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Analysis

A method for the determination of maleic anhydride content in copolymers

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SUMMARY

A simple and reliable non-aqueous direct titration method for the determination of anhydride content in maleic anhydride-vinyl acetate copolymers is described. The procedure involves reaction of the anhydride with a large excess of aniline followed by direct titration of the resulting monoacid with ethanolic NaOH using potentiometric or thymol blue end point detection. The method overcomes many of the disadvantages of previously published methods, and its application to other copolymers is considered.

INTRODUCTION

A variety of methods for the determination of maleic anhydride (MAnh) content of copolymers have been described (1-4). Bamford and Barb (4), and more recently, Ratzsch and Hue (5) have argued that the previous methods in the literature are unsuitable for accurate copolymer composition analyses for a variety of reasons. Ratzsch and Hue (5) proposed a method which they claimed overcame these problems, but, in this laboratory, the amount of MAnh monomer determined by their procedure was consistently 5-10% lower than the actual amounts (see Table 1). It was also found that the DMF used in their procedure had a very detrimental effect on the sharpness of the potentiometric end point. When acetone is substituted for DMF the change in potential at the end point increases from about 50 mV to around 250 mV.

Since ester monomers, such as vinyl acetate (VAc), are easily hydrolysed by hydroxide in aqueous systems, a non-aqueous method was sought to overcome the deficiencies of the Ratzsch and Hue method. The procedure which was found most suitable for MAnh - VAc copolymers was an adaptation of a method described by Kappelmeier (6) and Huber (7) for large samples of monomeric anhydrides. The method relies on the quantitative reaction of the anhydride in acetone solvent when treated with a large excess of aniline, followed by direct titration of the resulting monoacid in ethanol with ethanolic NaOH. The advantages inherent in this procedure are that: either potentiometric or thymol blue end point detection is possible, the reaction is quantitative, the titration is a direct titration, the copolymer is soluble even at the end point and there is no hydrolysis of ester groups.

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METHOD

A copolymer of MAnh and VAc containing preferably 0.3 - 1.5 mmol MAnh units is dissolved in a minimum of dry acetone (2 - 5 ml). When dissolution is complete pure, dry aniline (5 ml) is added and the mixture stirred well. The aniline in such large excess reacts rapidly and quantitatively with the anhydride in less than five minutes at room temperature to yield a pale yellow solution. To this solution is added ethanol (40 ml) and thymol blue indicator (2 drops saturated thymol blue in dioxan). The acid groups in the solution are then titrated with 0.05 M ethanolic NaOH to the first appearance of green colour of the indicator, or potentiometrically using an unmodified glass electrode with calomel reference.

The ethanolic NaOH was prepared by dissolving analytical grade NaOH in distilled ethanol. The solution was filtered into a polythene bottle and protected from the atmosphere. Before use the NaOH was standardized by dissolving 150 - 200 mg accurately weighed analytical grade benzoic acid in acetone (3 ml), adding ethanol (40 ml) and thymol blue indicator solution (2 drops) and titrating to the first appearance of green colour. Aniline was purified by distilling twice from zinc powder through a column packed with glass coils.

RESULTS AND DISCUSSION

Before titrating copolymer samples this method was tested using freshly sublimed MAnh monomer, and the results compared with those obtained using two other methods (Table 1). Typical potentiometric titration curves for this method showing the applicability of potentiometric and indicator end point detection for both polymeric and monomeric anhydride samples are shown in Figure 1.

The thymol blue end point was found to correspond to the potentiometric end point for both the anhydride determinations and the benzoic acid standardization to within the uncertainty of burette reading. The colour intensity of thymol blue in non-aqueous solvents is greater than that of phenolphthalein and is thus preferred for accurate end point recognition.

For samples containing more than 1.5 mmol MAnh a precipitate of the anilide was sometimes observed after addition of the aniline, however, this in all cases redissolved completely on addition of the ethanol.

A blank determination using the same volumes of each reagent should be run and the value deducted from sample measurements. A negligible blank was obtained in this work and no correction was applied. For solutions coloured other than yellow the correct end point colour for thymol blue must be determined by comparison with the potentiometric end point.

It is because MAnh - VAc copolymers are readily soluble in acetone that this solvent was chosen for the initial dissolution of copolymers, but in principle it should be possible to use other solvents where necessary, provided that the solvent is miscible with both aniline and ethanol. DMF, for example, has already been used successfully in this laboratory for copolymer samples which were not soluble in acetone.

TABLE 1

A Comparison of Several Analytical Methods

Method	MAnh actual (mmol)	MA found (mmol)	% Difference	End Point Detection
NaOH/HCl in acetone/ H_2O Back-titration (See refs 1, 8)	0.472 0.447 0.530	0.493 0.482 0.573	+4.4[a] +7.8 +8.1	Conductometric
n-butylamine/$HClO_4$ in dioxan. Back-titration. (See ref. 5)	0.750 0.612 0.675	0.692 0.582 0.616	-7.7[b] -4.9 -8.7	Potentiometric or methyl violet
Aniline/NaOH Direct titration (this method)	0.751 1.523 0.324	0.752 1.528 0.326	+0.13[c] +0.32 +0.62	Potentiometric or thymol blue

a. Large error is due to the "rounding" of the titration curve and also to back-titration.
b. Error is due to incomplete reaction of the amine and also to the back-titration.
c. Theoretical error ranges from ±1% for 0.3 mmol to ±0.4% for 1.5 mmol.

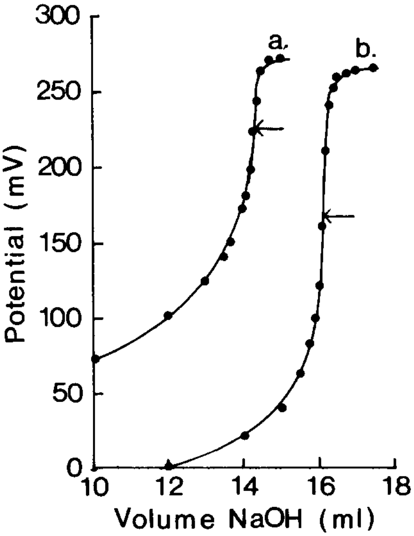

Fig.1 Typical titration curves for MAnh monomer and MAnh-VAC copolymers.

a. MAnh-VAC copolymer (0.666 mmol MAnh content)
b. MAnh (0.751 mmol actual)
← Thymol blue end point.

It must be noted that the method outlined here will give erroneously high anhydride contents for samples containing free carboxylic acid groups before the reaction with aniline.

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