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Gas Chromatographic Determination of Pyrolysis Products from Poly(2-Hydroxyethyl Methacrylate)

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Summary

Compared to poly(methyl methacrylate) (PMMA) or other poly(n-alkyl methacrylates), the thermal degradation of poly(2-hydroxyethyl methacrylate) (PHEMA)is rather complex, whereby the generated monomer (HEMA) is accompanied by a variety of other pyrolysis products. Besides HEMA, the dominating compounds were methacrylic acid and acetaldehyde, which could be established by gas chromatography.

Introduction

Due to its hydrophilic properties and its good compatibility with skin and tissue, poly(2-hydroxyethyl methacrylate) is used in human medicine, especially in ophthalmology.From this point of view, industrial wastes of this polymer are still of high value, and a recovering of degradation products of PHEMA should be discussed.

The course of the thermal degradation of PHEMA is highly influenced by the reactivity of the 2-hydroxy ethylester groups, which was reported by RÁZGA and PETRÁNEK (1). They found a relatively small monomer fraction of about 20 wt.-% (pyrolysis temp.: 500° C); besides ethylene dimethacrylate (EDMA), ethylene glycol, and some gaseous compounds, which were identified by means of mass spectrometric analysis. The gas chromatographic identification of the degradation products with the aid of authentic reference compounds, however, was not mentioned by the authors. To clear up this and to determine other unidentified pyrolysis products, a technical PHEMA was decomposed under N_2 in a suitable degradation equipment, the generated products condensed in methanol/ dry ice and characterized by gas chromatography with authentic reference compounds.

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Experimental

4 g pulverized PHEMA were pyrolyzed under N_2 in a little quarz tube, connected with three cooling traps, dipping in methanol/dry ice. The quarz tube was placed into a small vertical 500 W tube-oven (Fa. Horo, Stuttgart-Hedelfingen), whose temperature could be controlled with a thermocouple, connected with a 'Plastomatic-Regler'. The temperature was measured with a second thermocouple, located approximately in the middle of the oven between the wall of the quarz tube and the heating-coil, and was recorded with a digital temperature display (Digithermeter DG 800, Fa. Roth).

The chromatographic experiments were made with a Perkin-Elmer Sigma 2 gas chromatograph and a 6 ft x 1/8 inch ready packed column with 80/100 Carbopack C/0,1 % SP-100(poly(ethylene glycol)/nitroterephthalic acid). With a carrier gas flow (He) of 35,3 ml/min (at 30° C) and a detector sensitivity of 10 (FID), the following chromatographic conditions were adjusted: oven temp. initial = 40° C, time initial = 2 min, rate initial = 20° C/min, oven temp. final = 100° C, time final = 0 min, rate final = 10° C/min, oven temp. post = 200° C, time post = 300 min. The injected amount of the sample was 0,1 µl; the attenuations are given in the chromatogram (Fig.1).

Results and Discussion

The sample was heated within 6 min from room temperature to 650° C, whereby about 68 wt.-% (ref. to the initial amount of PHEMA) of a light yellow pyrolysate were collected in the traps. Apart from a neglecting char precipitation inside the quarz tube, the polymer was entirely decomposed to low molecular weight compounds. Already at temperatures in the region of 200°C, a small evolution of fluid degradation products was observed. Experiments up to 500° C with isothermal conditions, however, showed relativ large amounts of undecomposed PHEMA, slow reaction rates, and poor yields of pyrolysis products. This retarded desintegration of PHEMA (1) is obviously an indication for thermal induced curing reactions due to small contaminations of EDMA, diethylene glycolmonomethacrylate (DEMMA), and methacrylic acid in technical HEMA, which has been established by gas chromatographic investigations. Possible curing reactions involving the 2-hydroxy ethyl groups in PHEMA are therefore the formation of ethylene bridges,diethylene ether bridges (from DEMMA), and ester exchange reactions accompanied by liberation of ethylene glycol and diethylene glycol. The esterification of polymerized methacrylic acid contaminations with 2-hydroxy ethyl or diethylene glycol side-groups in PHEMA is a further explanation for cross-linking. Some essential pyrolysis products of PHEMA are HEMA, methacrylic acid, DEMMA, EDMA, diethylene glycol, ethylene glycol, and acetaldehyde (Fig. 1), which were

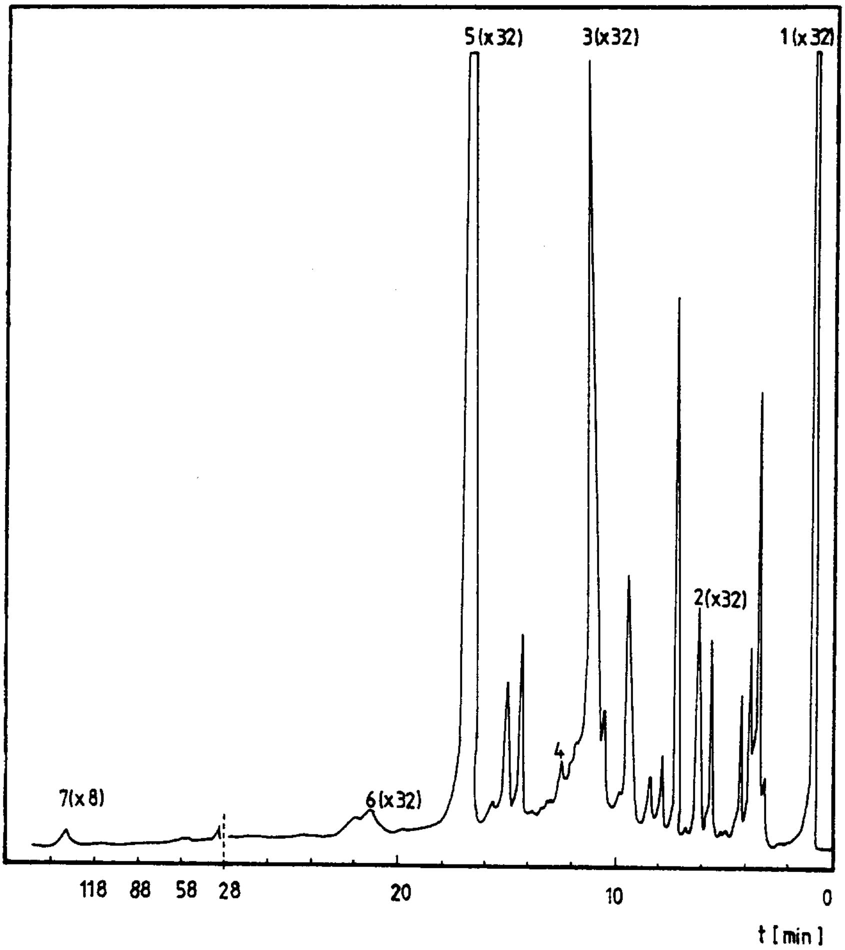
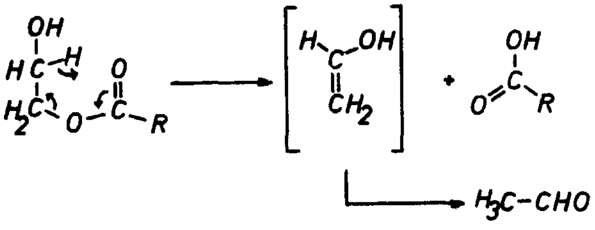
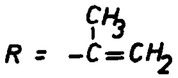


Fig. 1. Gas chromatographic separation of pyrolysis products from poly(2-hydroxyethyl methacrylate).Identified peaks: 1) acetaldehyde, 2) ethylene glycol, 3) methacrylic acid, 4) diethylene glycol, 5) HEMA, 6) DEMMA, 7) EDMA. At the dotted line the recorder speed was changed.

identified by comparision of retention values from authentic reference compounds. A typical degradation product of PHEMA is acetaldehyde (Fig. 1), which was not mentioned by RÁZGA and PETRÁNEK. Its formation can be explained via an ester pyrolysis of the monomer:





$R = -\overset{CH_3}{\overset{|}{C}}=CH_2$

With a yield of approximately 68 wt.-% liquid pyrolyzed products (at 650° C), a chromatographically determined HEMA- fraction of only maximal 25,7 wt.-% (ref. to the initial amount of PHEMA), and a wide spectrum of other degradation products, a recovering of pyrolyzed PHEMA wastes seems economically not very successful.

Reference

1. RÁZGA, J. and PETRÁNEK, J., Eur. Polym. J. 11, 805 (1975)

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