POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY TERT-BUTYL HYDROPEROXIDE–SULPHURIC ACID–ACETONE SYSTEM

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Dedicated to academician O. Wichterle on the occasion of his 70th birthday.

The radical polymerization of methyl methacrylate may be efficiently initiated by tert-butylhydroperoxide at 40°C and lower, deep below the temperatures of spontaneous hydroperoxide decomposition, when sulphuric acid simultaneously with ketones is used as the activator of peroxide decomposition. The initial reaction rate depends on concentration of initiator components, the exponents with regard to tert-butyl hydroperoxide, sulphuric acid and acetone being 0·25, 0·5 and 0·5, respectively. Water retards the hydroperoxide decomposition very efficiently and the polymerization rate is inversely proportional to the square root of water concentration in the system. Within the concentration range of hydroperoxide ($1 \,.\, 10^{-3} - 3 \,.\, 10^{-2}$ mol dm^{-3}), sulphuric acid $2{\cdot}62 \,.\, 10^{-2}$ mol dm^{-3} and acetone 0·2 mol dm^{-3} the observed initial polymerization rate varies from 14·4%/hour to 34·5%/hour at 40°C. The concentration of water, introduced into the system by the polymerization components, was 0·05% in all cases. The activating effect of ketones upon the acid catalyzed hydroperoxide decomposition is accounted for by the formation of ketone–H_2SO_4 adduct that facilitates the decomposition of hydroperoxide.

The research concerning initiating systems for radical polymerizations at temperatures close to that of ambient is very important from the viewpoint of energy requirements. Moreover, under these conditions the microstructure of the resulting polymer may be partially controlled. At these temperatures the fast radical production is usually achieved by the presence of redox systems whose individual components are thermally stable. Another way is seen in the application of thermally unstable peroxides.

During the methyl methacrylate polymerization an interesting accelerating effect of organic hydroperoxide decomposition was observed[1] in the presence of sulphuric acid. The amount of acid added should be relatively high to obtain realistic polymerization rates. When using this initiating system the polymer end-groups contain tert-butoxy and hydroxyl substituents but no sulphur containing groups. The acceleration of polymerization rate by sulphuric acid is attributed to a lower activation energy of a protonated hydroperoxide form with regard to the unprotonated hydroperoxide[2]. Approximately 30% of the decomposed hydroperoxide initiates the polymerization. This, when compared to some fast-initiating redox systems, represents 10 – 100 fold higher efficiency. On the other hand, already a small quantity of water, methanol or diethyl ether eliminates the catalytic influence of sulphuric acid.

In this work the hydroperoxide-H_2SO_4 initiating system was examined during the methyl methacrylate polymerization. It is known[3] that the radical decomposition of hydroperoxides may be accelerated by protonic acids as well as by other compounds. In our previous work[4] we observed the accelerating effect of carboxylic acids on the redox decomposition of hydroperoxides in the presence of aliphatic amines. In this study the sulphuric acid assisted tert-butyl hydroperoxide decomposition was followed in the presence of a variety of carbonyl compounds. Out of these, acetone was selected for a more detailed examination.

EXPERIMENTAL

Methyl methacrylate was purified using a common method[4]. The rate of its polymerization, initiated by 2,2'-azobisisobutyronitrile,was identical with the published data[5].Tert-butyl hydroperoxide, a Fluka commercial product, contained 20% of di-tert-butyl peroxide. Sulphuric acid and ketones employed were of analytical grade. For some experiments, acetone was dried over the molecular sieve Nalsit A4 (product of Lachema). The polymerization of methyl methacrylate was carried out under nitrogen in sealed glass ampoules and the conversion of monomer was determined gravimetrically by weighting the precipitated, dry polymer. The rate of polymerization was determined from the graphical dependence of gravimetrically determined conversion on time. For this purpose, six polymerizations of identical systems were carried out for varying length of time. Usually, the conversion did not exceed 10% even for the longest time intervals.

RESULTS AND DISCUSSION

In a first series of experiments the effect of various carbonyl-containing compounds was followed. The base polymerization system consisted of methyl methacrylate, concentrated sulphuric acid ($2{\cdot}6 \,.\, 10^{-2}$ mol dm^{-3}) and tert-butyl hydroperoxide ($1{\cdot}2 \,.\, 10^{-2}$ mol dm^{-3}). The amount of additives was 1·5 vol.% (or 1·5 wt.%), the temperature being maintained at 40°C. The results are indicative of a great variability in the effect of individual carbonyl compounds upon the polymerization (Table I). Significantly different effects upon the polymerization rate were observed even when comparing structurally similar carbonyl compounds. This indicates the important role of accompanying compounds which may actively participate in the production of primary radicals or may interfere with the efficiency of initiation in the polymerization process. It becomes thus obvious to examine to some detail the effect of only one carbonyl compound in order to elucidate this reaction. The most simple ketone — acetone, was selected for further experiments. The reaction rate in the water-free system depends on the concentration of basic components, the reaction order with regard to acetone and sulphuric acid is 0·5 in both cases (Fig. 1*a*). It follows that both acetone and sulphuric acid participate in the initiation reaction. The reaction order on hydroperoxide is, in the concentration region described, substantially lower, reaching only the value of 0·25 (Fig. 1*b*). This value suggests that a direct initiation of methyl methacrylate polymerization by hydroperoxide is considerably slower. This conclusion was further corroborated by the experiment. When either sulphuric acid or acetone was absent in the initiating system then the polymerization rate decreased substantially. Low value of reaction order on hydroperoxide and the necessity of hydroperoxide to be present indicate the consecutive character of the initiation

TABLE I

The influence of carbonyl compounds (1·5 vol.-%) upon the methyl methacrylate polymerization (monomer conversion in %/hour). Initiation by tert-butyl hydroperoxide (1·2 . 10^{-2} mol dm^{-3}) and sulphuric acid (2·6 . 10^{-2} mol dm^{-3}) at 40°C

Compound added	%/h	Compound added	%/h
—	1·6		
Cyclohexanone	52	Ethylene carbonate[a]	2·5
Acetone	27	Acetaldehyde	1·8
Cyclopentanone	24	Biacetyl	0·6
Acetylacetone	23	Acetic acid	0·25
Methylethyl ketone	11	Pyruvic acid	0
Acetophenone	5·5	Formaldehyde	0

[a] 1·5 wt.-%

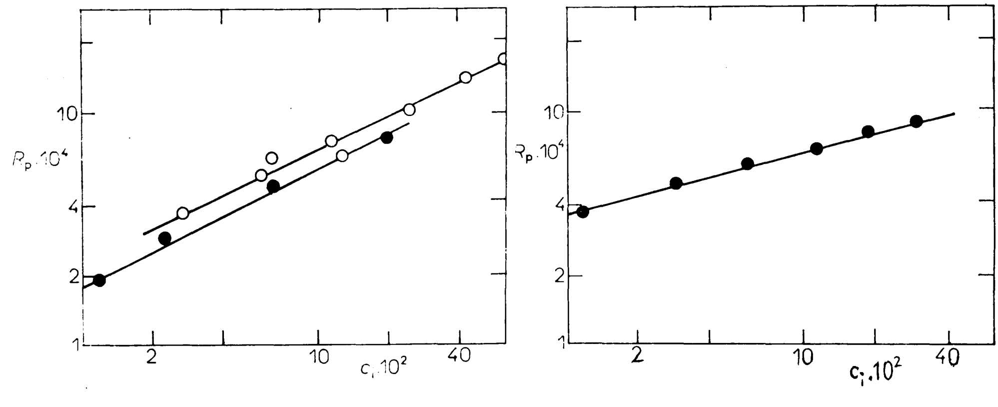

FIG. 1

The dependence of methyl methacrylate polymerization rate (in mol dm^{-3} s^{-1}) at 40°C upon the concentration of one component in a ternary initiation system (C_i in mol dm^{-3}): *a*) ● variable-acetone concentration, tert-butyl hydroperoxide and H_2SO_4 0·0117 mol dm^{-3}; ○ variable-H_2SO_4 concentration, tert-butyl hydroperoxide 0·0117 mol dm^{-3}, acetone 0·2 mol dm^{-3}; *b*) variable-tert-butyl hydroperoxide concentration, H_2SO_4 0·026 mol dm^{-3}, acetone 0·2 mol dm^{-3}

process, the reaction of acetone with acid being slower than the interaction of tert-butyl hydroperoxide with the products of the former step. The lowering of the reaction order with regard to hydroperoxide concentration may also be explained in terms of the degradative transfer of macroradicals on the non-protonated hydroperoxide giving rise to the formation of less active tert-butylperoxy radicals[1].

In the absence of acetone the polymerization rate is directly proportional to the concentration of sulphuric acid which signifies the reaction order being unity. This result suggests that the radical decomposition of one hydroperoxide molecule requires two molecules of sulphuric acid. When a comparable amount of a suitable carbonyl compound is present then the mechanism of initiation is substantially changed. In this connection it is worthwhile to note that the function of the carbonyl compound is, to some extent, fulfilled also by the methyl methacrylate. The polymerization of styrene, as the monomer approximately equally reactive, is substantially slower when initiated by tert-butyl hydroperoxide–sulphuric acid system. The kinetics correspond to a bimolecular initiation due to the interaction of hydroperoxide with monomer. The rate of polymerization will increase when methyl methacrylate is added to styrene or when the monomer is diluted with acetone.

The decrease in the peroxidic bond strength as a consequence of the presence of the added compounds is further manifested in runs where the methyl methacrylate polymerization was carried out at different temperatures. Within 17·5°C–50°C the overall temperature coefficient (E) was found to be 48 kJ mol^{-1} (Fig. 2). The commonly accepted relationship between the rate constants of elementary processes in the radical polymerization

$$K = (k_i/k_t)^{0.5} \, . \, k_p$$

and the values of $E_t \sim 0$ and E_p 21–25 kJ mol^{-1} for methyl methacrylate polymerization indicate that the rate of initiation is substantially less temperature dependent than

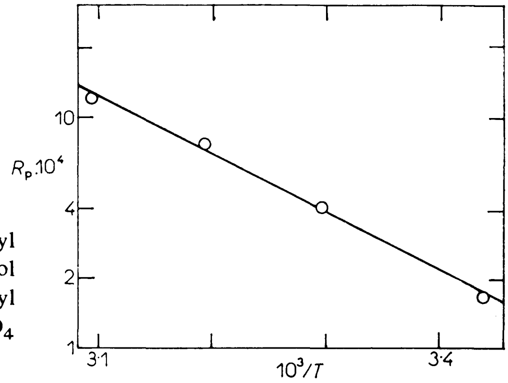

Fig. 2

The influence of temperature on the methyl methacrylate polymerization rate (in mol dm^{-3} s^{-1}) initiated by the system: tert-butyl hydroperoxide 0·0117 mol dm^{-3}, H_2SO_4 0·026 mol dm^{-3}, acetone 0·2 mol dm^{-3}

in the case of non-activated peroxidic initiation. The temperature coefficient E_i, estimated in this way, is 46 to 54 kJ mol^{-1}, this representing only $1/3 - 2/5$ from the value observed during the spontaneous thermal decomposition of peroxides and hydroperoxides. Low value of the temperature coefficient is advantageous particularly when the methyl methacrylate is polymerized in bulk. The rate of initiation is less dependent on temperature and the reaction starts at lower temperatures. These circumstances are favourable for the polymerization control at high monomer conversions.

Water is a typical accompanying substance present in carbonyl compounds. Its concentration is comparable to that of added initiators of polymerization; water significantly interferes with the formation of complexes of the acid with a carbonyl compound or with a hydroperoxide. The experiments with varying amount of water in the polymerization mixture confirmed this assumption (Fig. 3). It should also be noted that the polymerization rate is inversely proportional to the square root of water concentration in the system. The influence of water upon the polymerization may be accounted for by the hydration of sulphuric acid, this leading to the retardation of adduct formation with peroxide and acetone, resp. Thus hydroperoxide protonation which may be condisered as the cause of peroxidic bond weakening is restricted; according to this image, water will not lower the initiation efficiency but it will have a retarding influence on the hydroperoxide decomposition. Experi-

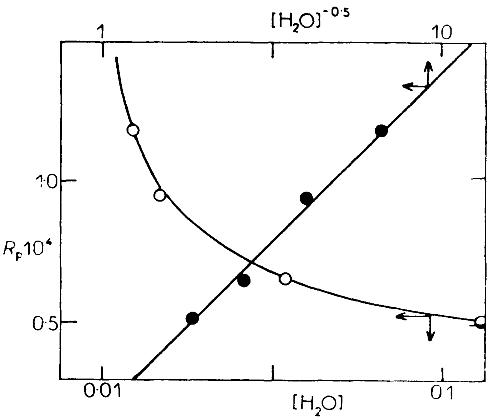

FIG. 3

The influence of water on methyl methacrylate polymerization rate (in mol dm^{-3} s^{-1}) initiated by the system tert-butyl hydroperoxide–H_2SO_4–acetone (in equimolar concentrations 0·0117 mol dm^{-3}) at 40°C

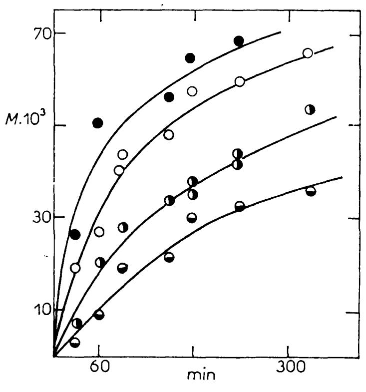

FIG. 4

Decomposition of tert-butyl hydroperoxide (0·149 mol dm^{-3}) in binary solvent acetone–water in the presence of H_2SO_4 0·088 mol dm^{-3}. Water concentration in acetone (in mol dm^{-3}): ● 0·025; ○ 0·255; ◑ 0·487; ⊖ 0·948. Temperature 19·5°C ments in which the hydroperoxide was decomposed in dried acetone as well as in acetone containing various quantities of water really indicate the decreasing rate of tert-butyl hydroperoxide decomposition (Fig. 4). A gradual decrease of the reaction rate in the course of reaction may thus be related to the formation of water, methanol and tert-butanol, the products which solvate the reactants and in this way retard the decomposition of tert-butyl hydroperoxide. We have experimentally confirmed that methanol, ethanol, butanol do not accelerate the methyl methacrylate polymerization initiated by hydroperoxide with sulphuric acid. Neither these alcohols increase the rate of hydroperoxide decomposition in inert solvent. In the presence of methyl methacrylate as a scavenger of primary radicals no retardation of the initiation reaction is observed. The primary radicals are not transformed into the deactivating compounds but these radicals are bonded to methyl methacrylate thus initiating the polymerization.

REFERENCES

1. Rizzardo E., Solomon D. H.: Macromol. Sci. Chem. A *14*, 33 (1980).
2. Quint G., Rizzardo E., Solomon D. H., Spurling T. H.: J. Macromol. Sci. Chem. A *15*, 527 (1981).
3. Solyanikov V. M., Petrov L. V., Charlampidi Ch. E.: Dokl. Akad. Nauk SSSR *223*, 1412 (1975).
4. Pavlinec J., Lazár M.: This Journal *42*, 3023 (1977).
5. Houwink R., Staverman A. J.: *Chemie und Technologie der Kunststoffe*, p. 254. Akad. Verlag, Leipzig 1962.

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