Polymer Bulletin 13, 77–82 (1985)

Polymer Bulletin

Monomeric Antioxidants. An ^{1}H-NMR Spectrometry Study of Their Homopolymerization

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SUMMARY

The polymerization behaviour of 3,5-di-tert-butyl-4-hydroxybenzylmethacrylate (I), trans-3,5-di-tert-butyl-4-hydroxycinnamic acid (II), 3,5-di-tert-butyl-4-hydroxystyrene (III) and N-(3,5-di-tert-butyl-4-hydroxybenzyl)maleimide (IV) was investigated. These monomeric antioxidants were polymerized in aromatic solvents, in the presence of usual radical initiators, by refluxing under nitrogen. An ^{1}H-NMR spectrometry method for the calculation of polymerization conversion was developed. The disappearance of the monomer double bond was followed using dibenzyl ether as an internal standard. The reactivity of these monomers, all showing the same antioxidant functionality, decreased in the order IV>I>III. The acid antioxidant (II) was not capable of polymerization.

INTRODUCTION

Antioxidants and light stabilizers are employed to improve the useful properties and extend the service life of polymers, by preventing or retarding degradation. For any particular stabilizer, its effectiveness depends on its concentration in the polymer. The concentration of the stabilizers in polymers decreases during processing and long-term use of the polymer, because of two processes: (i) chemical reactions of the stabilizers (POSPISIL 1979, SCOTT 1981a), and (ii) physical loss of stabilizers from polymers (LUSTON 1980, VINK 1980). The permanence of stabilizers in polymers depends on: (a) distribution and diffusion of stabilizers in polymers, (b) compatibility of stabilizers with polymers, (c) volatility of stabilizers, and (d) extractibility of stabilizers from polymers. Some approaches have been made to increase the permanence of stabilizers in polymers. Thus, volatility, extractibility and diffusion rate of stabilizers decrease with increasing their molecular weight. Consequently, polymeric stabilizers have been obtained by homopolymerization of the monomeric stabilizers. Such special monomers contain a polymerizable group and a functional group with antioxidant or UV stabilizing effect. Different polymers have been stabilized by adding either homopolymers of monomeric stabilizers or copolymers with a high content of stabilizing structure. A better improvement of the permanence may be obtained by chemical bonding of stabilizers "in" or "onto" polymer chains. Thus, monomeric stabilizers have been copolymerized with usual monomers, and bulk- or surface grafted onto polymers. These approaches are described in some review

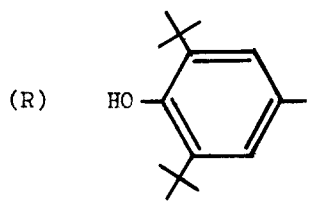
papers (GUGUMUS 1979, MUNTEANU et al. 1981, 1984, SCOTT 1981b).

Monomeric antioxidants of hindered phenolic structures may interfere with radical polymerization. Therefore, homopolymerization, random- and graft-copolymerization of such monomeric antioxidants are not allways possible.

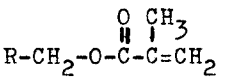
The purpose of our paper is to present the results of a preliminary study on the radical homopolymerization of some monomeric antioxidants, showing the same antioxidant functionality but different polymerizable groups. The homopolymerization of these monomeric antioxidants was followed by ^{1}H-NMR spectrometry.

EXPERIMENTAL

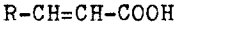
Synthesis of monomeric antioxidants



(R)



(I)



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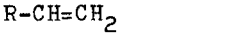
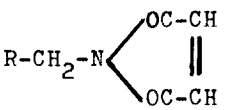


(III)



(IV)

Four monomeric antioxidants combining the same stabilizing functionality (R: 3,5-di-tert-butyl-4-hydroxyphenyl) were synthesized:

(I) 3,5-di-tert-butyl-4-hydroxybenzylmethacrylate was obtained from 3,5-di-tert-butyl-4-hydroxybenzylalkohol and methacryloyl chloride, in ethyl ether/pyridine solution, at -5°C to +5°C.

(II) trans-3,5-di-tert-butyl-4-hydroxycinnamic acid was obtained starting from 3,5-di-tert-butyl-4-hydroxytoluene, via oxidation to 3,5-di-tert-butyl-benzaldehyde and condensation with malonic acid according to Knoevenagel (solution of 8% NH_3 or $C_6H_5NH_2$ in ethanol, refluxed for 6 hours) or Doebner (pyridine solution, 5 days at room temperature, in the presence of piperidine).

(III) 3,5-di-tert-butyl-4-hydroxystyrene was obtained by thermal decarboxylation of the acid antioxidant (II) - a solution of 20% acid antioxidant in dimethylsulfoxide - at 130°C. Complete decarboxylation in 30 min.

(IV) N-(3,5-di-tert-butyl-4-hydroxybenzyl)maleimide was obtained from 2,6-di-tert-butylphenol and N-chloromethylmaleimide, in benzene solution, heating from 10-20°C to 50-60°C for 4 hours, $ZnCl_2$ catalyst (in the reaction product a part of the monomeric antioxidant is polymerized).

All monomeric antioxidants have been synthesized in inert medium, then purified by multiple recristallization from proper solvents. Spectral (IR and ^{1}H-NMR), elemental microanalysis and melting point determinations were used to characterize the purified monomeric antioxidants.

Homopolymerization of monomeric antioxidants

Solution polymerization was carried out in a 50 ml round-

bottomed flask fitted with thermometer, reflux condenser, gas inlet and a PTFE cork provided with an one ml syringe. Dibenzoylperoxide (BPO) and azobisisobutyronitrile (AIBN) were used as polymerization initiators, after purification by multiple recrystallization from proper solvents. Attempts to polymerize the monomeric antioxidants have been made in aromatic solvents: benzene, toluene and o-xylene, in the presence of BPO or AIBN, refluxing the solution under nitrogen. To determine the monomer conversion, directly from ^{1}H-NMR data, polymerization was performed in deuterated benzene. 10 mmol of the monomer, 3.5 mmol of the dibenzylether (DBE) as internal standard and the desired amount of polymerization initiator (0.02-2 mmol) were dissolved in 20 ml C_6D_6. The mixture was refluxed under nitrogen for 6 hours.

Measurement of monomer conversion by ^{1}H-NMR spectrometry

The conversion of monomeric antioxidants by polymerization was studied by ^{1}H-NMR spectrometry, by measuring the disappearance of the double bond. At 0, 10, 20, 30, 60, 120, 180 and 240 minutes reaction time, 0.5 ml solution was drawn out from the polymerization flask, with the aid of syringe, and injected directly in the measuring cell of the spectrometer. The cell was rapidly cooled to room temperature in an ice water bath.

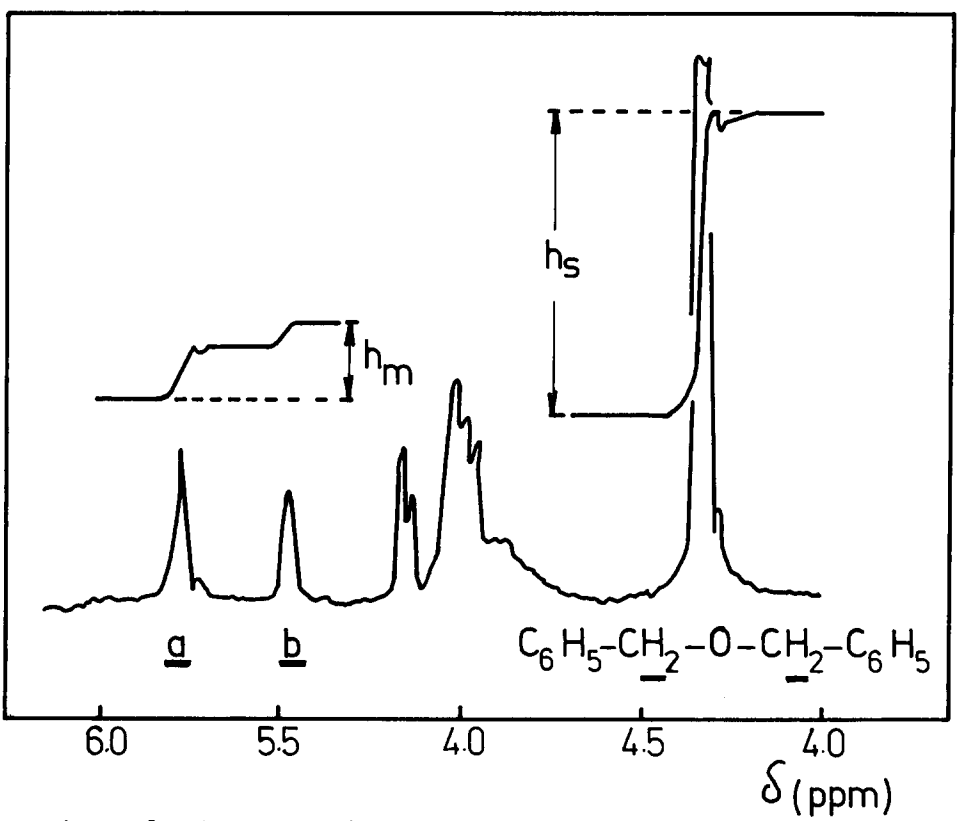


Figure 1. Measurement of conversion by polymerization of the R-CH=CH$_2$ antioxidant, by ^{1}H-NMR spectrometry.

^{1}H-NMR spectra of the C_6D_6 solutions (unreacted and polymerized antioxidant + DBE) were recorded on a TESLA BS-467 spectrometer, at 60 MHz and room temperature. The spectra were recorded between 6.5 and 4 ppm, i.e. the range corresponding to the signals of the protons of the double bond of the monomer. Although the ^{1}H-NMR spectrum of the methacrylate antioxidant (I) shows two signals for the two $>C=CH_2$ protons, only the signal at δ=6.17 ppm was chosen for analytical signal. Similar for the styrene antioxidant (III), among the four signals of the three $-CH=CH_2$ protons, the two signals at δ=5.5 and 5.8 ppm were used for analytical determination (peaks a and b in figure 1). All recorded spectra showed the signal at δ= 4.28 ppm, corresponding to the four $-CH_2-O-CH_2-$ protons of the DBE standard. The chosen analytical signals of the monomer and DBE were integrated and the corresponding heights h_m and h_s were measured. For each conversion 10 integrations were performed and the mean values of h_m and h_s were calculated. The ratio $R=h_s/h_m$ was calculated for both before polymerization (R_o) and every sample at a certain polymerization time (R_t). The ratio $100 \cdot R_o/R_t$ represents than the unpolymerized monomer and the ratio $100(1-R_o/R_t)$ represents the monomer conversion (both values expressed by weight percent).

RESULTS AND DISCUSSION

Attempts to polymerize the monomeric antioxidants have been carried out in aromatic solvents (benzene, toluene, o-xylene), at the boiling point of the solution (80-145^{o}C), in the presence of AIBN and BPO (0.02-2 mmol/mol). The acid antioxidant (II) could not be polymerized under these conditions. On the contrary, the maleimide antioxidant (IV) is very reactive. Even in the absence of radical initiators, the thermal polymerization proceeded very fast, so that it was not possible to follow the monomer conversion by ^{1}H-NMR spectrometry. This was possible only for the two other monomeric antioxidants (I and III).

The methacrylate antioxidant (I) exhibited an usual polymerization behaviour (figure 2). Monomer conversion increased with both polymerization time and initiator concentration (AIBN). After 2-2.5 hours the conversion reached its constant value. High limit conversions, i.e. over 70% were obtained with the AIBN concentration higher than 0.7 mmol/mol, but initiator concentrations exceeding 2-3 mmol/mol do not increase further significantly the limit value of the conversion.

The methacrylate monomer was capable of polymerization even in the presence of air, with a slight decrease of the conversion. For the same polymerization conditions the difference between the limit value of conversion, in the absence and presence of air was of about 7% (figure 2). This seems to be a very surprising result because general it is accepted that such monomeric antioxidants are not capable of radical polymerization in the presence of oxygen. However, in the absence of inert medium, it seems that the solvent vapours act as a protective screen against the oxygen penetration in the reaction mixture, because all polymerizations were performed by refluxing the solutions of monomers in aromatic solvents.

The styrene antioxidant (III) showed a similar polymerization behaviour (figure 3). For the same molar concentration, BPO seems to be more effective than AIBN.

The methacrylate antioxidant (I) was more reactive than the styrene one (III). Thus, for the same polymerization conditions,

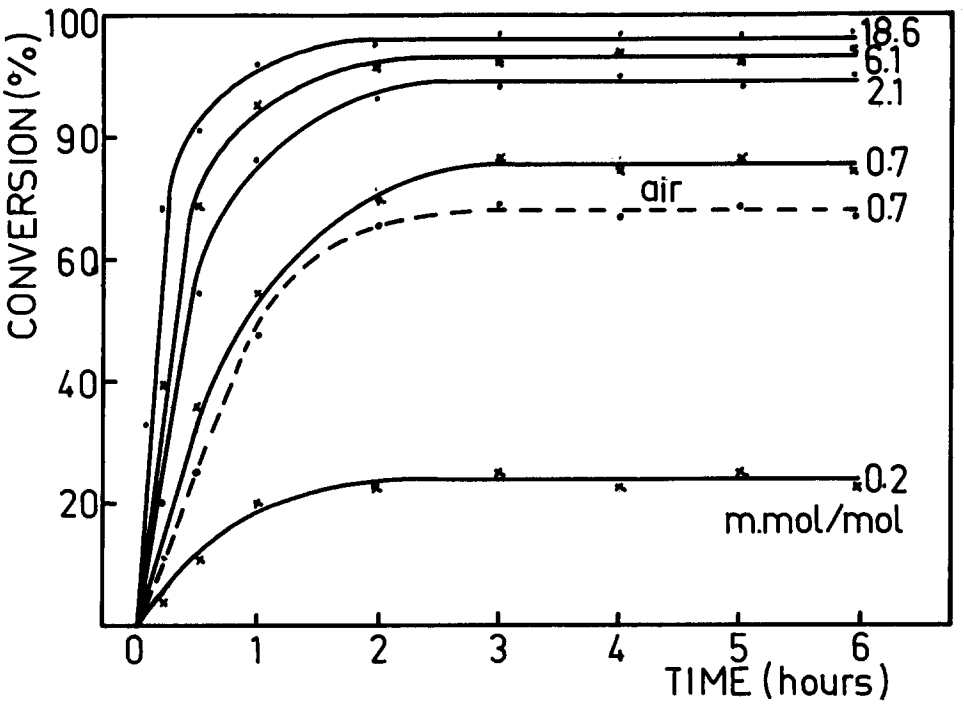


Figure 2. Monomer conversion versus polymerization time. $R\text{-}CH_2\text{-}OOC(CH_3)C{=}CH_2$ antioxidant, C_6D_6 solution, refluxed under nitrogen, at about 83°C, AIBN initiator

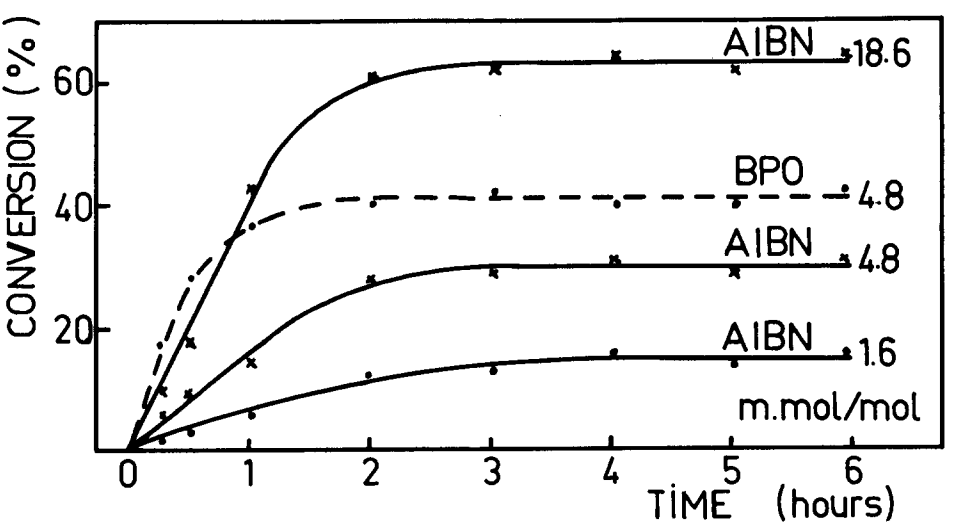


Figure 3. Monomer conversion versus polymerization time. $R\text{-}CH{=}CH_2$ antioxidant, C_6D_6 solution, refluxed under nitrogen, at about 83°C.

e.g. 18.6 mmol AIBN/mol monomer, C_6D_6 at reflux, the limit conversion was of 96% for the monomer (I) instead of 63% for the monomer (III).

CONCLUSIONS

The investigated monomeric antioxidants, combining the same stabilizing functionality of hindered phenolic structure (3,5-di-tert-butyl-4-hydroxyphenyl) but different polymerizable groups, showed a different behaviour in the solution radical polymerization. Except the acid antioxidant (II) all the monomeric antioxidants were capable of polymerization, their reactivity decreasing in the order IV>I>III. Of course, detailed studies are necessary. Such investigations, including the characterization of the polymers, are under progress and will be reported later.

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Accepted December 7, 1984