POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY ACTIVATED DECOMPOSITION OF HYDROPEROXIDES

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The radical polymerization at temperatures below 100°C can be efficiently initiated even by 7-cumenyl hydroperoxide or t-butyl hydroperoxide when the radical decomposition of hydroperoxide is accelerated by using a suitable activator. The rate of hydroperoxide-initiated polymerization of methyl methacrylate was examined in the presence of triethylamine and acetic acid; at 80°C methyl methacrylate containing $7.2 \text{ mmol} . \text{dm}^{-3}$ of 7-cumenyl hydroperoxide and equimolar concentrations of amine and acid polymerizes 6 times faster while the presence of amine or the acid alone accelerates the polymerization only 3 or 2.5 times, resp.; when the optimum concentration of the acid is exceeded further increasing the concentration of acid caused a decrease in the reaction rate. An analogous effect of amine and acid upon hydroperoxide decomposition can also be observed in benzene solutions. The activating effect of the amine–acid mixtures is accounted for by the formation of a hydroperoxide–amine–acid complex which is believed to be less thermally stable than hydroperoxide–amine or amine–acid complexes. Another explanation is seen in the formation of a hydroperoxy ester. The latter can, at given temperature, produce radicals necessary for the initiation process much faster than the original hydroperoxide.

The initiation of polymerization of vinyl monomers due to the decomposition of organic hydroperoxides is well known[1]. The rate of initiation is, in this case, substantially higher than the extrapolated rate of thermal decomposition of hydroperoxide in inert solvents. It follows that the initiation of polymerization process is a result of the interaction of vinyl monomer with hydroperoxide which eventually produces radicals capable of initiating the polymerization. Relatively high temperature necessary for achieving reasonable polymerization rates is the main disadvantage of these initiators. On the other hand, there are numerous polymerization procedures which require the low temperature initiation by an initiator whose decomposition rate is only little influenced by temperature. For this reason it appears attractive to activate the radical decomposition of hydroperoxides by suitable additives. Similar principle has already been employed in the case of diacyl peroxides where the peroxide decomposition rate is increased in the presence of tertiary dialkylaromatic amines. Especially the system consisting of dibenzoylperoxide and N-dialkylaniline has been studied to some detail. Also hydroperoxides can, however, easily react with amines, corresponding alcohol being formed in the yield exceeding 70% (see ref.[2]). The products and intermediates involved in the amine oxidation process will depend upon the type of amine[3] but stable N-oxyradicals and similar structures represent most significant components.

The first step in the reaction between an amine and a peroxidic compounds is believed[4] to proceed *via* a complex in which the transfer of the non-bonding electron from nitrogen to peroxide takes place, the ion-radical pair being a result of this process. In the second step the cation-radical

gives up its proton to the anion present in the complex. The radicals thus formed can either re-combine in the cage or they react with solvent molecules. Polar media enhance the stability of cation-radicals while an easy deprotonation of cation-radicals proceeds in non polar media. Whereas the combination of alkylaromatic amines with diacetyl peroxides is common and frequently employed in practice for the initiating of polymerization reactions, only little attention has been paid to the use of hydroperoxides with alkylamines[5].

Low efficiency of free radical production is a characteristic feature of some amine––peroxide initiating systems. The efficiency of initiation is strongly dependent not only on the polarity of solvent but also on the reactivity of molecules forming the wall of a cage. Therefore the compounds that are capable of forming associates with reaction components of the initiation system may influence not only the rate of production of free radicals but also the efficiency of their penetration into the reaction medium. Both effects influencing the initiation in the system amine–hydroperoxide are the subject of this work.

EXPERIMENTAL

Methylmethacrylate was rigorously purified using the usual method. After removing the stabiliser by shaking with 10% aqueous sodium hydroxide, followed by washing with distilled water and drying by anhydrous calcium chloride, the monomer was distilled at reduced pressure in nitrogen atmosphere; out of the middle fraction the required amount of monomer for experiments was distilled *in vacuo* prior to each experiment. The rate of polymerization of this monomer in the presence of 2,2'-azobisisobutyronitrile is in a good agreement with published values[6]. 7-Cumenyl-hydroperoxide was purified by its transformation to sodium salt; the peroxide was then obtained by adding solid carbon dioxide and the raw product was distilled at reduced pressure at temperature not exceeding 60°C. t-Butyl hydroperoxide was a Koch–Light Lab. Ltd. commercial product. Triethylamine, piperidine, acetic acid, acetanhydride, benzoic acid and bromine were of analytical grade.

The polymerization was carried out in a nitrogen atmosphere in sealed glass ampoules. The conversion of monomer to polymer was determined gravimetrically. The polymer was precipitated by adding heptane to ampoule contents. The rate of 7-cumenyl hydroperoxide decomposition in the presence of triethylamine, acids and methyl methacrylate was followed iodometrically.

RESULTS AND DISCUSSION

The addition of an equimolar amount of triethylamine causes approximately a three--fold increase in the polymerization rate of methyl methacrylate initiated by 7-cumenyl hydroperoxide at 80°C (from $2 \cdot 2\%$ h^{-1} to 6% h^{-1}), the initiator concentration being $7 \cdot 2$ mmol dm^{-3}. The rate is directly proportional to the square root of triethylamine concentration (Fig. 1) which suggests a usual course of both initiation and termination. Moreover, it follows that the rate of initiation is by an order of magnitude higher in the presence of triethylamine than during the initiation due to the 7-cumenyl hydroperoxide decomposition.

When another component is added, which is capable of interacting both with amine and hydroperoxide, then further effects upon the rate of free radical production may be expected. Thus the influence of organic acids was examined as these are known to react with hydroperoxides as well as to form charge-transfer complexes with amines[7]. The addition of acetic acid (Fig. 2) as well as of other organic acids accelerate the polymerization, the maximum rate being reached at the equimolar ratio of acid to triethylamine and 7-cumenyl hydroperoxide. Further increase in the acid concentration has a decelerating effect on the polymerization.

The explanation of this result is offered in form of a sum of the initiation rates of two-component initiators (hydroperoxide–amine and acid–amine)[8]. Such explanation is, however, in controversy with the fact that the system acetic acid–triethylamine without 7-cumenyl hydroperoxide (equimolar concentration 7·5, 30, and 150 mmol. . dm^{-3}, resp.) is not capable of initiating methylmethacrylate polymerization at 80°C. The polymerization does not proceed even when the acetic acid is replaced by a strong electron-accepting agent such as tetrachlorophthalanhydride. The latter substance was reported by Golshtein and coworkers[9,10] to be the most powerful initiator of methyl methacrylate polymerization. The authors, however, employed alkylaromatic amines, mainly N,N-dimethylaniline, this probably causing the difference from our observations. When the triethylamine in our experiments was replaced by N,N-dimethylaniline then, indeed, the two-component initiator amine–chloroanhydride exhibited the initiation effect in methyl methacrylate polymerization. On the other
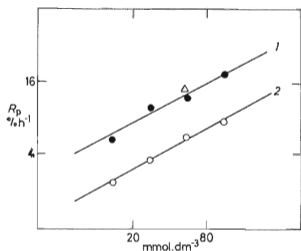

FIG. 1

Logarithmic Plot of the Initial Methyl Methacrylate Polymerization Rate at 80°C vs Triethylamine Concentration in the Presence of Hydroperoxides

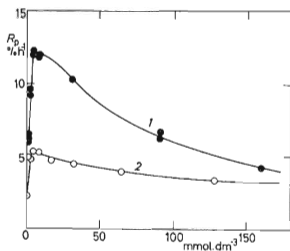Hydroperoxide (mmol . dm^{-3}): 1 7-cumenyl-(5·85), 2 t-butyl(10·5; △ 56).

FIG. 2

The Plot of the Initial Methyl Methacrylate Polymerization Rate at 80°C vs Acetic Acid Concentration

1 Initiation by 7-cumenyl hydroperoxide (7·5 mmol . dm^{-3}) and triethylamine (7·5 mmol . dm^{-3}), 2 in the absence of triethylamine.

hand the tetrachlorophthalanhydride appeared as a mild retarder in the polymerization initiated by 7-cumenyl hydroperoxide–dimethylaniline system (from $6·3\%\,h^{-1}$ to $5·6\%\,h^{-1}$; equimolar ratio of components $7·5\,mmol\,dm^{-3}$, 80°C).

Other explanation concerning the accelerating effect of acids upon methyl methacrylate polymerization initiated by 7-cumenyl hydroperoxide with triethylamine may be seen in faster decomposition of the hydroperoxide caused by the presence of an organic acid, the effect being similar as in the case of oxidation of hydrocarbons. The acid may also form an ester with hydroperoxide[11,12] which increases peroxide reactivity. The addition of acetic acid to 7-cumenyl hydroperoxide in methyl methacrylate will, indeed, cause an increase in polymerization rate even in the absence of amine (Fig. 2). The position of a maximum as well as the decrease in polymerization rate when the acid concentration is increased (curve 2 in Fig. 2) are the features which resemble the system containing amine, the only difference being that the acceleration of the polymerization is substantially less pronounced.

The decrease in polymerization rate at higher acid concentrations might be due to the increasing proportion of the nonradical decomposition of 7-cumenyl hydroperoxide. This hypothesis is, however, not in accordance with the observation of hydroperoxide decomposition in benzene in the presence of triethylamine and varying amount of acetic or benzoic acid (Fig. 3). The dependence of hydroperoxide decomposition rate on the acid concentration exhibits a maximum in the region of
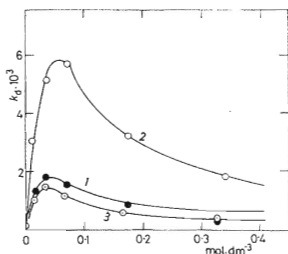

FIG. 3

The Dependence of the Rate Constant (k_d, $dm^3 . mol^{-1} . s^{-1}$) for Bimolecular Decomposition of 7-Cumenyl Hydroperoxide (40 mmol . dm^{-3}) in the Presence of Triethylamine (29 mmol . dm^{-3}) in Benzene at 60°C *1* and 80°C *2* Upon Acetic or Benzoic *3* Acid Concentration
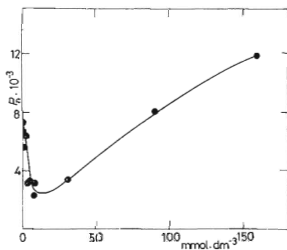
Fig. 4

The Dependence of the Average Degree of Polymerization of PMMA Obtained at 80°C Upon Acetic Acid Concentration Using 7-Cumenyl Hydroperoxide (7·5 mmol . dm^{-3}) and Triethylamine (7·5 mmol . dm^{-3}) Initiating System (conversion of monomer — c. 5%)

equimolar ratios of components. The dependence is analogous to that observed for methyl methacrylate polymerization rate dependence on acid concentration during 7-cumenyl hydroperoxide–triethylamine–acid initiation. It seems, therefore, more likely that the acceleration of polymerization is due to the enhanced production of free radicals induced by the activation of decomposition of the 7-cumenyl hydroperoxide––triethylamine complex by the added acids. Another possibility is seen in the decomposition of more reactive peroxyesters in the presence of the amine.

The hypothesis about the increased polymerization rate as a consequence of higher initiation rate is corroborated by the measurements of molecular weights of poly-(methyl methacrylate) prepared in runs shown in Fig. 2. Under conditions when the maximum decomposition rate of 7-cumenyl hydroperoxide as well as maximum polymerization rate is reached the polymer with the minimum polymerization degree is formed (Fig. 4). It cannot be excluded, however, that the activators besides accelerating the chemical decomposition of the original complex, thus forming free radicals, can also induce the formation of new complexes activator–amine and activator––hydroperoxide, resp. When the activator is present in an excess then the latter process is preferred. The decomposition of hydroperoxide is slowed down, both the initiation and polymerization rate being thus lower. This is quite plausible in view of the fact that triethylamine–organic acid complexes do not initiate the polymerization.

The activating effect of acids on hydroperoxide decomposition in the presence of amines is not restricted only to the system consisting of 7-cumenyl hydroperoxide and triethylamine. A similar effect of additives can also be observed in other systems (Table I). Besides the acetic acid also acetanhydride behaves similarly.

TABLE I

The Initial Rate of Methyl Methacrylate Polymerization (R_p) and Activation Energy (E) Initiated by Systems Consisting of Hydroperoxide, Piperidine and Acetanhydride

Initiating system (mmol . dm^{-3}): A 7-cumenyl hydroperoxide 7·21, piperidine 7·08; B system A and acetanhydride 8·45; C t-butyl hydroperoxide 8·03, piperidine 7·08; D system C and acetanhydride 8·45.

Initiating system	$R_p\% \text{ h}^{-1}$			E kJ mol^{-1}
	20°C	60°C	80°C	
A	0·16	4·7	25[a]	75 ± 6
B	0·44	4·8	20	59 ± 9
C	0·07	2·9	—	76
D	0·30	3·7	—	51

[a] Polymerization rate using 7-cumenyl hydroperoxide as an initiator was measured to be 2·2% h^{-1}.

The values of rate constants of the bimolecular decomposition of hydroperoxide––amine in the presence of monomer (Table II) are indicative of the activating effect of methyl methacrylate on 7-cumenyl hydroperoxide decomposition in the presence of triethylamine. Unlike the effect of acids, a monotonous increase of hydroperoxide decomposition rate is observed when increasing the monomer concentration. Especially pronounced increase in the hydroperoxide decomposition rate is seen when the system contains equimolar concentrations of amine and acid with regard to hydroperoxide, the neat methyl methacrylate being used as reaction medium. 7-Cumenyl hydroperoxide is, under these conditions, decomposed already at 60°C at the same rate as in benzene at 80°C (k_d equals $5 \cdot 5 . 10^{-3}$ and $5 \cdot 1 . 10^{-3}$ dm^3 mol^{-1} s^{-1}, resp.).

TABLE II

The Influence of Methyl Methacrylate upon the Rate of 7-Cumenyl Hydroperoxide Decomposition (35 mmol . dm^{-3}) in the Presence of Triethylamine (29 mmol . dm^{-3}) at 60°C in Benzene

Monomer mol . dm^{-3}	$k_d . 10^3$ dm^3 mol^{-1} s^{-1}	Monomer mol . dm^{-3}	$k_d . 10^3$ dm^3 mol^{-1} s^{-1}
0	0·05	1·00	0·39
0·04	0·11	1·00	1·78^a
0·16	0·19	8·95^b	5·55^a

^{a} Acetic acid (35 mmol . dm^{-3}) as another component. ^{b} Neat methyl methacrylate.

TABLE III

The Influence of Bromine Concentration Upon the Methyl Methacrylate Polymerization Rate Initiated by 7-Cumenyl Hydroperoxide ($5 \cdot 36$ mmol . dm^{-3}) and Triethylamine ($5 \cdot 42$ mmol . dm^{-3}) (concentrations calculated with regard to the monomer)

Bromine mmol . dm^{-3}	R_p% h^{-1}		E kJ mol^{-1}
	20°C	80°C	
—	0·10	1·65	56
1·1	0·08	1·09	54
4·4	0·21	1·71	43
15·6	0·42	4·71	46
62·5	0·28	3·43	51

In connection with the discussed values of hydroperoxide decomposition and polymerization rates we would like to point out that the increase in the polymerization rate does not correspond to the observed increase in the decomposition rate of 7-cumenyl hydroperoxide–triethylamine compound in the presence of acids. While the decomposition rate of hydroperoxide is almost 60 times higher the polymerization rate increases only twice. This suggests a considerable decrease in the efficiency of the initiation.

Amines are capable of forming molecular complexes both with halogens and acids. The products of their decomposition are ammonium and halogen ion radicals which can efficiently initiate the radical polymerization of methyl methacrylate. The amines containing only short alkyl chains in the molecule (shorter than butyl) when attached to a halogen proved to be ineffective in the initiation process[13,14]. When, however, a hydroperoxide is added to such a system we observed, within certain concentration range, an increase in the polymerization rate (Table III).

Although the position of infrared and raman absorption bands of both triethylamine and bromine is substantially changed following the formation of the bromine–triethylamine complex there are no literature data available concerning the interaction of molecular bromine with hydroperoxide. The interpretation of the observed data concerning the hydroperoxide–amine–bromine initiated polymerization is made even more difficult due to the occurrence of other chemical reactions of both molecular and atomic bromine with radicals and hydroperoxide. These factors might account for the relatively complex effect of the bromine additions to the triethylamine––hydroperoxide initiation system (Table III). Even here the increase in the rate of production of free radicals could be observed following the addition of a substance which interacts with one component of the redox system.

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