

# THE DETERMINATION OF ACETONE USING MASS SPECTROMETRY AFTER ACID HYDROLYSIS OF POLYMER ACETALS

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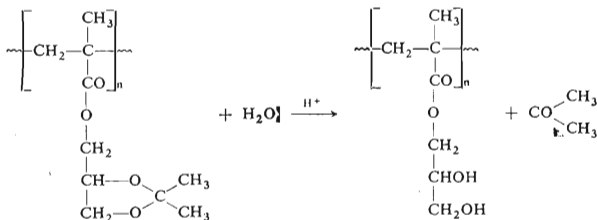
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A mass spectrometric method for the determination of acetone in the presence of polymers has been suggested. Perdeuterated acetone was used as the internal standard. The method was employed in a quantitative determination of (2,2-dimethyl-1,3-dioxolane-4-yl) methyl methacrylate units in copolymers with methyl methacrylate and in the determination of copolymerization parameters.

Acetals in side groupings of polymers behave similarly to low molecular weight ketone acetals which readily undergo acid hydrolysis while simultaneously splitting off the respective ketones. Poly[(2,2-dimethyl-1,3-dioxolane-4-yl)methyl methacrylate] was a typical example. Its hydrolysis gives rise to poly(2,3-dihydroxypropyl methacrylate) while acetone is released at the same time:



A reliable and simple analytical method of the determination of acetone would make possible, on the one hand, to investigate this reaction directly, and on the other, to determine the content of acetal units in the respective copolymers. The problem of determination of low-molecular weight compounds in systems which moreover contain polymeric compounds is however a complicated one. Direct use of *e.g.* gas chromatography is difficult, because the polymer would remain

in the injection space, and its thermal degradation (if any) would distort the results. Separation of the polymer followed by the determination of low-molecular weight components may also lead to inaccurate results due to the possible selective sorption of these compounds on the polymer. The method of quantitative mass spectrometry with an internal isotopic standard which is often applied especially in micro-analyses of biologically active compounds was chosen as the one best suited for the given concrete system<sup>1</sup>. A known amount of isotopically labelled standard added to the analyzed system makes possible an easy determination of the measured component on the basis of the intensity of characteristic peaks of the standard and of this component. The application of this method seems to be particularly advantageous for the following reasons: a) selective sorption of acetone on the polymer does not affect the results of acetone determination based on its concentration and on that of the standard in the gas phase; b) the determination may be carried out without isolation of the polymer, and with an appropriately chosen solvent also without removing the latter.

## EXPERIMENTAL

### Chemicals

The homopolymer of (2,2-dimethyl-1,3-dioxolane-4-yl)methyl methacrylate and of its copolymer with methyl methacrylate was prepared using the monomer of 99.5 mass % purity. Radical polymerization in the presence of 2,2'-azobis(isobutyronitrile) (0.05 mol/l) was carried out in toluene (concentration of monomers or of the mixture of comonomers was 1 mol/l) at 50°C up to a 10% conversion; the products were precipitated into light petroleum and washed several times. Freshly distilled ethylcellosolve (2-ethoxyethanol), content of impurities below 1 mass % (checked by gas chromatography), was used as solvent in the analysis of the products. Perdeuterated acetone (Merck), isotopic purity 99.5 mass %, served as the isotopic internal standard.

### Hydrolysis and Mass Spectrometry

The hydrolysis was carried out in sealed ampoules containing 1.9 g of a 4% polymer solution in ethylcellosolve, 0.18 g of water, 0.03 g of *p*-toluenesulphonic acid and 0.02 of perdeuterated acetone. The ampoules were placed in a thermostat. About 0.05 g of the mixture was transferred into the cell of the all-glass heated inlet system of an AEI-902 mass spectrometer. After cooling with liquid nitrogen the cell was evacuated, joined with the tank of the inlet system by means of a valve, and one part of acetone vapours with the solvent was transferred into the tank by distillation at -60°C. The mass spectra were recorded at the temperature of the ion source 150°C, electron energy 70 eV, emission 500 μA, accelerating voltage 8 kV and voltage on the multiplier 1.5 kV.

## RESULTS AND DISCUSSION

From the viewpoint of mass spectrometry and the condition of miscibility of the reaction mixture after the hydrolysis of the polymer of (2,2-dimethyl-1,3-dioxolane-4-yl)-

methyl methacrylate or of its copolymer with methyl methacrylate with water, 2-ethoxyethanol (ethylcellosolve) seems to be the most appropriate solvent; its signal height (intensity) of the fragment with the mass number to charge number ratio  $m/z$  58 (with the same mass as that of the molecular ion of undeuterated acetone) is only 1.7 rel.%.<sup>2</sup> The acetone content in analyzed samples of the reaction mixtures is often below 0.1%. Due to the high tension of ethylcellosolve, these amounts would be difficult to detect when being fed into the tank of the inlet system. Subcooling of the inlet cell and transfer of vapours from the cell into the tank by a low-temperature distillation provide conditions under which the concentrations of acetone and ethylcellosolve in the gas phase are of the same order of magnitude and can easily be measured. The most advantageous temperature of distillation transfer from the reaction mixture into the tank lies between  $-50$  and  $-60^\circ\text{C}$ . At this temperature, only ions of heavy and light acetone and ethylcellosolve are present in the mass spectra (Fig. 1).

By using calibration mixtures with constant composition (ethylcellosolve, water, *p*-toluenesulphonic acid and the standard) with various contents of undeuterated acetone (in the absence of the polymer), a calibration straight line was obtained in the coordinates  $(I_{58}-C)/I_{64}$  and  $G_H/G_D$  (Fig. 2), where  $C = 0.017I_{72}$  and  $G_H$ ,  $G_D$  are weight amounts of undeuterated acetone and of the standard in the mixture. The slope of this straight line (1.10) includes the whole isotopic effect of deuterium in the standard, *i.e.* differences in the ionization efficiency, vapour tensions and molecular weights of the heavy and light acetone.

In the acid reaction mixture the deuterium atom of perdeuterated acetone  $\text{C}_3\text{D}_6\text{O}$  is partly exchanged for the hydrogen atom from the solvent or from water. The exchange depends on time and reaction temperature. At  $35^\circ\text{C}$ , the exchange is about

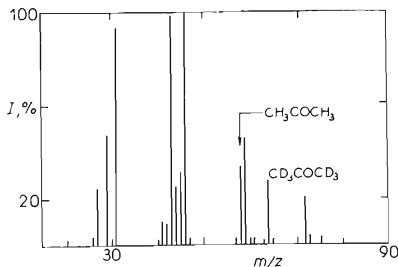


FIG. 1

Mass spectrum of the mixture after hydrolysis of the samples

25% within four hours. It is reflected in the increased intensities of molecular ions  $C_3D_3HO$ , ( $m/z$  63) or  $C_3D_4H_2O$  ( $m/z$  62). In a basic medium the method could not be used because  $D$  is very quickly exchanged for  $H$ . The effect of the partial isotopic exchange in the acid medium during the experiments was corrected by estimating the concentration of the standard on the basis of the sum of peak intensities 64, 63, 62 in the spectra. The peak intensities of deuterated acetone with a lower number of deuterium atoms were neglected. Corrections were also made for the contribution of ethylcellosolve to the intensity of the molecular ion of light acetone  $m/z$  58. Using the spectrum of pure ethylcellosolve, this contribution was found to be 1.7% of the fragment intensity of  $m/z$  72.

The amount of undeuterated acetone in the reaction mixture was determined from

$$G_H = \frac{G_D}{1.1} (I_{58} - C) / (I_{64} + I_{63} + I_{62}). \quad (1)$$

The reliability interval of acetone determination in artificially prepared mixtures in the absence of the polymer was  $\pm 1$  rel.%, which virtually represents the error in a mass spectrometric determination of the peak intensities.

The hydrolysis proceeds up to a 100% conversion for both the homopolymer, and copolymer at 35°C within 250 min unlike that of the acetal monomer, where a quantitative decomposition is reached within 140 min (Fig. 3). In repeated experiments the amount of acetone released in the case of the homopolymer corresponded to the theoretical one at a 100% conversion in the reliability interval  $\pm 2\%$  rel. on the significance level 0.01.

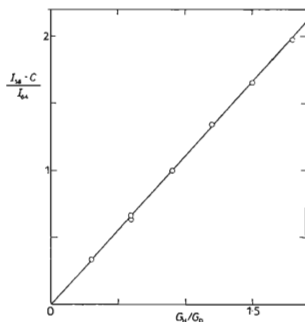


FIG. 2

The corrected relative peak  $(I_{58} - C) / I_{64}$  as a function of  $G_H / G_D$ . Meanings of symbols are given in the text

From the amount of acetone released after the hydrolysis of the copolymer samples prepared in this study, the composition of the copolymers and their copolymerization parameters were determined:  $[A]_0$ ,  $[B]_0$  – mol.% of (2,2-dimethyl-1,3-dioxolane-4-yl)methyl methacrylate and methyl methacrylate respectively, in the initial copolymerization mixture,  $[A]$ ,  $[B]$  being concentrations of the respective structural units in the copolymer.

Sample:

$[A]_0$ :	80.0	60.0	40.0	20.0
$[A]$ :	81.4	61.6	34.7	21.3

Using these data and the Mayo–Lewis method<sup>3</sup> by employing the relation

$$r_B = \frac{[A]_0 [B]}{[B]_0 [A]} \left( 1 - \frac{[A]_0}{[B]_0} r_A \right) - 1, \quad (2)$$

the copolymerization parameters were determined and compared with the values obtained by the Fineman–Ross method<sup>4</sup> based on the relation

$$F(f-1)/f = r_A m - r_B, \quad (3)$$

where  $m = F^2/f$ ,  $F = [A]_0/[B]_0$  and  $f = [A]/[B]$ ,

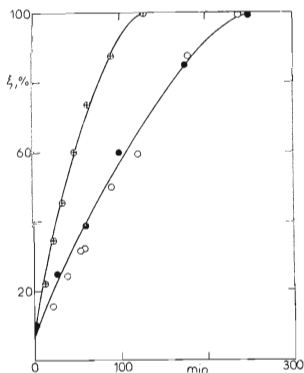


FIG. 3

Acid hydrolysis of acetal at 35°C ( $\xi$  reaction range):  $\oplus$  monomer,  $\circ$  homopolymer,  $\bullet$  copolymer with methyl methacrylate

and by the Kelen-Tüdös method<sup>5</sup> using the relation

$$Y = r_A X - (r_B/\alpha)(1 - X), \quad (4)$$

where  $Y = G/(\alpha + m)$ ,  $X = m/(\alpha + m)$ ,  $G = F(f - 1)/f$ ,  $\alpha \cong 1.0$ .

Relation:	Eq. (2)	Eq. (3)	Eq. (4)
$r_A$ :	1.03	1.12	1.09
$r_B$ :	0.89	0.97	0.95

The values of the copolymerization parameters are in a good agreement, especially with respect to relations (3) and (4).

The method of quantitative mass spectrometry with an isotopically labelled standard may also be employed in the determination of the copolymerization parameters of other acetals with other comonomers. If these copolymers were insoluble in ethylcellosolve, another solvent may be used, the mass spectrum of which does not interfere with the standard employed, or the interference may be reduced by using a suitable temperature in the measurement and then eliminated by calculation.

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