

Copolymers of Maleic Anhydride-¹⁴C and Vinyl Acetate as Standards in an Automated Titration Method for Combined Anhydride

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Synopsis

Copolymers of maleic anhydride and vinyl acetate containing 6 to 54 wt-% maleic anhydride were prepared in both toluene and methyl ethyl ketone by employing carboxyl-¹⁴C-labeled anhydride of demonstrated radiochemical purity. The standard copolymers thus prepared were used as reference materials in development of an automated titrimetric method for combined anhydride that had a standard deviation of 1.7 wt-% at an anhydride level of approximately 50%. The semimicrotechnique described is based on dissolution of the polymer in methyl ethyl ketone-aqueous alkali, addition of an aliquot of this solution to a slight excess of hydrochloric acid, and back titration of the excess of acid with standard alkali. The technique effectively prevents hydrolysis of the acetate groups of the copolymer.

INTRODUCTION

Copolymers of maleic anhydride and certain vinyl monomers have drawn considerable recent interest, not only because they have versatile practical applications, but also because the titration behavior of the corresponding hydrolyzed (succinic acid) copolymers deviates significantly from that of normal polyelectrolytes. This deviation, which occurs after neutralization of one half of the acidic function, has recently been explained by considering nearest-neighbor interactions between dicarboxylate groups.¹ Of further interest is the copolymerization of maleic anhydride with vinyl acetate in certain solvents, a reaction that yields alternating copolymers containing equimolar amounts of the monomers. Because of the susceptibility of the acetate group to hydrolysis, titration methods used in the precise study of this polymerization must be shown to have no significant effect on the ester while quantitatively determining the anhydride.

For titrating the acidic moiety of maleic anhydride copolymers, manual techniques, such as the early nonaqueous method based on dissolution of the copolymer in pyridine and addition of sodium methoxide,² have been augmented by more precise potentiometric methods employing automated instruments.^{1,3-5} Other analytical approaches include ultraviolet spectrophotometry,⁶ which has been suggested for determining the concentration of maleic anhydride-vinyl acetate copolymers in aqueous solution, and the use of both integrated infrared absorptivity and nuclear magnetic resonance⁷ for quantitative analysis of several olefin copolymers and their half-ester derivatives. An infrared procedure has also been described for the differential analysis of anhydride and carboxyl groups

in olefin copolymers.⁸ In addition, the dye interaction technique can be applied to copolymers of maleic anhydride and methyl methacrylate.⁹

Although several methods have thus been developed for determining combined maleic anhydride, none has been standardized with copolymers containing known amounts of this monomer, nor has the accuracy of either of the methods been verified by analysis of such standards. Copolymers of known composition can be prepared from radioactive monomers, however, and the availability of maleic anhydride-1,4-¹⁴C makes the preparation of such standard polymers feasible. Restriction of the labeled atoms to the carbonyl groups in the anhydride is necessary to avoid errors due to possible isotope effects during polymerization. Careful purification of the labeled anhydride is also necessary to remove significant radioactive impurities.

EXPERIMENTAL

Materials

Maleic anhydride-1,4-¹⁴C, obtained commercially (Mallinckrodt/Nuclear) at a specific activity of 4–12 millicuries/mole (mCi/mole), was diluted with maleic anhydride of the highest available purity as follows: 100 g nonradioactive maleic anhydride was dissolved with careful warming in 400 ml anhydrous diethyl ether to consume trace amounts of water. The ampoule containing the radioactive anhydride was then crushed beneath the surface of the solution. Crystallization was effected by slow cooling of the solution while swirling the flask, which was finally placed in an ice bath. The anhydride was collected, dried, and then recrystallized from anhydrous diethyl ether. The product was stored over phosphorus pentoxide. To determine the radiochemical purity of the anhydride, a portion was treated with an excess of aniline to form maleic acid monoanilide, which was recrystallized from a methanol–water mixture. Radioassays of these compounds were made in dioxane–naphthalene scintillator solution to determine the purity of the anhydride.

Dioxane–naphthalene scintillator solution. Naphthalene (200 g), PPO (2,5-diphenyloxazole) (14.0 g), and POPOP (1,4-bis-2-[5-phenyloxazolyl]-benzene) (0.60 g) were dissolved in dioxane (scintillation grade), the solution was diluted to 2 liters, and 200 ml methanol was added.

Toluene scintillator solution. PPO (15.0 g) and dimethyl-POPOP (0.90 g) were dissolved in 1 liter purified toluene. The scintillator concentration of this solution must be three times that of the usual toluene scintillator, since it is diluted 1:2 in assays by oxygen-flask combustion.

Ethanolamine:methanol, 1:3, used as absorbing medium for ¹⁴CO₂, was prepared from freshly distilled ethanolamine.

Toluene, hexane, and methyl ethyl ketone (MEK) were purified by stirring with freshly ground calcium hydride and distilling through a packed column in an argon atmosphere.

Sodium hydroxide, 0.045*N* aqueous, and hydrochloric acid, 0.05*N* aqueous. These solutions need not be standardized.

Potassium hydroxide, 0.05*N* in ethanol, standardized.

Vinyl acetate, polymerization grade, was distilled under argon immediately before use.

Azobisisobutyronitrile and benzoyl peroxide, commercial grade, were used as received.

Apparatus and Equipment

A Radiometer automatic titrator, Model TT2, was used with 2.5-ml automatic buret ABU 11 and recorder SBR3 for all titrations. A glass indicator electrode, G202C, was employed in conjunction with a calomel reference electrode, K401.

A Packard liquid scintillation spectrometer, Model 3303, was used for radioassays.

Polymerization tubes and conventional pint and quart bottles were employed for the preparation of polymers.

Schöniger flasks, 2-liter, with platinum baskets, were used for combustion of samples for radioassay.

Procedures

Preparation of Labeled Polymers. Polymerization vessels were flushed with argon, then charged with the labeled maleic anhydride, solvent, vinyl acetate, and initiator. The bottles were sealed with Teflon-lined caps and argon was again added; the tubes were again flushed with argon before sealing. After polymerization under the desired time and temperature conditions, the polymers made in toluene were collected on a glass frit and washed with dried toluene; the polymers made in MEK were precipitated with dried hexane, dissolved in toluene, and reprecipitated with hexane. All polymers were dried at room temperature in vacuum over phosphorus pentoxide.

Radioassay of Labeled Compounds and Polymers. Radioassays of the maleic anhydride and its monoanilide for estimating radiochemical purity were made in dioxane-naphthalene scintillator solution since both of these compounds are easily soluble in dioxane. Specimens were weighed into 50- or 100-ml volumetric flasks, and 15-ml aliquots of solution were taken. All polymers were assayed by oxygen-flask combustion because of their limited solubility in scintillation solvents. Specimens of 40–80 mg of the anhydride, monoanilide, and copolymers were burned in a 2-liter flask, and 15-ml of 1:3 ethanolamine:methanol was added after placing the flask in an ice bath. After the contents of the flask had reached room temperature, an aliquot of 10 ml was removed and added to 5 ml of the concentrated scintillator solution in toluene.

$$\% \text{ radiochemical purity} = (100) \left(\frac{\text{molar sp. act. of monoanilide}}{\text{molar sp. act. of anhydride}} \right)$$

$$\text{wt-\% anhydride in polymer} = (100) \left(\frac{\text{sp. act. of polymer, mCi/g}}{\text{sp. act. of anhydride, mCi/g}} \right)$$

The wt-% anhydride in the polymer so calculated is uncorrected for radiochemical purity of the anhydride.

Titrimetric Determination of Maleic Anhydride in Copolymers. Specimens of ca. 100 mg were weighed into 100-ml volumetric flasks and dissolved in 5 ml purified MEK. Dilute sodium hydroxide solution (ca. 0.045*N*) was then added to volume. After 30–45 min, aliquots of 5 ml were removed and added to a 50-ml beaker containing 5 ml of ca. 0.05*N* hydrochloric acid and 5 ml water. The excess acid was then titrated with standard 0.05*N* KOH in 99% ethanol, and the end-point was determined from the recorder tracing of pH versus volume of titrant. Volumes were read to the nearest 0.001 ml. A blank determination was performed in the same manner.

RESULTS AND DISCUSSION

Purification of Labeled Maleic Anhydride

Because of its high reactivity toward adventitious moisture, maleic anhydride must be handled carefully. In the case of the labeled compound, this ease of hydration requires the accurate determination of radiochemical purity, or the proportion of activity present as the anhydride. Treatment of the anhydride with an excess of aniline gives a quantitative yield of a derivative that is easily purified and assayed. The two lots of labeled anhydride used in this work had radiochemical purities of 99.8% and 98.8% as determined from the molar specific activities of the anhydride and monoanilide.

Preparation of Copolymers of Maleic Anhydride and Vinyl Acetate

Copolymers containing 5% to 50% maleic anhydride are desirable for standardizing and evaluating analytical methods for combined monomer. The preparation of copolymers containing substantially less than 50% of the anhydride is complicated, however, by the strong tendency of this monomer to yield alternating copolymers containing equimolar amounts of the reactants. This phenomenon is partly dependent on the ability of the anhydride to exchange electrons with the comonomer, but other factors, such as resonance effects, polar interactions, and steric requirements, are involved.¹⁰ For maleic anhydride-vinyl acetate copolymer, this alternation is reflected by the low value of the product of the reactivity ratios, i.e., $r_1r_2 = 0.002$ at 75°C.¹⁰ Early studies indicated that in the presence of an excess of vinyl acetate, initial formation of a 1:1 copolymer is followed by homopolymerization of the vinyl acetate.¹¹ A later investigation suggested that, with benzoyl peroxide in toluene at 70°C, formation of the 1:1 copolymer was followed by formation of a copolymer containing 2 moles of acetate per mole of anhydride.¹² Current interpretations of alternation favor a mechanism involving a donor-acceptor charge-transfer complex formed from the comonomers, and the existence of several such complexes of maleic anhydride has been demonstrated.¹³

The standard radioactive copolymers prepared in the present work were made in both toluene and MEK with either azobisisobutyronitrile (AIBN) or benzoyl peroxide as initiator. The nitrile has a first-order decomposition that is little influenced by the solvent; its lower transfer constant also results in higher molecular weight polymers than are obtained with the peroxide. Polymerization conditions used in preparing the labeled copolymers are given in Table I.

The fraction of charged maleic anhydride actually incorporated into copolymers prepared in toluene reflects the pronounced tendency of this monomer to form 1:1 products under the conditions used. For the polymers made in this solvent, the minimum maleic anhydride content of 31.0% at 70°C with 0.3 part of peroxide and a 95/5 charge ratio is close to the 29.5% found after 8 hr at a 90/10 charge ratio under the same conditions.¹²

Substitution of MEK for toluene permitted the preparation of polymers containing as little as 6% of the anhydride, presumably by reducing charge-transfer complex formation. The polymerizations in MEK were accompanied by a red-purple color that remained in the polymer even after its purification by a double precipitation with hexane. These two polymers were of relatively low molecular weight, as evidenced by their easy solubility in toluene.

TABLE I
Preparation Conditions for Standard Copolymers

Polymer designation	Solvent used	Initiator used	Initiator concn ^a	Temp., °C	Time, hr	Polymer container	Monomer concn, w/v%	Anhydride, wt-%	
								Charged	Found ^b
A	Toluene	AIBN	0.5	60	18	Pt. Bottle	10	45.3	50.5
B	Toluene	AIBN	0.5	60	18	Pt. Bottle	10	10.3	42.2
C	Toluene	AIBN	0.5	60	18	Pt. Bottle	10	24.5	44.7
D	Toluene	AIBN	0.5	60	18	Qt. Bottle	10	44.8	49.0
E	Toluene	Benz. Per.	0.3	70	24	Tube	50	5.1	31.0
F	Toluene	AIBN	0.5	60	18	Pt. Bottle	10	44.6	54.1
G	MEK	AIBN	0.5	70	22.5	Tube	58	5.2	6.3
H	MEK	AIBN	0.5	70	18	Tube	62	14.9	23.2

^a Parts per hundred parts monomers.

^b From radioactivity data.

Titrimetric Determination of Combined Maleic Anhydride

A characteristic of hydrolyzed maleic anhydride copolymers that has been studied in detail is their pronounced deviation from normal polyelectrolyte titration behavior after neutralization of one half of the carboxyl groups. Hydrolyzed copolymers made with ethylene or methyl vinyl ether were titrated with 0.1*M* tetrabutylammonium hydroxide in 0.1*M* tetrabutylammonium chloride, and pH versus α was plotted ($\alpha = 2$ for complete neutralization).⁵ The inflexion point at $\alpha = 1$ was more well defined for the methyl vinyl ether copolymer than for the ethylene copolymer. The difference between pK_1^0 and pK_2^0 for both copolymers was more than a unit larger than that for succinic acid,¹⁴ and this result gives support to the hypothesis that the two carboxylate groups in maleic acid polymers are sterically restrained to remain in the *cis* position.¹⁵

The two intrinsic pK 's of hydrolyzed copolymers of maleic anhydride with hydrocarbons are dependent on the number of carbon atoms in the hydrocarbon; one pK is decreased and the other increased as the number of carbon atoms in the comonomer is increased. In titration, sharper endpoints are observed as the molecular weight of the alkyl comonomer is increased from ethylene to 2-methyl-1-pentene.⁴ The analyses were performed by hydrolyzing in excess alkali and back titrating with acid in 0.1*M* KCl solution. The inflexion point was poorly defined for the copolymer with ethylene.

Direct potentiometric titrations in pure water of the hydrolyzed copolymers with methyl, ethyl, *n*-butyl, and *n*-hexyl vinyl ethers were also done in a study of hydrophobic bonding.⁵ All copolymers exhibited a well-defined equivalence point at $\alpha = 1$, indicating two successive ionization constants of different orders of magnitude. Titrations of copolymers of maleic anhydride with various unsaturated acetates have been performed and significant differences were observed in the behavior of these copolymers.¹⁶

Analytical methods for maleic anhydride in its copolymers with vinyl acetate must take into account the susceptibility of the acetate to hydrolysis. Extremely rigorous conditions, such as heating 10 hr at 90°C in 0.1*N* alkali,⁴ cannot be used, nor can hydrolysis in water for 30 min at 90°C.¹⁵ Dissolution of vinyl ether copolymers in water at room temperature simply by shaking proceeded slowly, was unsuitable for polymers containing lower concentrations of the anhydride, and permitted degradation.⁵ Although treatment of the copolymers with reagents that react with the anhydride groups to yield other titratable groups is feasible,¹⁷ this approach is largely restricted to copolymers of lower molecular weight.

In the present work, the observation was made that, if the polymer is first dissolved in a small quantity of MEK and dilute aqueous alkali is added, the anhydride groups are hydrolyzed rapidly without hydrolysis of the acetate. The reaction can be followed by removing aliquots, adding them to a measured excess of acid, and titrating the excess of acid with standard alkali. Results observed in the application of this method to a typical 1:1 copolymer are given in Table II.

These data confirm the stability of the acetate group over the 6-hr reaction time. On the basis of the above results, the standard deviation is 1.66% anhydride at the average level of 51.8%, corresponding to a coefficient of variation of 3.2%.

TABLE II
Hydrolysis of a 1:1 Copolymer at Room Temperature^a

Reaction time, min	Maleic anhydride, wt %	Reaction time, min	Maleic anhydride, wt %
15	53.0	150	50.6
30	52.9	180	52.1
45	50.0	240	52.4
60	51.6	300	51.3
90	52.6	360	52.1
120	50.9		

^a Sample A.

TABLE III
Maleic Anhydride Content by Isotopic and Titrimetric Methods

Polymer designation	Maleic anhydride, wt %		Relative deviation of titration result from isotopic result, %
	Titrimetrically	Isotopically	
Polymers Made in Toluene			
A	51.8	50.5	+2.6
B	44.6	42.2	+5.7
C	47.1	44.7	+5.4
D	47.7	49.0	-2.6
E	32.2	31.0	+3.9
F	53.4	54.1	-1.3
Polymers Made in MEK			
G	7.3	6.3	+15.8
H	26.2	23.2	+12.9

The method was applied to a total of eight labeled copolymers, and the results are compared with the isotopically derived maleic anhydride contents in Table III. The percentages of anhydride obtained from radioactivity data are corrected for radiochemical purity of the monomer.

Without regard to sign, the average relative deviation of the titrimetric data from the isotopic data is 3.6% for the polymers made in toluene. The higher (positive) deviations observed with polymers prepared in MEK may involve the solvent, but may also reflect the higher relative deviations to be expected of the titrimetric method at lower anhydride contents. The titration curves obtained in the direct titration of aqueous solutions of maleic anhydride-vinyl acetate copolymers in the present work exhibited the poorly defined inflection points previously reported for copolymers of the anhydride with ethylene⁴ and the lower alkyl vinyl ethers.⁵ The back titration technique is particularly advantageous with copolymers containing low concentrations of anhydride, since it overcomes the adverse titration characteristics of such polymers, which have marginal solubility in water. It is, therefore, especially useful with polymers containing only minor amounts of anhydride. In the analyses of the two lots of twice-recrystallized (labeled) maleic anhydride used in preparing the copolymers, recoveries were 98.7% and 98.8%.

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