Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Rizzardo, E. and Solomon, D. H.(1977) 'Acid-Induced Free-Radical Decomposition of Hydroperoxides and Peroxides: New Low-Temperature Initiator Systems for Vinyl Polymerization', Journal of Macromolecular Science, Part A, 11: 9, 1697 — 1700

To link to this Article: DOI: 10.1080/00222337708063086

URL: http://dx.doi.org/10.1080/00222337708063086

J. MACROMOL. SCI.–CHEM., A11(9), pp. 1697-1700 (1977)

Acid-Induced Free-Radical Decomposition of Hydroperoxides and Peroxides: New Low-Temperature Initiator Systems for Vinyl Polymerization

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ABSTRACT

Evidence for an acid-induced free-radical breakdown of tert-butyl hydroperoxide and di-tert-butyl peroxide at room temperature has been obtained from polymerization experiments with methyl methacrylate and styrene.

INTRODUCTION

The acid-catalyzed decomposition of organic hydroperoxides has been studied extensively, and it is generally accepted that the reaction proceeds via heterolysis of the O–O bond with migration of an aryl or alkyl group to the electron-deficient oxygen [1-5]. Acidic mineral fillers have been shown to decompose hydroperoxides in a similar fashion [6] and are known to promote, for example, the decomposition of cumyl hydroperoxide in filled rubber composites. In this case it was proposed that homolytic fission of the hydroperoxide did not occur to any significant extent, thus preventing vulcanization or crosslinking of the polymer system.

In contrast to the reaction above, we have observed the rapid autoxidation of unsaturated compounds such as oleic acid and its derivatives on acidic mineral surfaces [7]. Certain aspects of this oxidation can be rationalized by assuming that the decomposition of the hydroperoxides, via a free-radical path, is facilitated on the acidic surface.

We now report on experiments which show conclusively that certain hydroperoxides and peroxides can decompose with formation of active radicals in strongly acidic media.

RESULTS AND DISCUSSION

tert-Butylhydroperoxide (TBHP) or di-tert-butyl peroxide initiated the polymerization of methyl methacrylate (MMA) at room temperature or below in the presence of various strongly acidic substances such as perchloric acid, sulfuric acid, hydrochloric acid, trifluoromethanesulfonic acid, trifluoroacetic acid, and BF_3 etherate. Acids or peroxides alone do not induce polymerization of pure MMA at the temperatures of our experiments.

The radical nature of the reaction was established from the polymerization of a 1:1 mixture of styrene and MMA with TBHP (0.05 $\underline{M}$) and sulfuric acid (0.05 $\underline{M}$). The proton magnetic resonance spectra showed that the copolymers contain approximately equal numbers of styrene and MMA units and were similar to those produced when benzoyl peroxide or azobisisobutyronitrile were used as the initiators [8, 9]. A cationic polymerization process would have been expected to give polymers consisting almost exclusively of styrene units, while an anionic process would have preferentially incorporated MMA in the polymer chains [9]. Further, the yield of poly(methyl methacrylate) (PMMA) was greatly reduced when the reaction (MMA-TBHP-H^+) was carried out in the presence of typical free-radical retarders such as hydroquinone or oxygen.

Unlike TBHP, a mixture of cumyl hydroperoxide (CHP) and acid did not induce polymerization of MMA. Since benzylic hydroperoxides are far more susceptible to the ionic acid-catalyzed rearrangement [1, 3], it is probable that the proportion of CHP decomposing to active radicals is either extremely small or nonexistent. It is well to recall, however, that the heterolytic decompositon of CHP produces phenol and this is likely to inhibit or retard any radical reaction.

With regard to the efficiency of the initiator in the system MMA-TBHP-H^+ we can report at this stage an estimate made under a specific set of conditions. In 3 hr at 25°C, bulk MMA (4.62 g) containing TBHP (0.086 M) and H_2SO_4 (0.1 M) gave PMMA (0.39 g) of viscosity-average molecular weight ($\overline{M}_v$) of 2.6×10^5 while consuming 1.8×10^{-5} mole of TBHP. Assuming the average number of initiator fragments per molecule of PMMA as 1.15 [10] (termination mainly by disproportionation) and taking $\overline{M}_v$ as the upper limit for the number-average molecular weight it can be concluded that at least 5% of the TBHP is decomposing to give radicals capable of initiating MMA polymerization.

The recent report [11] of the spontaneous polymerization of autoxidized (aged) MMA by the action of H_2SO_4 is in keeping with our findings although it is somewhat surprising, in view of our results, that H_2SO_4 should be a specific catalyst for the decomposition of MMA peroxides into active radicals.

A detailed study will now be undertaken with the aim of elucidating the mechanism of this interesting and potentially useful reaction.

EXPERIMENTAL

MMA and TBHP were purified by fractional distillation at reduced pressure and stored in the dark at 4°C. The MMA was shown to be free of peroxides before it was used [12].

The polymerizations were performed on deoxygenated solutions under nitrogen in a sealed tube.

Yields of polymer were determined gravimetrically after precipitating with methanol and drying to constant weight.

Intrinsic viscosities were obtained with acetone solutions of the polymer at 25°C. The viscosity-average molecular weights were calculated by using the relation $(\eta) = 5.3 \times 10^{-3}\ \overline{M}_v^{0.73}$ml/g [13].

Peroxides were determined by iodometric titrations [14].

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Accepted by editor March 30, 1977
Received for publication April 22, 1977