

## POLYMERISATION OF METHYL METHACRYLATE INITIATED WITH N-BROMOSUCCINIMIDE

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Kinetics of polymerisation of methyl methacrylate initiated by N-bromosuccinimide was studied in the temperature range of 41–85°C. The overall energy of activation was found to be 10.5 kcal/mol and the transfer constant with respect to the initiator 1.3. An initiation mechanism is put forward. Also an inhibition effect of styrene on the polymerisation or on the copolymerisation with methyl methacrylate is discussed.

N-bromosuccinimide (*I*) is known as a selective brominating agent and the radical nature of its action is generally accepted. Its ability of initiating polymerisation is mentioned in papers by Dannley and Esayian<sup>1</sup> and by Otsu and Yamaguchi<sup>2</sup>. The authors of the first paper have found that imide *I* initiates polymerisation of methyl methacrylate but does not initiate either the styrene polymerisation or the copolymerisation of this couple of monomers. The authors of the second paper have focused their attention to a cocatalytic effect of reduced nickel on the initiation effectiveness of the imide. Up to now no more detailed information about the course of polymerisation is known. Nevertheless, the facts mentioned above are interesting enough as to initiate investigation of the origin of an unusual behaviour of the imide *I* as the initiator. If the initiation should proceed via a radical mechanism, then its failure to initiate styrene polymerisation is difficult to understand but what is even more surprising is a strong inhibition effect of styrene on methyl methacrylate polymerisation. It is known that at the copolymerisation of these two monomers initiated by common radical initiators the rate of copolymerisation decreases with increasing styrene concentration but it does not lead to a complete inhibition<sup>3</sup>.

The main aim of the present study was to obtain more detailed information about the kinetics of methyl methacrylate polymerisation initiated by N-bromosuccinimide and also to help in elucidation the styrene inhibition effect on the polymerisation reaction.

### EXPERIMENTAL

N-Bromosuccinimide, Lachema, Brno, m.p. 177°C (nitromethane; ref.<sup>4</sup> gives 178°C); benzoyl peroxide, m.p. 108°C (chloroform); 2,2'-azobis(isobutyronitrile), m.p. 103.5°C (ethyl ether). Methyl methacrylate, Považské chemické závody, Žilina, stabilised by hydroquinone, was freed from stabiliser by five-time washing with 10% sodium hydroxide solution and then with water to neutral reaction. After drying with calcium chloride it was twice distilled under reduced pressure of nitrogen<sup>5</sup>. The kinetics of methyl methacrylate polymerisation was followed by the gravi-

metrical determination of the conversion of monomer to polymer. The polymerisation was performed in sealed glass ampoules under nitrogen and in dark (U. V. light induces catalyst decomposition). The ampoules were removed in selected time intervals, cooled to room temperature, opened and the polymer was precipitated by the excess of methanol containing 5% of water. The average molecular weight of poly(methyl methacrylate) was determined from the intrinsic viscosity<sup>6</sup> according to  $[\eta] = 8.69 \cdot 10^{-5} \bar{M}_n^{0.76}$ . The viscosity of benzene solution was determined at 30°C.

## DISCUSSION

Table I summarizes both the effect of N-bromosuccinimide (*I*) concentration (initiator) and temperature on the molecular weight of poly(methyl methacrylate) formed. At the temperature of 60°C the radical polymerisation follows the usual square-root relation between the rate of polymerisation ( $R_p$ ) and the initiator concentration ( $[I]$ ). The value of the exponent *n* in the following equation

$$R_p = k[I]^n, \quad (1)$$

was determined from the linear dependence  $\log R_p$  vs  $\log [I]$  and found to be 0.48. This value should indicate that no anomalous process takes place at the termination reaction. The rates of polymerisation were calculated from initial linear parts of the conversion curves (Fig. 1). The Arrhenius plot gives a linear dependence (Fig. 2),

TABLE I

Rate of Reaction ( $R_p$ ) and Polymer Molecular Weight ( $\bar{M}_n$ ) at the Polymerisation of Methyl Methacrylate in the Presence of N-Bromosuccinimide as the Initiator (*I*)

| Temperature<br>°C | $[I] \cdot 10^2$<br>mol/l | $R_p \cdot 10^5$<br>mol/l · s | $\bar{M}_n$       | Conversion <sup>a</sup><br>% |
|-------------------|---------------------------|-------------------------------|-------------------|------------------------------|
| 60                | 1.41                      | 1.66                          | 610 000           | 3.5                          |
| 60                | 2.81                      | 2.30                          | 219 000           | 6.5                          |
| 60                | 5.62                      | 3.23                          | 89 000<br>142 000 | 5.5<br>9.1                   |
| 60                | 11.24 <sup>b</sup>        | 4.27                          | —                 | —                            |
| 60                | 39.35 <sup>c</sup>        | 5.21                          | —                 | —                            |
| 80                | 5.29                      | 8.42                          | 56 000<br>199 000 | 4.0<br>10.1                  |

<sup>a</sup> Conversion of monomer to polymer at which the molecular weight was determined. <sup>b</sup> Initiator was completely dissolved only at the polymerisation temperature. <sup>c</sup> Part of the initiator was undissolved in the monomer even during the polymerisation.

the overall energy of activation ( $E$ ) being 10.5 kcal/mol. The relatively low value of  $E$  is due to a low energy of activation of the initiation reaction ( $E_i$ ). From the value of  $E$  and from the known values of activation energies of the elementary reactions, *i.e.* for propagation and termination being 4.7 kcal/mol and 0.4 kcal/mol, respectively, (ref.<sup>7</sup>) follows that the value of  $E_i$  is 12.0 kcal/mol. The direct determination of  $E_i$  from the rate of initiation determined by measuring the inhibition periods (6.5 min at 82.5°C; 35 min at 41°C) in the presence of diphenylpicrylhydrazyl ( $1.04 \cdot 10^{-4}$  mol/l) gives the value of 8.6 kcal/mol. The rate of polymerisation was measured at imide I concentration of 0.078 mol/l and at the temperature of 41°C and 85°C. Under these conditions the measured rates of initiation are the following:  $4.95 \cdot 10^{-8}$  mol/l . s and  $2.83 \cdot 10^{-7}$  mol/l . s.

The initiation rates, which were determined in the presence of the selected inhibitor, are unusually high with respect to the observed rates of polymerisation. At the same concentration of imide I and of benzoyl peroxide (0.078 mol/l) and at 60°C, the polymerisation initiated by imide I is 80-times slower than that initiated by benzoyl peroxide. Such a high difference in the rate of polymerisation would correspond to a 6400-times lower rate of initiation if imide I is used instead of benzoyl peroxide. But the directly measured rate of initiation of methyl methacrylate polymerisation in the presence of imide I is similar to the initiation rate of benzoyl peroxide (about  $1.5 \cdot 10^{-7}$  mol/l . s).

Besides a low effectiveness of initiation the methyl methacrylate polymerisation initiated by imide I is also distinguished by a marked transfer of the growing radical

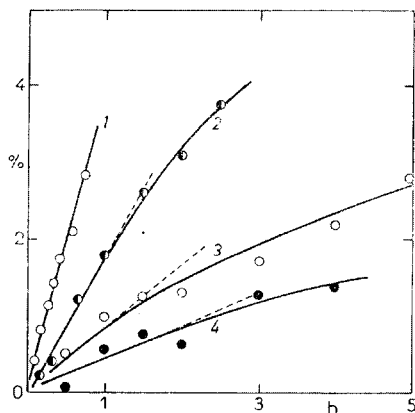


FIG. 1

Effect of Temperature on the Course of Polymerisation of Methyl Methacrylate at N-Bromosuccinimide Concentration of 0.0485 mol/l

Temperatures (°C): 1 85, 2 70, 3 55, 4 41.

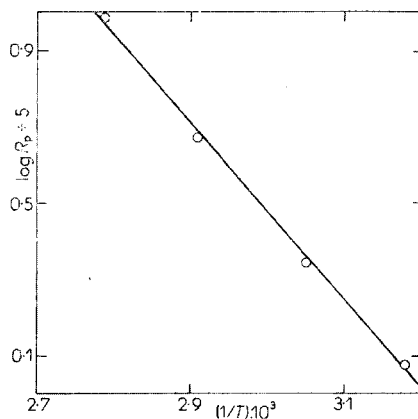


FIG. 2

Arrhenius' Plot -- Rate of Polymerisation vs Temperature for Methyl Methacrylate Polymerisation

N-Bromosuccinimide Concentration 0.0485 mol/l.

to imide I. The number-average molecular weight of poly(methyl methacrylate) prepared with the use of 2,2'-azobis(isobutyronitrile) as initiator at 60°C and at the conversion of 6.6% was  $8.5 \cdot 10^5$ . When imide I was added to this system (1.3%) the conversion increased to 7%, but the number-average molecular weight dropped to the value of  $3.2 \cdot 10^5$ . The retardation effect of the transfer agent on the rate of polymerisation has not been observed.

The transfer constant ( $C_I$ ) with respect to imide I has been determined with the use of Mayo's equation generalised for any kind of initiation and termination<sup>8,9</sup>, providing that the viscosity of the starting polymerisation mixture is constant:

$$\frac{1}{\bar{P}_n} = (1 + \lambda) \cdot \frac{1}{2} \delta^2 \frac{R_p}{[M]^2} + C_M + C_I \frac{[I]}{[M]} \quad (2)$$

$\bar{P}_n$  is the average degree of polymerisation,  $\lambda$  represents a part of termination due to disproportionation<sup>10</sup> and the value of the fraction being  $(1 + \lambda)/2 = 0.875$ .  $\delta^2$  represents the ratio of the termination rate constant and the square of the propagation rate constant; the value being 72 (ref.<sup>11</sup>),  $[M]$  is monomer concentration,  $C_M$  is the transfer constant with respect to monomer ( $1 \cdot 10^{-5}$  according to ref.<sup>12</sup>). The value of the transfer constant of poly(methyl methacrylate) radical with imide I at 60°C is 1.3 (Fig. 3) as it was obtained by a graphical solution of the equation (2). The value is by 3 to 5 orders higher than transfer constants of usual initiators, such as 2,2-azobis(isobutyronitrile) used in comparative experiments. A marked transfer with initiator – imide I – is also indicated by an increase of polymer molecular weight with conversion, even at such low conversions up to 10% (Table I, line 3 and 4, line 7 and 8). This fact is ascribed to a decrease of the transfer agent concentration

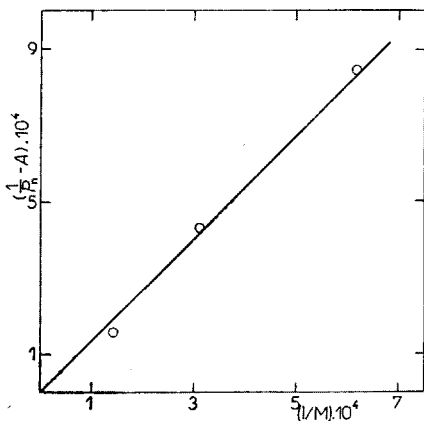


FIG. 3

Graphical Representation of Mayo's Equation for Determining the Transfer Constant with Respect to N-Bromosuccinimide (Eq. (2))

Temperature 60°C, concentration of 2,2-azobis(isobutyronitrile)  $5 \cdot 10^{-3}$  mol/l,  $A = (1 + \lambda) \frac{1}{2} \delta^2 (R_p/[M]^2) + C_M$ .

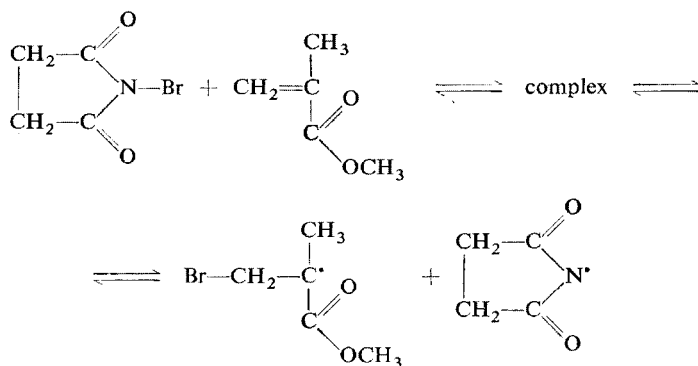
in the course of polymerisation due to a high reactivity of imide I in substitution reactions with macroradicals.

In our experiments we have not succeeded to initiate polymerisation of styrene with imide I. At  $[I] = 8 \cdot 10^{-2}$  mol/l (1.5% wt.) no polymerisation of styrene took place after 3 hours at 60° and 80°C. We have observed that the presence of styrene, even at low concentrations, retards the polymerisation (or copolymerisation) of methyl methacrylate initiated by imide I ( $5.6 \cdot 10^{-2}$  mol/l) at 60°C. This is documented by the following data:

|   |     |     |     |      |      |     |     |
|---|-----|-----|-----|------|------|-----|-----|
| Styrene concentration, $10^{-2}$ mol/l: | 0   | 4.3 | 8.6 | 12.8 | 21.2 | 174 | 348 |
| Conversion of monomers after 5 h, %:    | 5.0 | 4.2 | 3.8 | 3.8  | 3.5  | 0   | 0   |

N-bromosuccinimide, however, reacts with styrene. The changes of I.R. spectrum of the solution of styrene and imide I in chloroform are observable even at room temperature. The decrease of absorbance of vinyl double bond at 1310, 1630 and  $1635 \text{ cm}^{-1}$  was detected. The absorption bands at 1130, 1467 and  $2880 \text{ cm}^{-1}$  indicate the presence of  $\text{C}-\text{H}$  bond formed by saturation of styrene vinyl group<sup>13</sup>. The decrease of imide I concentration at the reaction with styrene is documented by a newly formed absorption band at  $600 \text{ cm}^{-1}$  (which can be assigned to  $\text{C}-\text{Br}$  bond) and simultaneously by a decrease of the absorbance at  $640 \text{ cm}^{-1}$  (disappearance of  $\text{N}-\text{Br}$  bond)<sup>14</sup>.

The proposed mechanism of the polymerisation induced by N-bromosuccinimide is based on the known fact that imide I — while in solution — does not act as a specific brominating agent to allylic position, but the addition of bromine on double bonds is a preferable reaction<sup>15</sup>. At the same time, we have to assume that the bromination proceeds at a direct interaction with methyl methacrylate. The observed relatively low energy of activation of the initiation reaction as well as a different initiation of different monomers are the facts which are against the assumption of direct spontaneous radical decomposition of the nitrogen-bromine bond. On this basis we can write as the initiation reaction a bimolecular equilibrium reaction leading to a relatively stable complex: This mechanism enables us to explain the difference between



the rate of initiation determined from the inhibition period and from the rate of polymerisation. The presence of compounds which are able to react with radicals

formed as a result of the monomer–initiator complex decomposition enhances the rate of radical formation. This is just the case when we are comparing the reaction rate of primary radicals with monomer or with stable radicals. Besides this, we can quite reasonably assume that diphenylpicrylhydrazyl reacts preferably and directly with N-bromosuccinimide and thus its fast disappearance is observed.

According to the above stated idea the inhibition action of styrene consists in the formation of more stable complex with N-bromosuccinimide which does not dissociate to radicals which would be able to initiate polymerisation of styrene or of methyl methacrylate but directly forms a reaction addition product. The imide is then consumed by this reaction and therefore it can not play any marked role in the initiation reaction with methyl methacrylate. By the presence of the complex, *i.e.* a potential pair of radicals, we can explain also a high transfer reaction which does not retard polymerisation as it is observed in case of highly active transfer agents.

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