# Infrared and Nuclear Magnetic Resonance of Maleic Anhydride Copolymers and Their Half Esters

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## Synopsis

Infrared and NMR group-type methods for the analysis of the anhydride content of maleic anhydride copolymers such as poly(maleic anhydride–co–α-olefin) and the half ester content of their reaction products with alcohols are described. The infrared analyses are based on the integrated absorptivities of the anhydride carbonyl and the combination of the acid and ester carbonyl. The NMR method is based on the intensities of the various chemically shifted groups in the copolymer. The use of dimethyl sulfoxide as an auxiliary solvent has made the infrared analysis possible.

## Introduction

Recent interest in the maleic anhydride copolymers, such as poly-(maleic anhydride–co–α-olefin) and their subsequent reaction products with alcohols, has led to the need for a simple method to determine the anhydride content of the copolymer as well as the half ester content of the reaction product.

Conventional chemical methods, such as nonaqueous titrimetry, frequently are not suitable for the analysis of polymeric material. Therefore, a method of analysis with the use of infrared absorption spectrophotometry in the wavelength region characteristic of carbonyl has been developed for the determination of the anhydride content as well as the acid and/or ester present in such copolymers.

Various investigators[1–4] have successfully used infrared absorption methods for the quantitative analysis of polymers. The infrared method, which is to be described, is a group-type procedure[5,6] in which integrated absorptivities, rather than those obtained from peak values, are used. The relative insolubility of the copolymers in conventional infrared solvents also posed a problem. It was found that dimethyl sulfoxide could be used as a solubilizing agent for the copolymers and for other carbonyl-containing compounds. As a result of this we are now able to extend the analysis to

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include aromatic anhydrides, acids and esters which hitherto had not been amenable to such analyses because of their insolubility.

## Experimental

A Perkin-Elmer Model 221 recording infrared spectrophotometer equipped with a NaCl prism was used to obtain all of the infrared data. A NaCl cell with a path length of 0.183 mm was used to obtain all data. The anhydrides, esters, and acids were all of the highest purity available. The purity ranged from 95 to 99% and was checked by mass spectrometry, gas-liquid chromatography, and nuclear magnetic resonance methods. The maleic acid and maleic anhydrides were recrystallized for this work. The solvents used were Fisher's certified reagents, methylene chloride (spectro-analyzed) and dimethyl sulfoxide (when needed). The concentrations of the compounds which were calibrated ranged from $8 \times 10^{-3}$ to $32 \times 10^{-3}$ mole of carbonyl-containing compound per liter.

Integrated absorptivities were calculated for all of the compounds in the carbonyl region. The integrals were obtained by means of a special ball-and-disk type integrator built by Perkin-Elmer Corporation. The integral of the anhydride carbonyl extended from $5.20\ \mu$ ($1923\ cm^{-1}$) to $5.65\ \mu$ ($1770\ cm^{-1}$). The second integral, for the ester and/or acid carbonyl, ranged from $5.65\ \mu$ ($1770\ cm^{-1}$) to $6.00\ \mu$ ($1667\ cm^{-1}$). The solvent formed the baseline in these regions (see Fig. 1).
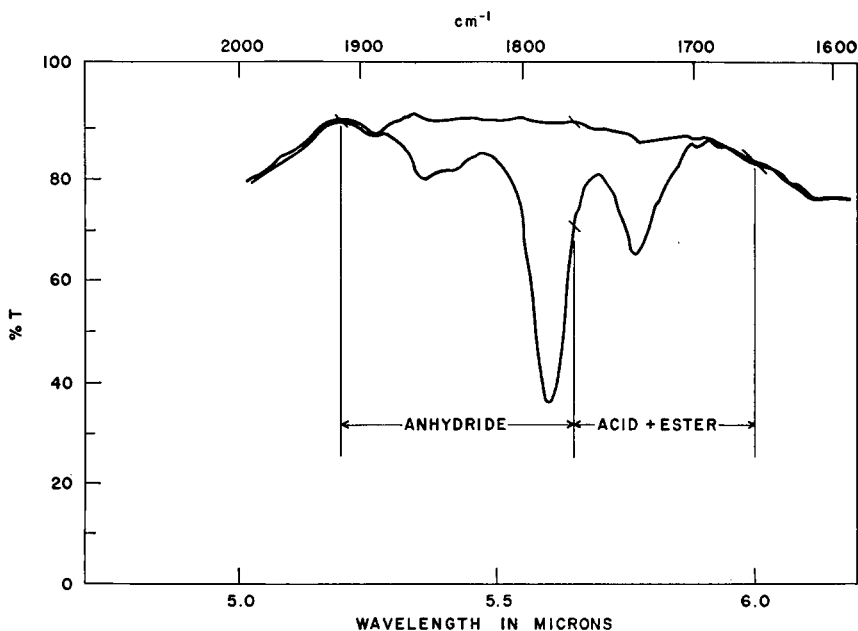


Fig. 1. Partially esterified maleic anhydride copolymer baseline. Solvent: DMSO–MeCl$_2$, 1:9.

Samples were usually run in methylene chloride (0.1 g/10 ml). When the sample is insoluble in methylene chloride, the weighed portion is solubilized in 1 ml of dimethyl sulfoxide to which 9 ml of methylene chloride was added. This procedure holds the polymer in solution for the analysis. A new baseline with the solvent dimethyl sulfoxide (DMSO)–methylene chloride (MeCl$_2$) 1:9 was then required. On occasion, we found it necessary to use additional dimethyl sulfoxide to keep a polymer in solution followed by methylene chloride to a volume of 10 ml; the solvent baseline was then redetermined accordingly.

The NMR spectra were run at 60 Mcps on a Varian HA-60 spectrometer at room temperature in acetone-$d_6$ solution. Tetramethylsilane (TMS) was used as internal calibration standard for the purpose of obtaining chemical shifts. Unfortunately, the individual absorption lines are broadened, resulting in considerable overlap, and the expected spin–spin couplings are not resolved under these conditions. However, the assignment of the various absorption lines can be made on the basis of reference spectra and the expected chemical shifts for the various groups. Absorption intensities were obtained after the overlapping lines were resolved by drawing symmetric absorption curves.

## Results and Discussion

The anhydrides used for the calibration, in the copolymer analysis, were maleic, succinic, and dodecenyl succinic. They were chosen because maleic anhydride is one of the starting materials, succinic anhydride approximates the product in that it is a saturated anhydride, and dodecenyl succinic anhydride tests the effect of a long side chain. The absorptivities for these anhydrides are found in Table I. Dodecenyl succinic anhydride which had

TABLE I
Absorptivities of Anhydrides[a]

| Anhydrides | Solvent | Absorptivity $\times$ 10$^{-4}$, l/mol-cm$^2$ | |
|---|---|---|---|
| | | 5.2–5.65 $\mu$ (1923–1770 cm$^{-1}$) | 5.65–6.00 $\mu$ (1770–1667 cm$^{-1}$) |
| Maleic | MeCl$_2$ | 2.26 | 0.27 |
| Succinic | MeCl$_2$ | 2.15 | 0.30 |
| Dodecenyl succinic | MeCl$_2$ | 2.31 | 0.28 |
| Dodecenyl succinic from branched-chain $\alpha$-olefins | MeCl$_2$ | 2.35 | 0.24 |
| Dodecenyl succinic from branched-chain $\alpha$-olefins | MeCl$_2$ + DMSO (9:1) | 2.22 | 0.27 |
| Average absorptivity | | 2.23 | 0.27 |

[a] Absorptivity = integrated absorbance (cm$^{-1}$)/concentration (mol/l) $\times$ cell length (cm).

been made from both straight-chain and branched-chain $\alpha$-olefins was used in the calibration. The effect of dimethyl sulfoxide on the absorptivity of this anhydride (see Table I) is well within the experimental error of the analysis. The group-type absorptivity, used to calculate the anhydride content of the copolymer, was obtained by averaging the absorptivities of the anhydrides listed in Table I.

The analysis can be applied to any copolymer of type I:



I
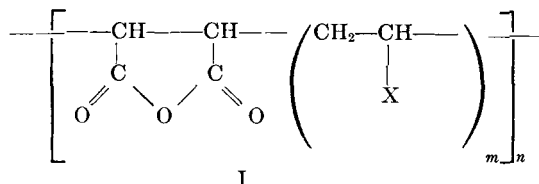
where X may be the alkyl, phenyl, or ester, etc., part of the $\alpha$-olefin and where $m \geq 1$. Calculation for the anhydride content only will be as follows:

$$\text{Mol anhydride/g sample} = \left(\frac{\text{Integrated absorbance}}{\text{Absorptivity} \times \text{cell length}}\right) \text{g sample/}$$

The molar anhydride content determined above can be used to calculate the anhydride to olefin ratio (A/O) of the copolymer.

$$\text{A/O} = \frac{\text{Mol anhydride/g sample}}{1.00 - \text{mol anhydride/g sample}}$$

When the maleic anhydride copolymers are reacted with alcohols they yield half esters which have many commercial uses. The reaction product has the general structure II:



II
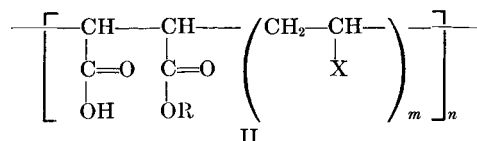
where X and $m$ are as defined previously and where, if X is an ester, special calculations will be required. In order to determine how successful such a reaction has been, it is necessary to know both the total carbonyl content of the half ester as well as any residual anhydride carbonyl. The analysis, therefore, involves the determination of anhydride carbonyl (5.20–5.65 $\mu$) and the total carbonyl of the half-ester region (5.65–6.00 $\mu$) which arises from both acid and ester carbonyl. It is impractical by infrared absorption to separate the acid and ester carbonyl due to overlap of their respective absorption bands in this region. Qualitatively one can tell, by inspection of the spectrum in the long-wavelength region, whether a half ester, diester, or diacid has been made or whether one type predominates over the other. This is based on the appearance of an absorption band in the region 8.00 $\mu$ (1250 cm$^{-1}$) to 8.50 $\mu$ (1176 cm$^{-1}$) which is suggestive of an ester and simi-

larly the appearance of an absorption arising around 10.6 $\mu$ (940 cm$^{-1}$) which suggests an acid.   Calibration compounds used for this part of the analysis were the diesters and diacids which are listed in Table II.   Dimethyl sulfoxide was required for the acids and its effect is illustrated for one of the esters. The average absorptivity for both types of compound becomes the group-type absorptivity used to determine the acid-ester carbonyl content.

TABLE II
Absorptivities of Diesters and Diacids[a]

| Compounds | Solvent | Absorptivity $\times 10^{-4}$, 1/mol-cm$^2$ | |
| | | 5.20–5.65 $\mu$ (1934–1770 cm$^{-1}$) | 5.65–6.00 $\mu$ (1770–1667 cm$^{-1}$) |
|---|---|---|---|
| Diethyl succinate | MeCl$_2$ + DMSO (9:1) | 0.09 | 1.78 |
| Diethyl succinate | MeCl$_2$ | 0.18 | 1.78 |
| Di-$n$-butyl succinate | MeCl$_2$ | 0.58 | 1.90 |
| Succinic acid | MeCl$_2$ + DMSO (9:1) | 0.12 | 2.19 |
| Maleic acid | MeCl$_2$ + DMSO (9:1) | 0.06 | 1.75 |
| | Average absorptivity | 0.21 | 1.88 |

[a] Absorptivity = integrated absorbance (cm$^{-1}$)/concentration (mol/l) $\times$ cell length (cm).

The calculations for the acid-ester carbonyl as well as the anhydride carbonyl were handled by setting up a simple binary matrix with the use of the data in Tables I and II, i.e.,

$$A_1 = a_{11}x_1 + a_{12}x_2$$

$$A_2 = a_{21}x_1 + a_{22}x_2$$

where $A_i$ is the integrated absorbance at band $i$, $a_{ij}$ is absorptivity of group-type $j$ at band $i$, $x_j$ is the number of moles per liter of $j$th group type.   The final values are reported in moles per gram, which simply involves a division by weight of sample per liter in grams, i.e.,

$$\text{Moles/gram of sample} = \frac{\text{moles/liter of the } j\text{th group type}}{\text{grams sample/liter} \times \text{cell length}}$$

The results of the analysis of a group of maleic anhydride copolymers and their half esters have been summarized in Table III.   These copolymers were made under reaction conditions which required an olefin to anhydride ratio of 1:1 (i.e., $m = 1.0$).   As a result, it was possible to obtain theoretical

TABLE III

Analyses of Maleic Anhydride Copolymers (I) and Their Half Ester (II)

| Sample description | | | Anhydride, mmol/g | C=O (acid + ester), mmol/g | Total C=O (as dicarbonyl compounds), mmol/g | | Calculated $m$ |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Number | X | R | | | Found | Theoretical | |
| 8778 | $C_3$ | — | 3.55 | 0.14 | 3.69 | 4.20 | 1.24 |
| 8789E | $C_3$ | $C_1$ | 0.22 | 2.99 | 3.21 | 3.70 | 1.30 |
| 8714E | $C_3$ | $C_1$ | 0.13 | 3.54 | 3.67 | 3.70 | 1.01 |
| 8783E | $C_3$ | $C_3$ | 0.25 | 2.77 | 3.02 | 3.33 | 1.14 |
| 8782E | $C_3$ | $C_4$ | 0.12 | 2.69 | 2.81 | 3.21 | 1.31 |
| 87-132A | $C_4$ | — | 5.17 | 0.19 | 5.36 | 5.49 | 1.05 |
| 7-53 | $C_4$ | $C_1$ | 0.03 | 4.24 | 4.27 | 4.67 | 1.24 |
| 7-40 | $C_4$ | $C_1$ | 0.32 | 4.06 | 4.38 | 4.67 | 1.17 |
| 8746A | $C_4$ | — | 0.26 | 5.35 | 5.61 | 5.49 | 0.95 |
| 8791A | $C_4$ | — | 4.56 | 0.41 | 4.97 | 5.49 | 1.23 |
| 8781A | $C_4$ | — | 4.62 | 0.27 | 4.89 | 5.49 | 1.26 |
| 8739A | $C_4$ | — | 4.86 | 0.36 | 5.22 | 5.49 | 1.12 |
| 8784E | $C_4$ | $C_4$ | 0.14 | 3.46 | 3.60 | 3.91 | 1.26 |
| 8785E | $C_4$ | $C_4$ | 0.19 | 3.48 | 3.67 | 3.91 | 1.19 |
| 878E | $C_4$ | $C_4$ | 0 | 3.65 | 3.91 | 3.91 | 1.21 |

values for the molar anhydride content of the copolymer and for the carbonyl of its half ester by calculating the reciprocal of the gram molecular weight of the predicted repeating unit in each case. A comparison of the analytical values with the theoretical values listed in Table III indicates very good agreement assuming the condition $m = 1$ has been met.

By allowing $m$ to be a variable parameter, it is possible to calculate $m$ for each sample from the above data; these results are listed in the last column of Table III. By grouping separately the anhydride copolymers, half esters, and samples 87-132A, 7-53, 7-40 which were known to be interrelated, and average value for $m$ with its standard deviation was found to be $1.18 \pm 0.08$. This value indicates a good internal consistency in the results.

By analyzing such copolymers for both anhydride and acid-ester carbonyl, one can tell if the copolymer has remained stable or hydrolyzed by picking up water. In the case of their reaction products with alcohols, the analysis will give information as to the extent of the reaction by indicating the presence or absence of anhydride.

## NMR Studies

This section reports the results of the high resolution nuclear magnetic resonance (NMR) analysis[7] for anhydride content, relative amounts of ester and/or acid, and any unreacted maleic anhydride present of certain poly(maleic anhydride–co–$\alpha$-olefins) (III) and of the products (IV) of this reaction with various aliphatic alcohols.
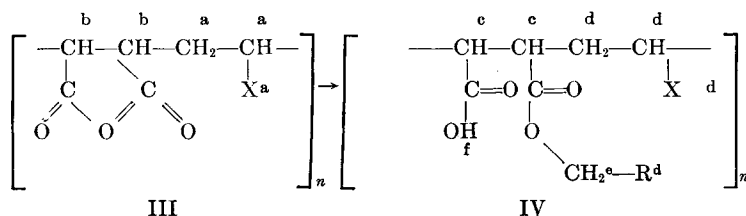


The chemical shifts of the various types of protons in III and IV are as follows: $a = 0.7$–$2.6$ ppm; $b = 3.25$ ppm; $c = 2.8$ ppm; $d = 0.7$–$2.3$ ppm; $e = 4.0$ ppm ($3.7$ for O—CH$_3$); $f < 9.0$ ppm. All chemical shifts are from tetramethylsilane (TMS), which was used as internal standard. Carbomethoxyl and carboxylic acid signals are sharp, as expected, since there is no spin-spin coupling that could cause line broadening.

Since the relative intensities of the various signals are related directly to the number of protons for each functional group, one can readily obtain the amounts of the various components of interest in each sample. For example comparison of the intensity of anhydride protons (b) to the sum of the intensities of —COOH and —COOCH$_3$ or —COOCH$_2$— (normalized for the appropriate number of protons) yields the relative amounts of unreacted and reacted anhydride. Also, comparison of the —COOH intensity to that of —COCH$_3$ or —COOCH$_2$— yields the relative amounts of acid and ester

TABLE IV
NMR and IR Analyses

| Sample | | | Reacted anhydride, % of total | | Unreacted anhydride, % of total | | Distribution of reacted anhydride | | Number of aliphatic protons | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No. | X | R | NMR | IR | NMR | IR | Acid, % | Ester, % | Experimental | Theoretical[a] |
| 7-50 | $C_4$ | $n\text{-}C_4$ | 93 | 99 | 7 | 1 | 56 | 44 | 15.0 | 14.9 |
| 87-78 | $C_8$ | — | 0 | 4 | 100 | 96 | 0 | 0 | 20.7 | 20.0 |
| 7-47 | $C_8$ | $n\text{-}C_4$ | 91 | 100 | 9 | 0 | 48 | 52 | 23.0 | 23.3 |
| 87-89 | $C_8$ | $C_1$ | 80 | 93 | 20 | 7 | 57 | 43 | 18.0 | 20.0 |
| 87-132 | $C_4$ | — | 0 | 3 | 100 | 97 | 0 | 0 | 10.0 | 12.0 |
| 7-53 | $C_4$ | $C_1$ | 94 | 99 | 6 | 1 | 57 | 43 | 9.5 | 12.0 |
| 7-40 | $C_4$ | $C_1$ | 86 | 93 | 14 | 7 | 57 | 43 | 9.0 | 12.0 |
| 7-54A | $C_4$ | $n\text{-}C_4$ | 96 | 100 | 4 | 0 | 38 | 62 | 18.0 | 16.2 |

[a] Assuming 1:1 polymerization.

present. Table IV shows the relative amounts of the various components present in the samples examined, and for comparison, the results obtained by infrared spectroscopy. The agreement between the two techniques is generally good, especially in view of the fact that the NMR absorption lines overlap considerably.

The intensity of the alkyl chain protons from 0.9 to about 2.3 ppm will be contributed to by part of the ester if the alcohol used in the reaction with the anhydride is other than methanol. In fact, only the proton alpha to the carboxy group (e) will not contribute to this region. In addition, such contributions will be proportional to the amount of ester formed and to the number of protons in the ester chain. For example, from the spectrum of sample 7-50 and on the basis of the intensity of the anhydride protons there are 15 protons contributing to this alkyl region. Assuming one anhydride unit to one olefin unit polymerization, one expects $N + Y(M-2)$ protons for the aliphatic proton group; for sample 7-50 this equals 14.9 in very good agreement with the experimental count of 15. (Here, $N$ is the number of protons from the olefin chain; $Y$ is the ester formed expressed as a fraction of the total anhydride; and $M$ is the number of protons in the ester.) The last two columns of Table IV summarize these calculations for all the samples examined and compare them to the actual number of protons determined from the spectra.

Samples 87-89 and 7-47 were prepared from 87-78. The good agreement within the series between actual and expected aliphatic protons for a one anhydride unit to one olefin unit polymerization is reassuring with respect to the correctness of the approach.

Samples 7-53 and 7-40 were prepared from 87-132. It is noted that for all three samples the actual number of aliphatic protons is less than the expected number. Although this discrepancy could perhaps be attributed to such experimental error as the poor resolution of the spectral bands, the consistency of the deviation suggests that on the average there may be more anhydride units than olefin units per polymer chain.

Note that three of the samples examined (87-132, 7-53, and 7-40) had approximately 5% unreacted maleic anhydride present, as revealed by the resonance at 7.4 ppm.

## Conclusions

The infrared method described is simple, and about 45 min is required to complete a determination. The NMR method is equally direct. Both offer excellent control possibilities, and their accuracies are well within the limits of group-type procedures.

As a result of the necessity to solubilize copolymer reaction products, we found that we were also able to solubilize various aliphatic and aromatic acids as well as aromatic anhydrides in a similar manner. Integrated absorptivities for a group of these compounds have been summarized in Table V. It is therefore quite possible to extend this type of analytical procedure to such materials.

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TABLE V

Absorptivities for Other Carbonyl-Containing Compounds Requiring DMSO as a Solubilizing Agent

| Compound | Solvent | Absorptivity $\times 10^{-4}$, l/mol-cm$^2$ | |
|---|---|---|---|
| | | 5.25–5.65 $\mu$ (1923–1770 cm$^{-1}$) | 5.65–6.00 $\mu$ (1770–1667 cm$^{-1}$) |
| Phthalic anhydride | MeCl$_2$ + DMSO (9:1) | 2.64 | 0.09 |
| Benzophenone tetra-carboxylic dianhydride | MeCl$_2$ + DMSO (9:1) | 5.29 | 0.59 |
| Oxalic acid | MeCl$_2$ + DMSO (9:1) | 0.98 | 1.69 |
| Benzoic acid | MeCl$_2$ + DMSO (9:1) | 0.59 | 1.23 |
| Phthalic acid | MeCl$_2$ + DMSO (9:1) | 0.76 | 2.40 |

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