyrene (Ref.64)			
Galvinoxyl	100	0.26	from consumption of inhibitor
Kolesch's radical	100	0.28	from consumption of inhibitor

There exist two hypotheses about the structure of the intermediate: according to one of them, it is PTHN and according to the other it is a biradical. We shall consider which hypothesis corresponds better to the thermopolymerisation inhibition data. The increase of the electronegativity of the halogen atoms in tetrahalogenobenzoquinone lowers the constant k (the reaction constant ρ is then -1).[72] On this basis, it was concluded that there exists a stage in which the halogenoquinone is subjected to the electrophilic attack by the intermediate.[72] The reactions of halogenoquinones with hydrocarbons are usually accompanied by the abstraction of hydrogen atoms. For example, 3,4,8,9-tetrahydronaphthalene, which is an analogue of PTHN, affords naphthalene on reaction with chloranil.[73] In such cases the reaction rate constant has the maximum value for quinones with the most electronegative substituents.[74] If the intermediate is PTHN, one may expect the opposite variation of the constant k on passing from chloranil to iodanil compared with that actually observed. For this reason, the occurrence of the process via a mechanism of the Diels—Alder type is ruled out.

The rate constant k for the reactions of methyl derivatives and p-benzoquinone diminishes with increase in the number of substituents and in the presence of four methyl groups cannot be measured. A similar trend has been observed in the series benzoquinone > naphthoquinone > anthraquinone.[71] This means that an unsubstituted ring carbon atom participates in the reaction of the intermediate with quinone. This conclusion has been confirmed quantitatively by the constancy of the values of k referred to a single reaction centre. An analogous deviation of the reactivity of methylquinones has been observed in reactions with methyl[75] and styryl[76] radicals; the specific constant then also remains invariant.

Since there are quantitative and qualitative analogies between the reactions of quinones with radicals and the intermediate, presumably the intermediate has a radical natur and hence should consist of a biradical. In practice it is unlikely that the rate constants for the reaction of Kolesch's radical with the intermediate would increase by 3—4 orders of magnitude on passing from H-PTHN to F-PTHN (pentafluorostyrene). It is also difficult to imagine the abstraction of a CH_3 group by diphenylpicrylhydrazyl from the PTHN formed from vinylmesitylene.[32] Finally, it has been established recently[77] that, when a nitroxy-radical is introduced at the beginning of the reaction, PTHN is not formed. On the other hand, the rate constant for its destruction in a pseudo-first order reaction with respect to Z is independent of the radical concentration. Hence PTHN is consumed unimolecularly, evidently isomerising to phenyltetralin, while the acceptor reacts with its precursor.[77] There is no doubt that this precursor can only be a biradical. Accordingly, the transfer of a hydrogen atom to the inhibitor is a result of disproportionation; the increased yield of phenyldihydronaphthalene under these conditions[66,78,79] is therefore determined by the reactions



One of the most convincing pieces of evidence for the existence of an intermediate of type PTHN is the conversion of nitroxy-radicals and DPPH radicals into hydroxylamine and hydrazine respectively.[66,78-80] However, hydroxylamine can also be formed as a result of the decomposition of its ether (recombination product).[81] On the other hand, the amount of hydroxylamine formed is only 20% of theoretical.[80] Without going into details, we may note that the change in the composition of the reaction products on treatment with DPPH, quoted by Kopecky and Hall[78] and Wiesner and Mehnert,[79] is inconsistent with the formation of an intermediate of the type of PTHN, since in this case one would expect anomalously high acceptance coefficients. Consequently the fact presented above cannot be regarded as rigorous proof of the involvement of PTHN in the reaction with stable radicals. The structure and composition of the products of the reactions of sulphur and benzoquinone are evidence against a bicyclic structure of the intermediate.[72]

Thus the structure of the products and the kinetics of the reactions of inhibitors fail to confirm, in our view, the concept of the triene structure of the intermediate and make it necessary to give preference to the hypothesis of its biradical nature.

4. The Mechanism of the Thermopolymerisation of Styrene and Vinyl-aromatic Compounds

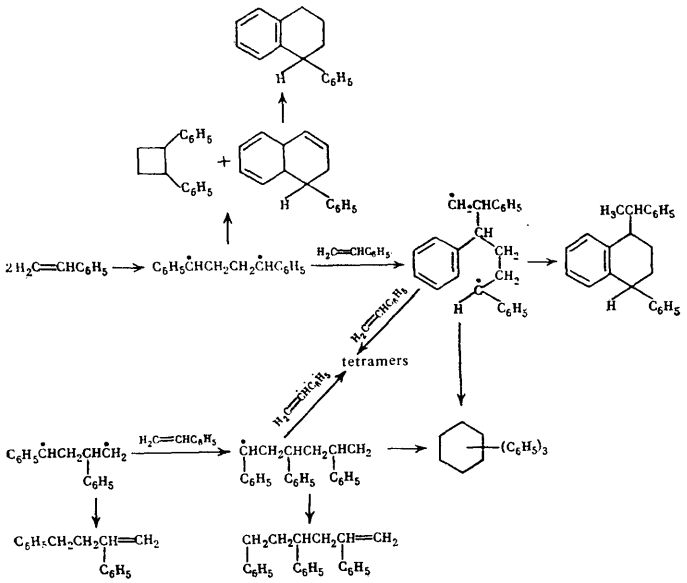
Since the main experimental data have been obtained for styrene, we shall initially analyse those concerning the mechanism of the thermopolymerisation of the above monomer.

Tetraline oligomers (PT, PPET), on the formation of which the current ideas about the thermopolymerisation mechanism are based, are not the only low-molecular-weight products of this process. Their yield is several times smaller than the overall yield of the oligomeric fraction. Together with these, linear unsaturated dimers and trimers have been identified: 1,3-diphenylbut-3-ene, 1,3,5-triphenylhex-5-ene, and triphenylcyclohexanes[11-13,82] and in the case of α-methylstyrene an unsaturated linear dimer.[46] This finding does not fit

within the framework of Mayo's mechanism. In order to eliminate the contradiction, a number of workers postulated, taking into account the presence of the same olefinic compounds in the products of the thermal reaction of polystyrene, their pyrolytic formation under conditions of either chromatographic analysis[13] or direct polymerisation.[11,12]

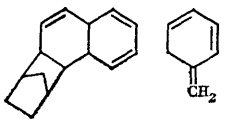
However, in the chromatography of solutions of polystyrene in ethylbenzene, subjected to preliminary heat treatment, oligomers were not detected.[72] The finding that the fraction of linear unsaturated oligomers of 1,3-diphenylbut-3-ene (DPB) and 1,3,5-triphenylhex-5-ene (TPH) decreases with increasing styrene concentration also conflicts with the above hypothesis.[12] Hence it follows that the low-molecular-weight compounds indicated are the main and not secondary thermopolymerisation products.

On the other hand, the presence of all the oligomers noted can be readily accounted for, without contradiction, within the framework of the biradical mechanism. Presumably the olifinic derivatives are formed as a result of the intramolecular disproportionation of the corresponding dimeric and trimeric biradicals, while cyclohexane derivatives are produced by their recombination and tetralin derivatives are formed via alkylation. Furthermore, the lowest biradicals can be converted into the highest by reaction with styrene molecules and then can give rise to oligomers in unimolecular reactions. This has been confirmed by the presence of tetramers among the polymerisation products[12,82] and agrees with the decrease of the fractional yield of DPB and TPH with increase in the concentration of styrene.



We shall now proceed to the discussion of the initiation mechanism. A kinetic isotope effect close to 2 has been found not only in the initiation reaction but also in the trimerisation reaction.[12] The rate of destruction of DPPH in the polymerisation of pentadeuteriostyrene is also smaller by a factor of two than in the reaction involving the non-deuteriated monomer. As already mentioned, this process is second order with respect to the monomer and its rate is limited by that of the stage involving the formation of the intermediate, which participates, according to current ideas, also in the initiation reaction. For this reason, the manifestation of isotope effects in the initiation reaction may be a consequence of their occurrence in the stage where the intermediate is formed. At the same time, on replacement of hydrogen by deuterium in the *ortho*-position, the kinetic isotope effect in the DPPH destruction process is 0.75 in the case of the thermopolymerisation reaction.[83] This indicates merely an uncertainty in the influence of the nature of the *ortho*-substituent on the formation of the intermediate, i.e. the given effect cannot be regarded as proof that the mechanism involving the generation of free radicals operates.

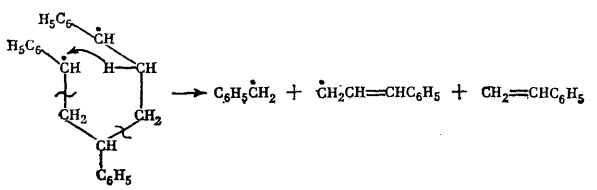
The PTHN concentration, established by UV spectroscopy, does not remain constant over several hours.[16,17] Consequently if PTHN were responsible for the formation of the initiating radicals, then the polymerisation process would not be stationary. For this reason, it is believed that[16,17] the isomer with the axial C_6H_5 group, assumed to be more reactive than the other isomers, participates in the initiation. However, as already mentioned, this intermediate should be produced via a biradical. Finally, the characteristic features of the formation of tetralin oligomers require that stationary conditions hold throughout the intermediate and not only in a fraction of the latter. It has been established[20] that close analogues of PTHN such as compounds of the type



only reduce the molecular weight of the polymer without influencing the rate of initiation. The increase of the latter has been noted only when markedly different model compounds, which can in principle themselves react with styrene to form biradicals, are used.

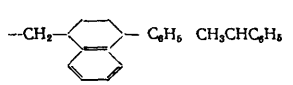
The capacity of pentafluorostyrene for thermopolymerisation cannot be explained on the basis of the structure of an intermediate of the type of PTHN. Indeed, in this case a fluorine atom should be abstracted from PTHN by a monomer molecule, which is extremely doubtful.

A possession of an initiating capacity (even though it is a weak capacity) by the biradical formed from cyclodiazo-compounds is of fundamental importance. We may note that the types of biradicals involved in the formation of monoradicals in thermopolymerisation can be various. The data of a study whose authors[84] concluded that the macromolecules have benzyl and phenylpropenyl end groups are extremely interesting in this sense. Clearly, PTHN cannot be their source. It is also unlikely that they arise in the thermal decomposition of dimers, since the rate of this reaction should be extremely low and the dimer $C_6H_5CH_2CH_2CH_2{=}CHC_6H_5$ has not been detected. Apparently the trimeric biradical



should be regarded as the source of initiating radicals.

In low-molecular-weight products of the thermopolymerisation of styrene in the presence of $FeCl_3$, the following fragments have been discovered:[85]



It has been suggested that they are due to the primary initiating radicals, which confirms Mayo's mechanism. However, they could be formed in other ways. Thus the phenyltetralin

fragment can arise on chain transfer via PTHN and the phenylethyl fragment enters into the composition of the trimer.

We shall now confirm the available data on the polymerisation of styrene and other vinyl-aromatic compounds. The thermal reactions of these monomers are characterised by a series of common features: the formation of dimers having related structures (vinylthiophen, vinylfuran), the same order of the initiation reaction with respect to monomers, which is 3 (for VT, VF, 2-methyl-5-VP, and indene). It is noteworthy that also in the case of vinyl-aromatic compounds a dimeric intermediate participates in the formation of the initiating radicals. In principle, it can also be the adduct formed as a result of the Diels–Alder condensation. This possibility exists for VF, VT, VP, and β-VN, but is realisation in the case of indene, acenaphthalene, and α-VN is extremely problematical, since it requires the occurrence of fairly complex multistage rearrangements. One can therefore assume that there exists only one mechanism of the thermopolymerisation of all vinyl-aromatic monomers.

Thus the biradical mechanisms make it possible to account for the majority of experimental data, including those which do not fit within the framework of Mayo's mechanism.

Table 2. Kinetic parameters of the initiation process in the thermopolymerisation of acrylates.

Monomer	A_i, litre mol^{-1}s^{-1}	E_i, kJ mol^{-1}	t, °C	w_i, mol litre^{-1}s^{-1}	Refs.
Butyl methacrylate	—	—	80	$3\cdot10^{-13}$	[86]
Methyl acrylate	—	—	80	$5.3\cdot10^{-12}$	[86]
Methyl methacrylate	0.36	92	90	$1.7\cdot10^{-12}$	[87]
ditto	—	—	90	$1.7\cdot10^{-12}$	[86]
»	$1.1\cdot10^{-4}$	84	90	10^{-16}	[1]
»	—	—	0	$6.3\cdot10^{-13}$	[88]
Ethyl methacrylate	$10^{3.17}$	138.3	90	$1.5\cdot10^{-15}$	[89]
Methyl methacrylate	$10^{3.17}$	138.3	90	$1.5\cdot10^{-15}$	[89]
α-Chloroacrylate	$10^{6.96}$	148	80	$1.2\cdot10^{-15}$*	[89]
β-Chloroacrylate	$10^{6.9}$	158	80	$7.9\cdot10^{-16}$*	[89]

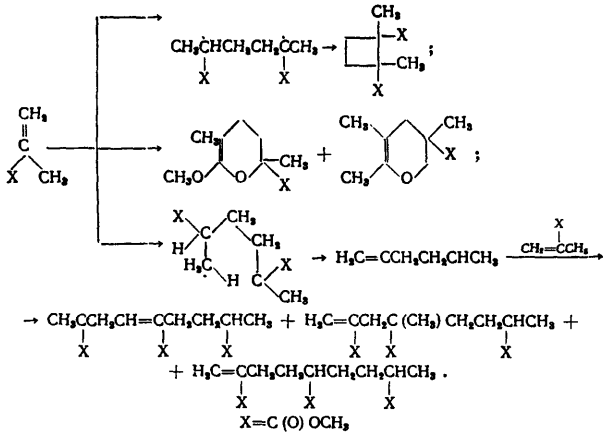
*Bimolecular initiation rate constants.

III. OXYGEN-CONTAINING MONOMERS

1. Acrylates

The kinetic data for bimolecular reactions initiating the polymerisation of acrylates in bulk, obtained in different studies or calculated by ourselves from published results, are presented in Table 2. In the analysis of the data in Table 2, the non-reproducibility of the rate of initiation of methyl methacrylate (MMA) is striking. It has been suggested[88] that this may be caused by the generation of an inhibitor in the thermal reaction. Indeed the rate of increase of viscosity for a fairly low degree of conversion diminishes as the process proceeds. Analysis shows that its reciprocal fits satisfactorily on the linear time plot. This is consistent with the hypothesis put forward by Bamford and Dewar.[88] The rate of initiation of the polymerisation of MMA at 0 °C [88] is fairly high (Table 2). According to the hypothesis of Stickler and Meyerhoff,[90] this can be caused by the accelerating effect of impurities, while pure MMA polymerises at a low rate. However, in this case one should expect a different type of time variation of the rate of increase of viscosity.

According to the data in Table 2, α-substituents (H, CH_3, C_2H_5, C_4H_9) do not exert a significant influence on w_i. An exception is Cl, whose introduction into the α-position increases the rate of initiation of polymerisation. The absolute rates of initiation quoted in a number of studies[86,87,89] differ from one another by three orders of magnitude. This can probably be explained by the causes noted above. Among the low-molecular-weight products, dimers of three types as well as linear trimers have been detected. These are formed via the following tentative mechanisms:

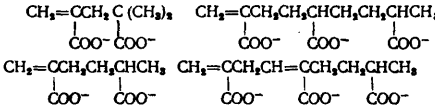


The main product is a linear dimer, the bimolecular rate constant for the formation of which is given by[91–94]

$$k\ (\text{litre mol}^{-1}\text{s}^{-1}) = 1{,}3\cdot10^{13}\exp(-107{,}2/RT).$$

Initiation is achieved as a result of the decomposition of the dimeric biradical.

In the polymerisation of methacrylic acid salts, the following products were identified in the solid phase:[95]



A reaction mechanism has been proposed, in which the formation of biradicals is postulated in the first stage.[95]

The inhibition of the thermopolymerisation of acrylates by stable nitroxy-radicals—di(ethoxyphenyl)nitrogen oxide (I), the 4-hydroxy-2,2′,6,6′-tetramethylpiperidin-1-yloxy-radical (II), and the 4-benzoyl-2,2′,6,6′-tetramethylpiperidin-1-yloxy-radical—has been investigated.[86] In all cases, with the exception of methyl acrylate, the dependence of τ on $[In]_0$ is non-linear and resembles the corresponding dependence found for styrene. The results of the treatment of these data by Kurbatov's method[72] are presented in Table 3. Overall, a satisfactory agreement is observed between the rate constants calculated for different conditions. An exception is the value for the polymerisation of butyl methacrylate inhibited by compound (II). On the other hand, the values of w_i obtained using these compounds (I) and (II) agree satisfactorily. The linear dependence of τ on $[In]_0$ observed for the methyl acrylate–radical (I) pair shows that the radical is consumed in accordance with a zero-order law. The process rate constant is 6.75×10^{-9} mol litre^{-1} s^{-1}. This value exceeds almost by three orders of magnitude the rate of initiation found in experiments with the radical (III) and should therefore represent the product $nk_0[M]^2$.

The constant $k_{i,n}$ for the process involving MMA is much too high compared with that found under initiated conditions, while the value of w_i is consistent with that found by Lingnau

and Meyerhoff.[89] The constants k for MMA and other monomers of this series are similar. This can be associated with the effect of strong secondary inhibition in the chain process or with the generation of an "internal" inhibitor, which reacts with alkyl radicals, as stated above. It is of interest that this feature is characteristic solely of MMA.

Table 3. The rates of initiation and the rate constants for the inhibition of the polymerisation of acrylates by nitroxyradicals (calculated from data of Trubnikov et al.[86]).

Radical	k_{in}, litre mol^{-1}s^{-1}	k_{in}^*, litre mol^{-1}s^{-1}	w_i, mol litre^{-1}s^{-1}	10^4k, s^{-1}
Butyl methacrylate, 80 °C				
(I)	$2.4\cdot10^6$	$5.7\cdot10^6$	$1.5\cdot10^{-11}$	2.7
(II)	$0.3\cdot10^6$	$30\cdot10^6$	$2.3\cdot10^{-11}$	0.60
Methyl acrylate, 80 °C				
(I)	—	—	—	$\leqslant$0.1(88° C)
(III)	$4.8\cdot10^5$	$7\cdot10^5$	$3.2\cdot10^{-12}$	1.5
Methyl methacrylate, 90 °C				
(II)	$460\cdot10^5$	$6\cdot10^5$	$4.0\cdot10^{-15}$	0.42

*The inhibition rate constants found under the conditions of initiated polymerisation.[86]

The set of data obtained in the analysis of the characteristics of the inhibition and of the composition and structure of the low-molecular-weight products shows that the thermopolymerisation of acrylate entails the formation of an intermediate, which reacts unimolecularly with the molecules of the inhibitor and the monomer. In the case considered such an intermediate can only be a dimeric biradical. By analogy with styrene, the formation of dimers in the scheme presented above can be represented as a result of its interaction with the monomer and the subsequent unimolecular disproportionation.

2. Vinyl Acetate

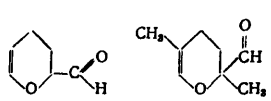
Calculated data based on the results of Starkweather and Taylor[96] have shown that the best agreement between the overall polymerisation rate constants is achieved when a kinetic order with respect to the monomer of 2.5 is adopted. One can then obtain the following expression for the rate of initiation (at 80–110 °C):

$$w_i \text{ (mol litre}^{-1}\text{s}^{-1}) = 4.8\cdot10^{18}\exp(-167.2/kT)\,[\text{M}]^{2.5}.$$

It is close to that found[1] by another method. This means that the initiating radicals are formed in the thermopolymerisation of vinyl acetate with participation of monomer molecules.

3. Acrolein, Methacrolein, and Acrylic Acid

The primary products of the reaction of aldehydes are the corresponding dihydropyrans, formed as a result of 2,4-cycloaddition:[97–100]



Acrylic acid gives rise to a linear unsaturated dimer—acryloylhydracrylic acid.[99] Only the acrolein dimer is formed in the presence of hydroquinone.[99] The activation energy for the thermopolymerisation is 65.4 kJ mol^{-1}. In the presence of an amine inhibitor (whose structure and concentration have not been reported), it increases to 118.8 kJ mol^{-1}.[98] On this basis, it has been concluded that the inhibitor is active in the dimerisation stage.[98]

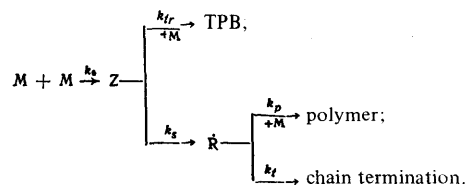
If the reaction takes place under inhibited conditions, the increment in the observed activation energy should be $0.5(E_i + E_t) - E_{in}$, where E_i, E_t, and E_{in} are the activation energies for initiation, chain termination, and the interaction of radicals with the inhibitor. For $E_{in} \cong 15$–25 kJ mol^{-1}, the quantity E_i, calculated on the basis of experiments with and without participation of the inhibitor, is 12–140 kJ mol^{-1} (the values of E_p and E_t were taken from Ham[101]), which means that the thermopolymerisation of acrolein proceeds via a radical-chain mechanism and that dimerisation is the accompanying process.

IV. MONOMERS OF THE ACETYLENE SERIES

Among the products of the thermopolymerisation of vinylacetylene, diethynylcyclobutane and the polymer which is a polyene according to the latest data[103,104] were detected.[102] The kinetic studies were performed in relation to ethynylaromatic compounds: phenylacetylene (PA), 5-ethynyl-2-methylpyridine,[105,106] and 3-ethynylphenyl phenyl ether.[107]

Apart from the polymer, 1,3,5- and 1,2,4-triphenylbenzenes (TPB),[106] whose overall yield was ~10%, were found among the products of the reaction involving PA. Since the overall rate of polymerisation is described by a kinetic equation whose order is close to two, it has been suggested that the initiators are biradicals or more precisely that one of the isomers is formed by the "tail to tail" combination of two monomer molecules, since the lowest activation energy is then expected; TPB arises as a result of the interaction of the biradicals with a monomer molecule.[106]

Analysis of the above data[106] shows that, both for PA and ethynylpyridine, the observed polymerisation rate constant, calculated subject to the condition that the reaction is of second order, is not invariant and depends on the monomer concentration. The relation $[\text{M}]^3/w = a + b[\text{M}]$, where a and b are constants, hold satisfactorily under these conditions (Fig.1). This result conflicts with the mechanism of the initiation of polymerisation by biradicals. The present author's analysis of the kinetic schemes has shown that unimolecular and bimolecular destruction of biradicals should correspond not to second order with respect to the monomer but to a higher or lower order. Hence the experimental reaction order and the dependence of the rate constant on the monomer concentration lead to the conclusion that the initiation reaction involves the formation of an intermediate Z. On this basis, one can postulate that the polymerisation mechanism is described by the following scheme:



According to this scheme, the intermediate gives rise to initiating radicals in the unimolecular reaction and to TPB in the bimolecular reaction. Chain termination takes place linearly, as has been established by Pickard and Jones.[107]

Under conditions stationary with respect to Z and $\dot{R}$, the expressions for the rate of polymerisation and trimerisation are as follows:

$$w = \frac{k_0 k_p k_s [M]^3}{k_t (k_s + k_{tr}[M])}; \quad (1)$$

$$w_{tr} = \frac{k_0 k_{tr} [M]^3}{k_s + k_{tr}[M]}. \quad (2)$$

Evidently the former agrees with the empirical relation.

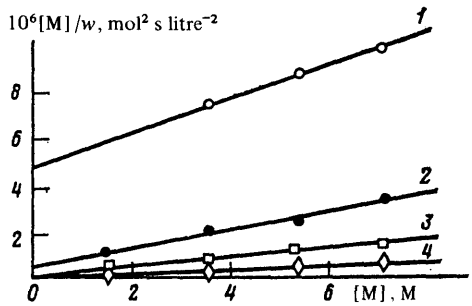


Figure 1. Dependence of the reciprocal of the measured third order rate constant for the polymerisation of phenylacetylene on its concentration at different temperatures (°C): 1) 125; 2) 140; 3) 155; 4) 170 (according to the data of Bantsyrev et al.[106]).

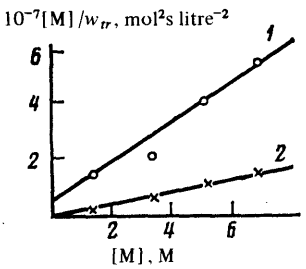


Figure 2. Dependence of the reciprocal of the third order rate constant for the formation of 1,2,4-triphenylbenzene (line *1*), and 1,3,5-triphenylbenzene (line *2*) at 140 °C on the phenylacetylene concentration (according to the data of Bantsyrev et al.[106]).

Treatment in terms of the second equation of data on the rate of formation of TPB isomers, which can be calculated from the results of Bantsyrev et al.,[106] confirms the validity of the proposed mechanism (Fig.2). The difference between the slopes of the linear relations in Fig.2 indicates unequal rates of generation of the precursors of the different TPB isomers. The constant k_0 is 1.5×10^{-7} litre mol^{-1} s^{-1} for 1,2,4-TPB and 5×10^{-7} litre mol^{-1} s^{-1} for 1,3,5-TPB. The straight line corresponding to 1,3,5-TPB intersects the ordinate axis near zero; consequently k_s/k_{tr} is vanishingly small. Thus the intermediate preceding 1,3,5-TPB does not participate in the initiating reaction. For 1,2,4-TPB, the above quantity, estimated from kinetic data for both polymerisation and trimerisation, is 5–6 mol litre^{-1}.

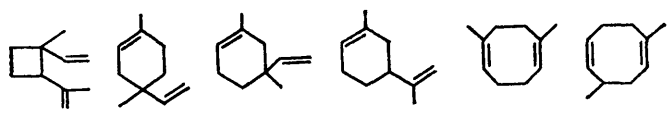
As regards the nature of the intermediate, there is no doubt that it is a biradical. Thus two types of paramagnetic species were detected by EPR in the thermopolymerisation of PA in the presence of spin trapping agents.[108] Analysis of the spectra permitted the conclusion that they arise as a result of the acceptance of the polymeric monoradical and biradical.

V. DIENE MONOMERS

1. Derivatives of Butadiene and Cyclic Dienes

The majority of publications concerning the thermal reactions of hydrocarbons of the divinyl series refer to the study of low-molecular-weight cyclic products formed as a result of the [2 + 4]cycloaddition. The polymerisation kinetics have been investigated only in a few early studies and to an extremely limited extent. We shall deal here with data which are of fundamental interest.

The thermal reactions of diene hydrocarbons of the divinyl series were accompanied by the formation of a polymer and dimers of three main types: derivatives of cyclobutane, vinylcyclohex-3-ene, and cyclo-octa-1,5-diene. Mainly 1-vinylcyclohex-3-ene and 4–5% of 1,2-divinylcyclobutane are formed from divinyl itself.[109] Isoprene gives rise to all the possible dimers:[110,111]

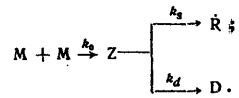


The low-molecular-weight products of the reaction of *cis*-piperylene are only the six- and eight-membered dimers, while *trans*-piperylene gives rise to 80% of four-membered products.[111] The biisopropenyl dimer consists exclusively of dimethyl-4,6-dimenthene.[112]

The polymerisation of methylallenes leads to the formation of dimethylenecyclobutanes, which subsequently participate in secondary reactions.[113] Cyclopentadiene dimerises with an activation energy of 69 kJ mol^{-1} and the reaction is reversible.[111,114] Trimers are formed in a very small amount as a result of the cycloaddition of the monomer to the dimer.[115] Cyclohexadiene reacts via two pathways: dimerisation and polymerisation.[116]

The polymerisation reaction of all the dienes investigated is of second order with respect to the monomer. This order persists also when the reaction is carried out in dimethylformamide.[117] The results of kinetic studies are presented in Table 4. Since the overall polymerisation is a second order reaction, we may conclude that the initiation is a bimolecular process. Assuming that the activation energy for the bimolecular termination of the kinetic chains E_t is close to 8 kJ mol^{-1}, while $A_t = 10^7 - 10^8$ litre mol^{-1} s^{-1} as for the majority of monomers, we obtain $E_i \approx 92$ kJ mol^{-1} and $A_i \approx 8$ to 80 litre mol^{-1} s^{-1} for isoprene, while the corresponding values for biisopropenyl are 88 kJ mol^{-1} and 0.1–1 litre mol^{-1} s^{-1} respectively. The constants k_p were taken from Kauffmann et al.[16] (p.120) and Starinchikova and Svetlov[127] (p.342). Since the pre-exponential factors A_i found are fairly low, one can assume that the initiation rate constant is an effective quantity. This is possible only when the radicals are

formed via an intermediate Z, which is also converted competitively, for example, into dimers. The reaction mechanism can be formally represented schematically as follows:



According to this scheme, the rate of initiation is defined by the expression

$$w_i = k_0 k_s [M]^2/(k_s + k_d).$$

Then, assuming that $k_s \ll k_d$ and adopting $E_d \cong 84-92$ kJ mol^{-1} and $A_d \cong 10^6-10^7$ litre mol^{-1} s^{-1}, we obtain $E_s - E_d \cong 0$ and $A_s/A_d \cong 10^{-6}-10^{-4}$. It is noteworthy that no measurements were made of the initiation reaction order on the basis of concentration; one cannot rule out that it amounts to 2.5 and that the rate constant k_s actually characterises a bimolecular process.

Table 4. Kinetic parameters of the reactions involving the formation of polymers (P) and dimers (D) from diene monomers.

Monomer	Reaction product	E, kJ mol^{-1}	A, litre mol^{-1}s^{-1}	Refs.
Isoprene	(VII)	94	$1.8\cdot10^7$	[118]
»	(V) + (VI) *	90	$1.4\cdot10^6$	[118]
»	D	104	$7.9\cdot10^7$	[119]
»	P	78,6	$3.4\cdot10^7$	[118]
Biisopropenyl	D	92	$2.1\cdot10^6$	[118]
»	P	73	$2.2\cdot10^5$	[118]
cis-Piperylene	D	93	$2.1\cdot10^5$	[111]
trans-Piperylene	D	81,5	$8.7\cdot10^4$	[111]
Cyclopentadiene	D	62	$4.0\cdot10^5$	[111]
1,2-Dimethylallene	D	116	$3.4\cdot10^7$	[113]
Cyclohexa-1,3-diene	D	86	$4\cdot10^4$	[116]
»	P	96,5	$1.7\cdot10^6$	[116]

*Gapon[118] called this product the second dimer, while according to Nazarov et al.[110] it is a mixture of compounds (V) and (VI).

In our view the intermediate is none other than a biradical. The formation of biradicals in the thermopolymerisation of dienes has been confirmed by the presence of four-membered cyclic dimers. It has been established[119] that the volume of the transition state in the dimerisation of isoprene is greater by 21–23 cm^3 mol^{-1} than the volume of the dimer. On passing from six-membered rings to the corresponding linear hydrocarbons, the same increase in specific volume occurs. On this basis, it has been concluded that the intermediate is indeed a biradical. The dimerisation of 1,4-dideuteriobutadiene is accompanied by a decrease of the stereospecificity of the dienophile component by 10%.[121]

2. Chloroprene

The thermopolymerisation of chloroprene is accompanied by the formation of products of the same type as for other 1,3-dienes, namely compounds corresponding to divinylcyclobutane (X),[122] two vinylcyclohexene (XI) isomers, and cyclooctadiene.[123] The first two products predominate at high temperatures (95 °C) and the compound of type (X) isomerises to (XI). The polymer is linear *cis*-polychloroprene.[124]

The dimers and the polymer are formed in accordance with a second-order law at different rates and with different activation energies; the latter differ little for the 4- and 6-membered isomers, amounting to 84–86 kJ mol^{-1}.[124,125] Typical inhibitors suppress the formation of the polymer but do not affect dimerisation,[124] DPPH being converted under these conditions into the corresponding hydrazine.

However, a number of significant differences make it necessary to regard the mechanism of the thermopolymerisation of chloroprene as extremely stereospecific and different from the mechanism of the reactions of other dienes. At the end of the induction period, associated with the exhaustion of the inhibitor, the concentration of the dimer falls, tending to ~1 wt.%, while the polymer is formed at a constant rate.[125] If the reaction is carried out without an inhibitor, then the concentration of dimers increases from a certain initial value to a limiting value, which is also close to 1 wt.%. These findings enabled the authors[124] to reach the unusual conclusion that the polymer is formed exclusively from the dimer; there is no doubt about its validity.

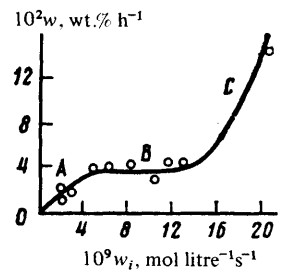


Figure 3. Dependence of the rate of polymerisation of chloroprene on the rate of initiation at 35 °C.[125]

The method used in the preliminary treatment of the monomer, especially, the degree of elimination of oxygen from the latter and the degree of its reduction, exerts the main influence on the rate of polymerisation. Chloroprene dimers do not polymerise, but the introduction of the monomer renders this process possible. The authors[125] suggested that the polymerisation initiator is an oxidised form of the monomer, which is not determined as the peroxide. The relation between the rates of polymerisation and initiation of chloroprene (the latter was estimated from the consumption of DPPH) is characterised by the presence of different sections *A*, *B*, and *C* (Fig.3) whose existence has been explained as follows.[125] After the careful removal of oxygen, the concentration of catalytic species Y is small and the rate of polymerisation is lower than that of dimerisation. Indeed, along section *A*, the sum of the concentrations of the dimers and the polymer is approximately equal to the concentration of the dimers formed in the presence of the inhibitor. Along section *B*, the rate of polymerisation is constant and equal to the rate of dimerisation in the presence of the inhibitor regardless of the rate of initiation. This means that [Y] is large and the rate of conversion of the dimers into the polymer is much higher than the rate of their formation. In order to explain section *C* of the curve, the monomer brought into contact with oxygen was employed and there is no doubt that the increase in the rate of polymerisation in this region is associated with the influence of a polyperoxide.[126]

Taking into account all the facts described, one may conclude that the monomer contains catalytic species which lead to the polymerisation of the dimers via ring opening. In the presence of inhibitors, these species are not destroyed. Therefore, there should exist an active centre (I), originating from the catalytic compound Y. It participates in the kinetic chain propagation and termination reactions and in the latter case the catalyst Y is regenerated.

We believe that the following mechanism is most probable:

$$M + M \xrightarrow{k_0} D; \quad D + Y \xrightarrow{k_s} I; \quad D + I \xrightarrow{k_p} P; \quad I \xrightarrow{k_t} \text{chain termination.}$$

The steady concentration of dimers can be found from the equation which follows from the above scheme:

$$0.5\left(\frac{k_t}{k_0 k_p k_s [Y][M]^2}\right)^{0.5} \ln\frac{([D]_{st} + [D])([D]_{st} - [D]_0)}{([D]_{st} - [D])([D]_{st} + [D]_0)} = t, \qquad (3)$$

where $[D]_{st}$ is the stationary concentration of the dimer.

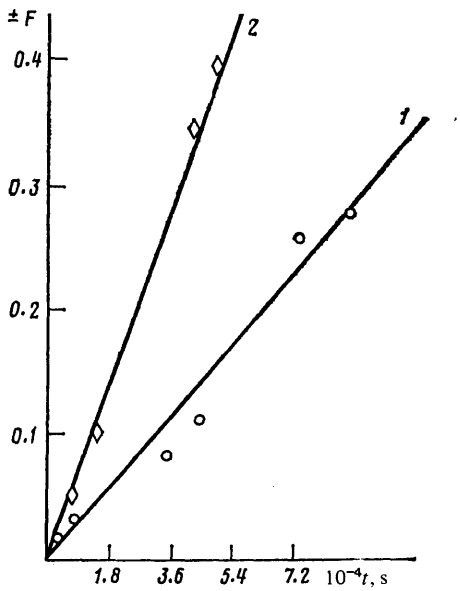


Figure 4. Semilogarithmic representation of the kinetics of the attainment of a stationary chloroprene concentration (at 35 °C): 1) calculation based on the accumulation of the dimer; 2) calculated based on the consumption of the dimer (according to the data of Billingham et al.[125]).

Calculation of the change in the concentration of the dimers by this equation both in experiments with the inhibitor and without it makes it possible to obtain the linear relations presented in Fig.4. In the second case, the sign of the function

$$F = \ln\frac{([D]_{st} + [D])([D]_{st} - [D]_0)}{([D]_{st} - [D])([D]_{st} + [D]_0)}$$

is negative. Since it is impossible to determine $[D]_{st}$ accurately from the data presented, we assumed that it is approximately 1%. If it is ~1.5%, then the sign of F becomes positive.

Evidently the authors[125] used monomer specimens with different concentrations [Y], which determine $[D]_{st}$. The validity of the formal relations, which also show that [I] ≪ [Y], is of fundamental importance.

Within the framework of the scheme presented above, the rate of polymerisation is described by the expression

$$w = \frac{k_p k_s}{k_t}[Y][D]^2. \qquad (4)$$

After substituting in Eqn.(4) the expression for the steady concentration of the dimers, we obtain

$$w = \frac{k_p k_s}{k_t}[Y][D]_{st}\left(\frac{\beta e^{-\alpha t} - 1}{\beta e^{\alpha t} + 1}\right),$$

where

$$\alpha = 2\left(\frac{k_0 k_p k_s [Y][M]^2}{k_t}\right)^{0.5}; \quad \beta = \frac{[D]_{st} + [D]_0}{[D]_{st} - [D]_0}.$$

Since

$$[D]_{st} = \left(\frac{k_0 k_t [M]^2}{k_p k_s [Y]}\right),$$

it follows that, for large values of [Y], $w = k_0[M]^2$.

Two questions are of decisive important for the mechanism of the thermopolymerisation of chloroprene: (a) the nature of the catalytic species and of the active centre; (b) the mechanism of the ring opening. It is as yet difficult to give a definite answer to these questions.

On the grounds that substances tending to undergo homolytic reactions exhibit an inhibiting activity, presumably I is a radical in nature and diphenylpicrylhydrazine is formed as a result of a disproportionation reaction. Then the interaction of the dimer and Y should result in the formation of an extremely specific radical, which reacts with the dimer but not with the monomer. The equality of the rates of dimerisation and polymerisation suggests either the involvement of the dimers of all types in the second process or the establishment of equilibrium between them via the intermediate. There exists also the view that the rearrangement proceeds via the formation of a biradical.[121] This may explain the observed characteristics of the polymerisation, although the mechanism of the stabilisation of the biradicals by the catalytic species is obscure.

3. Divinyl Sulphide

The elementary units of the polymer macromolecules formed from divinyl sulphide have the thiophane structure.[127] The order of the overall polymerisation reaction with respect to the monomer is 2.1 and the activation energy is 50.2 kJ mol^{-1}. The activation energy for thermal initiation (62 kJ mol^{-1}) and the pre-exponential factor for the rate constant (~10^3 litre mol^{-1} s^{-1}) can be estimated from the data of Starinchikova and Svetlov.[127]

VI. ETHYLENE

The thermal reactions of ethylene have been investigated in the gas and liquid phases. At temperatures below 400 °C, polymerisation mainly takes place[128] (p.125). The primary reaction products detected consisted of 31.7% of butenes, 12.6% of cyclobutanes, and also propene and higher olefins. The activation energy for the formation of lower hydrocarbons is 475 kJ mol^{-1}. The kinetic order of the polymerisation

reaction with respect to ethylene at sufficiently high conversions is close to two but at early stages it amounts to 2.3 to 2.5.[129]

The polymerisation of ethylene in solution in naphthalene is characterised by a kinetic order of 2.6, an activation energy of 170 kJ mol^{-1}, and a pre-exponential factor of $10^{10.1}$ litre mol^{-1} s^{-1}.[129] It has been suggested[129] that the reaction order observed is determined by the stage involving the formation of the intermediate. It is believed[128] that the initiating radicals arise when a hydrogen atom is transferred from one ethylene molecule to another. The observed activation energy for the initiation stage is consistent with this hypothesis but one cannot rule out the possibility of the formation of the tetramethylene biradical as the intermediate.[128]

The data of Russell and Hottel[129] permit the conclusion that the order of the initiation reaction with respect to ethylene is 3. When w_i (mol litre^{-1} s^{-1}) $= 10^{15}\exp(-272/RT)[M]^3$.

Bearing in mind that the reaction considered is of third order and also taking into account the formation of cyclobutane and butene, its mechanism can be represented by the following scheme involving the tetramethylene biradical:

$$2H_2C{=}CH_2 \rightarrow \dot{C}H_2CH_2CH_2\dot{C}H_2- \begin{cases} \rightarrow n\text{-}C_4H_8 + \text{cyclo-}C_4H_8, \\ \rightarrow 2\dot{R} \rightarrow \text{polymer}. \end{cases}$$

Chlorotrifluoroethylene and tetrafluoroethylene give rise to only the corresponding cyclobutane derivatives.[130]

VII. CONCLUSION

Analysis of the results of the study of the thermopolymerisation of monomers of different classes permits certain general conclusions concerning the mechanism of this reaction.

The low-molecular-weight products of the given process can be various but as a rule they are dimers. Phenylacetylene gives rise to the trimer only. Mixtures of different dimers and trimers are produced from styrene and MMA and tetramers have also been detected.

The polymerisation of all monomers, with the exception of chloroprene, proceeds in accordance with the classical radical-chain mechanism. The initiating radicals are generated via an intermediate which is in most cases a biradical. Although the formation of PTHN as an intermediate has in fact been postulated for styrene, a number of results conflict with this hypothesis. There is probably no point in assuming a special exceptional mechanism for this monomer, which does not exhibit any anomalous properties. The third order of the initiation stage with respect to the monomer shows that the radicals are formed as a result of the interaction of the dimeric biradical with the monomer, which subsequently decomposes, producing, for example, in the case of styrene, the benzyl and phenylpropenyl radicals. Judging from the fairly low pre-exponential factors in the expressions for the initiation rate constants, the third kinetic order is to be expected for MMA, isoprene, bi-isopropenyl, indene, and divinyl sulphate. The primary radical is then preferentially converted into the dimer, which is confirmed in many instances either by the absence of trimers or by their low yield. On the other hand, when the competing reaction of the biradical with the monomer takes place to an appreciable extent, the reaction order may become less than three, falling to two. In order to establish the true reaction order, detailed kinetic studies are required and these have been by no means always carried out. In contrast to other monomers, in the polymerisation of phenylacetylene monoradicals arise in the decomposition of a dimeric biradical, whose reaction with the monomer leads to the formation of triphenylbenzene. The initiating radicals are not formed at all or are formed with a low yield in the thermopolymerisation of trifluorostyrene and acrylonitrile[101] (p.221), whose only products are the corresponding four-membered dimers.[131] A similar situation has been observed for α- and β-halogenostyrenes.

It is noteworthy that, when the classical values of the pre-exponential factors are used for the rate constants for the elementary stages involved in the initiation process, it is impossible to account for the high pre-exponential factors in the expression for the initiation rate constants for monomers such as ethylene and vinyl acetate, which amount to ~10^{15} and 10^{18} litre^2 mol^{-2} s^{-1} respectively. On the other hand, this can be explained by the fairly low values of A for the stages where the biradicals are converted into low-molecular-weight compounds or for their reversible decomposition with formation of the monomer and, on the other, by the more complex expression for the overall rate constant, which is determined by the characteristic features of the mechanism.

In contrast to other methods of generating similar reactive species, such as the decomposition of cyclic diazo-compounds or the thermolysis of cyclobutanes, in the thermal reaction of the monomers there is a possibility of the formation of biradicals with different configurations. It has been noted correctly[121] that the "uncoiled" forms of biradicals are less susceptible to unimolecular recombination, since for the occurrence of the latter it is essential that the biradical should assume a cyclic form, from which the cyclic dimer can be readily produced. Indeed, inhibitors do not influence the formation of diphenylcyclobutane in the decomposition of tetrahydropyridazines and in the thermal reaction of styrene.[19] The rate of generation of the initiating monoradicals is also extremely low. Biradicals in an acyclic conformation are capable of reacting unimolecularly also via disproportionation and alkylation. There is also a possibility of a bimolecular reaction, for example, the reaction with the monomer. Judging from data of Kirchner and Burhholz,[12] the ratio k_d/k_{tr} for styrene should be 2.3. Since the deviation from the zero order of the DPPH destruction reaction occurs at the concentration (DPPH) $\cong 10^{-5}$ M,[63] it follows that $k_b/k_{tr} \cong 8.7 \times 10^5$.

The rate constants for the destruction of biradicals generated in the photochemical reactions of ketones (Norrish type 2 reactions) in the presence of various acceptors (oxygen, bipyridyl hydrochloride, dibutyl selenoketone) are (4–6) × 10^9 mol^{-1} s^{-1},[132,133] i.e. exceed significantly in absolute magnitude the constants known for monoradicals. A similar phenomenon had been observed earlier for nitroxy-biradicals.[134] In order to account for this finding, the concept of the adiabatic nature of the reactions was resorted to[134] (pp.378, 386). If it is assumed that the rate constants for the reactions of the dimeric styrene biradicals with DPPH are also diffusion dependent, it is possible to calculate $k_{tr} \cong 5 \times 10^3$ litre mol^{-1} s^{-1} and $k_d \cong 10^4$ s^{-1}. The latter quantity may be too low, but even in the case of cyclic biradicals, whose conversion into a state favourable for recombination requires virtually no rotation about the C–C bonds, there exists a competing reaction with divinyl.[135]

The question whether the initiating radicals and all the low-molecular-weight compounds are formed via the same intermediate is of fundamental importance. There is perhaps no doubt that this is true (a) for styrene, because it is supported by evidence obtained in the study of the thermopolymerisation kinetics, the structures of the compounds produced, and the influence of radical acceptors and (b) for

monomers whose thermopolymerisation gives rise preferentially to oligomers with a linear structure, which are formed via an intermediate (methacrylates).

However, for the monomers giving rise to low-molecular-weight 2,4-cycloaddition products, the answer to the question posed above is not unambiguous. The possibility of the formation of small amounts of four-membered or linear dimers cannot be ruled out even in those cases where the main product is a six-membered compound (2,3-dimethylbutadiene). On the other hand, there exists the hypothesis that 2,4-cycloaddition reactions take place via two competing mechanisms: synchronous and biradical.[136] The second pathway may be responsible for the initiation of the polymerisation. According to most investigators, the activation energy for the biradical process should be significantly higher than for the synchronous process[121] and its contribution should be correspondingly lower.

Thus in the given case the problem also reduces to the familiar problem of the mechanism of pericyclic reactions. Having analysed numerous facts, Firestone[121] concluded that the biradical mechanism makes it possible to explain virtually all the experimental data, while the synchronous mechanism is inconsistent with many of them.

Overall, one may conclude that there exists a general mechanism of the thermal reactions of many monomers. Specific differences may be observed for individual representatives of substances of this kind.

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