On Oxidative Thermal Destruction of Three-dimensional Polyester Methacrylate*

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The kinetics of MDF-2-based oxidative thermal destruction of polyester methacrylate has been studied. The effective energy of activation calculated by oxygen absorption in the interval from 160 to 200°C amounts to 24.1 kcal mole^{-1}. Analysis of the destruction products seems to indicate that oxygen initiates the process by interacting first of all with $-CH_2-$ groups that are in the α-position to the ester methacryl group. A new effective inhibitor of the thermal and oxidative destruction of three-dimensional polyester methacrylates, poly-2-methyl-5-ethynyl-pyridine, has been found.

Multifunctional unsaturated esters with polymerizable acryl or methacryl terminal groups are used to obtain reinforced plastics, insulating compounds, varnish, glues, and other materials. The polymerization of such unsaturated esters involves the formation of three-dimensional polymers whose properties are a function of the structure and size of the bridge [1]. The kinetics and the mechanism behind the destruction of three-dimensional polymers of this type have not yet been practically studied.

This paper is concerned with oxidative thermal destruction of a most widespread three-dimensional polyester methacrylate, a polymer based on α,ω-dimethacrylate--diethyleneglycol phthalate with the average polymerization factor $n = 2$ (MDF-2) whose structure is shown in Chart 1.

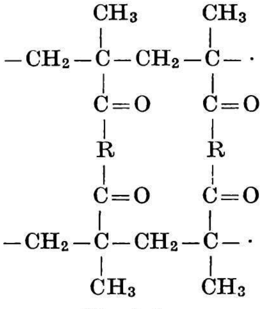

Chart 1

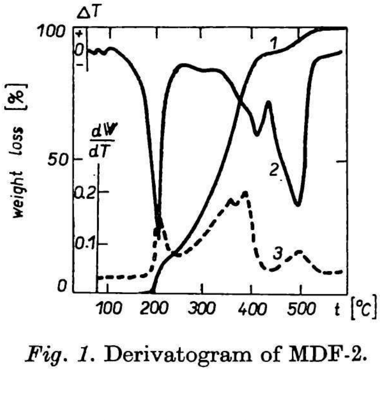

Fig. 1. Derivatogram of MDF-2.

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Experimental

The unsaturated oligomeric ester MDF-2 was obtained and purified by the well-known procedure [1] and described by the following indices: bromic number 43.6 g Br/100 g; saponification number 465 mg KOH/g; the molecular weight calculated for double bonds determined by the ozonization method [2], 590; by the heat of condensation [3] in methyl ethyl ketone, 540 (calculated molecular weight 714). Thin-layer chromatography in the initial oligomer revealed 6 components which were fractions with n 0, 1, 2, 3, and higher.

The oligomer was polymerized in thin layer *in vacuo* (10^{-2} mmHg) at 76°C with 2% benzoyl peroxide as initiator. The conversion of polymerization was found by the bromic number and the reduced intensity of the absorption band (1636 cm^{-1}). The conversion of polymerization thus obtained is about 95%. To remove the unreacted products, the polymer films were heated *in vacuo* (10^{-3} mmHg) at 140°C for 40 hours. According to the ozonization data, there were practically no (below 1%) double bonds in such films.

Thermogravimetric experiments have been carried out on a derivatograph ("MOM", Hungary, the system designed by F. Paulik, I. Paulik, and L. Erdey) between room temperature and 500°C at a heating rate of 3 deg min^{-1} in air and *in vacuo.*

The kinetics of polymer oxidation at low temperatures (160–200°C) was studied on a conventional stationary unit [5]. The samples in all tests were thin (0.03–0.05 mm) films. At this thickness oxygen diffusion does not limit the rate of polymer oxidation. The weight of samples was 50 mg. The initial pressure in the system varied within 50–500 mmHg.

To examine the detailed mechanism of the oxidative thermal destruction of three-dimensional polyester methacrylate, polymer films were obtained directly on optical KBr cells and were stepwise heated from 100 to 350°C with increments of 15°/min. After exposition from 2 hours to 30 minutes at high temperatures the i.r. spectra of the samples were measured on a spectrometer IKS-14.

Results and Discussion

Earlier studies of thermal destruction have established that the nature of pyrolytic reactions depends on heating conditions [4]. At mild temperatures (up to 280°C), thermal destruction of this network-structured polyester methacrylate is similar to the destruction of the linear analog and is in fact the depolymerization of network aggregates unhampered by numerous crosslinks. Both vinyl groups of the bridge spare in this process independently. Experimental data led to the assumption that the networks depolymerization is initiated with the rupture of strained C–C bonds caused by the polydispersion of the initial polymer. At temperatures over 280°C depolymerization is accompanied with the rupture of ester bonds, decarboxylation, *etc.*

We wished to find the effect of oxygen on the destruction of this polymer.

Fig. 1 shows the derivatographic curve of the oxidative thermal destruction of the polymer MDF-2 at heating rate of 3 deg min^{-1}. Comparison of derivatograms representing the heating in air and *in vacuo* seems to indicate that oxygen intensifies the process in that intensive decomposition starts at lower temperatures. The enthalpy characteristics of the process change abruptly. Instead of the two endothermic peaks in the thermogram *in vacuo*, exothermic peaks are observed in the 150–240°C, 340–440°C, and 40–530°C temperature ranges for destruction in air. The exothermic effects result from the interaction of oxygen with the polymer and its fragments that form in destruction and crosslinking. In the 270—340°C temperature range the total heat is zero since th exothermic effects are overlapped by the endothermic processes of polymer destructio and the removal of low molecular products from the system.

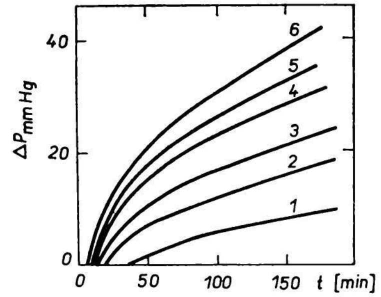


Fig. 2. Curves of oxygen absorption by polymer films of MDF-2, 0.05 mm thick at 180°C.
1. 50 mm; *2.* 100 mm; *3.* 150 mm; *4.* 200 mm; *5.* 250 mm; *6.* 300 mm.

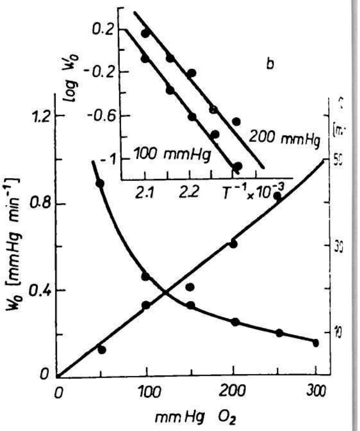


Fig. 3. Initial oxidation rate and induc- tion period *vs.* pressure: *b* — lg W_0 *vs.* 1/T.

Figs. 2 and 3 show the kinetics of oxygen absorption by the MDF-2 polymer at 180° and 50—300 mmHg, and the dependence of the induction period and the initial oxidation rate on oxygen pressure in the system. The initial polymer oxidation rate at constant oxygen pressure depends exponentially on temperature. The effective activation energ of polymer thermal oxidation was found to be 24.1 kcal mole^{-1}.

With increasing temperature the i.r. spectra of samples revealed alternating increas and decrease in optical density of absorption bands.

Even at the earliest oxidation stages (100—150°C) the i.r. spectra showed increas of absorption bands at 1645 and 825 cm^{-1} that were associated to stretching C=C an deformation C—H vibrations of the methacryl group double bond (Fig. 4). This indicate that oxidation involves the destruction of the main chain of polyester methacrylate

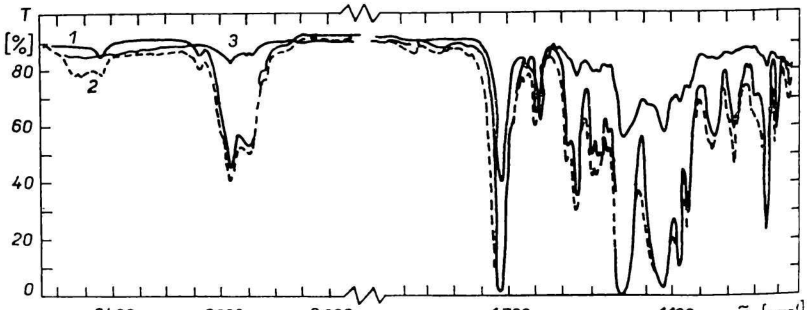


Fig. 4. Infrared spectra: *1.* initial polymer film; *2.* film heated at 170°C; *3.* film heate at 290°C in air.

The resulting macroradicals seem to decompose according to the depolymerization mechanism.

Thermal destruction of three-dimensional polyester methacrylate has already been reported [4] to result from the rupture of the most strained carbon—carbon bonds in the main chain of a macromolecule. The rupture of such bonds may share in the initiation of polyester methacrylate destruction in the oxidizing medium, but the chief contributor to the initiation of free-radical oxidation is the interaction of polymer with oxygen

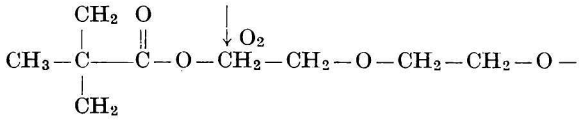
$$\mathrm{RH + O_2 \rightarrow R\cdot + H\dot{O}_2}$$

$$\mathrm{RH + O_2 + RH \rightarrow 2R\cdot + H_2O_2}.$$

This is directly confirmed by the observed dependence of the induction period and the initial oxidation rate of three-dimensional polymer on oxygen pressure.

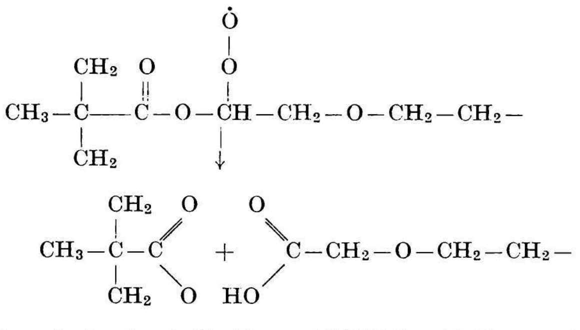
Three-dimensional polymer oxidation is accompanied by intensive rupture of bridges as evidenced by the appearance of the band $\nu(\mathrm{C{=}O})$ (3550 $\mathrm{cm^{-1}}$) in the i.r. spectra of heated samples and by the change in the ratio of absorption bands $\nu(\mathrm{C{=}O})$ and $\nu(\mathrm{C{-}O{-}C})$ (1735, 1290, 1155 $\mathrm{cm^{-1}}$) and $\nu(\mathrm{C{-}H})$ (2890, 2970 $\mathrm{cm^{-1}}$) and benzene ring (1595, 790 $\mathrm{cm^{-1}}$).

The traces of methacrylic acid at the earliest stages of three-dimensional polyester methacrylate oxidation lead to the conclusion that oxygen attacks primarily the C—H bonds of methylene groups that are in the α-position to the ester methacryl group



$$\mathrm{CH_3{-}\overset{\overset{\large CH_2}{|}}{\underset{\underset{\large CH_2}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{|}{\downarrow O_2}}{CH_2}{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}}$$

The resulting peroxide radicals share then in the development of the chain or are isomerized with the rupture of the C—O bond, which leads to the appearance of acyl radicals



More detailed analysis of volatile thermal MDF-2 oxidation products reveals certain elementary reactions of the process.

The network structure of polyester methacrylate affects the nature of the oxidative thermal destruction, which is felt above all in the fact that at relatively low temperatures and sufficiently high pressure of the medium the oligomers which are the products of the main bond rupture and macroradicals depolymerization are very slowly removed from the system. As a result, the probability of a reverse polymerization reaction and secondary reactions of polymer oxidation increases.

Effective inhibitors are needed if the free radical process of three-dimensional polyester methacrylates is to be prevented.

Thermal and oxidative stabilization of network-structured polyester methacrylates is an unsolved problem. The introduction of a stabilizer into a finished nonmelting polymer is hard to accomplish, while the use of standard stabilizers such as amines or phenols into reactive oligomer before crosslinking makes this solidification practically impossible. The polymer stabilization for reactive oligoester methacrylates was solved by using certain polymer compounds with a system of conjugated bonds [1].

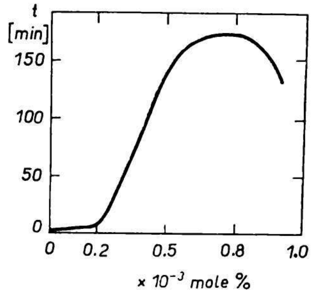


Fig. 5. Oxygen absorption induction period *vs.* percentage of PEP addition.

We have suggested a new effective stabilizer, poly-2-methyl-5-ethynyl-pyridine (PEP) [5]. This compound dissolves easily in organic solvents and oligomer does not hamper oligomer polymerization at low temperature ($\leqslant$ 70°C) and is an effective inhibitor of polyester methacrylate oxidation at high ageing temperatures ($>$ 150°C). Thus when 3×10^{-3} mole % PEP are introduced, MDF-2 starts to decompose intensively at 230°C, while without this addition this temperature at the heating rate of 3 deg min^{-1} is 190°C. The shape of the curve of the induction period *vs.* the inhibitor concentration shown in Fig. 5 enables so classify this compound as strong inhibitor.

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