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Determination of Copolymer Composition by Quantitative Infrared Analysis*

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ABSTRACT

Infrared spectroscopic analysis was used in the determination of the copolymer composition of itaconic anhydride copolymers. The results are in close agreement with those obtained by elemental analysis. The method is of great value in determining the composition of copolymers which contain strongly absorbing groups and the composition of which could not be realized by using elemental analysis.

INTRODUCTION

Infrared spectroscopy has been widely used in the identification of functional groups as well as the fine structure of high polymers. It can be used in the determination of the composition of copolymers which have strongly absorbing functional groups [1].

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In this paper, the copolymer composition of itaconic anhydride–vinyl acetate copolymers, which could not be determined by elemental analysis, was obtained by using infrared quantitative analysis.

In order to check the reliability of the results, the copolymer composition for three other systems, namely: itaconic anhydride–2-chloroethyl acrylate, itaconic anhydride–styrene, and itaconic anhydride–p-methoxystyrene was determined by both elemental and infrared analyses.

EXPERIMENTAL

Purification of Acetonitrile

Spectrograde acetonitrile was dried and distilled over phosphorus pentoxide according to the method described by Weissberger [2].

Infrared Measurement

The infrared spectra were obtained by using a Perkin-Elmer-237B spectrometer equipped with matching 0.5 mm sodium chloride cells. A Keuffel and Esser compensating planimeter was used to measure the peak areas.

Solutions (0.5%) of poly(itaconic anhydride) as well as of the homopolymer or the model compound of each of the comonomers, were prepared in anhydrous acetonitrile. Mixtures of varying compositions of these solutions were prepared and their spectra were obtained. The peak areas for the anhydride peak at 1864 cm^{-1} were measured, and a standard curve was obtained, in each case, by plotting the percent anhydride content against the peak area.

To determine the copolymer composition, spectra were obtained for 0.5% solutions of the copolymer and the areas of the peak at 1864 cm^{-1} were measured in the same manner. The percent anhydride content was then determined by using the standard curve, and the mole fraction of the anhydride moiety in the copolymer was calculated by the following procedure. Let A = percent of itaconic anhydride moiety in copolymer; $B = 100 - A$ = percent of comonomer moiety in copolymer; M = molecular weight of comonomer. Then the number of moles x of itaconic anhydride moiety in 100 g polymer is $x = A/112$ and the number of moles y of comonomer moiety in 100 g polymer is $y = B/M$ and the mole fraction of itaconic anhydride moiety in the copolymer is $x/(x + y)$.

RESULTS

Itaconic Anhydride–2-Chloroethyl Acrylate

The copolymer composition of these polymers was obtained by elemental analysis for chlorine as well as infrared analysis. Figure 1 shows the spectra of poly(itaconic anhydride) and of poly(2-chloroethyl acrylate). Figure 2 shows the carbonyl absorbances of mixtures of poly(itaconic anhydride) and poly(2-chloroethyl acrylate) of varying anhydride content. The plot of the peak area against the percent anhydride content is shown in Fig. 3. Table 1 lists the copolymer compositions of different itaconic anhydride–2-chloroethyl acrylate copolymers.

Itaconic Anhydride–Vinyl Acetate

The spectrum of poly(vinyl acetate) is shown in Fig. 1. The carbonyl absorbances of mixtures of poly(itaconic anhydride) and poly(vinyl acetate) with different anhydride contents and those for mixtures of poly(itaconic anhydride) and sec-butyl acetate are shown in Figs. 4 and 5. Plots of the peak area against the percent anhydride content for these different mixtures are shown in Fig. 6. Table 2 lists the copolymer composition of different itaconic anhydride–vinyl acetate copolymers.

Itaconic Anhydride–Styrene

Polystyrene was insoluble in acetonitrile, and a standard curve was obtained by diluting the stock solution of poly(itaconic anhydride) into 80, 60, 40, and 20% of the original concentration (0.5%). The spectra for these dilutions were obtained, and the carbonyl absorbances are shown in Fig. 7. The plot of the peak area against poly(itaconic anhydride) concentration is shown in Fig. 8. Table 3 gives the copolymer composition of the different itaconic anhydride–styrene copolymers determined both by elemental analysis for carbon and infrared analysis.

Itaconic Anhydride–p-Methoxystyrene

The standard curve was obtained by using mixtures of poly(itaconic anhydride) and the model compound of the comonomer unit, p-(sec-butyl)-anisole. Figure 9 shows the carbonyl absorbances for the

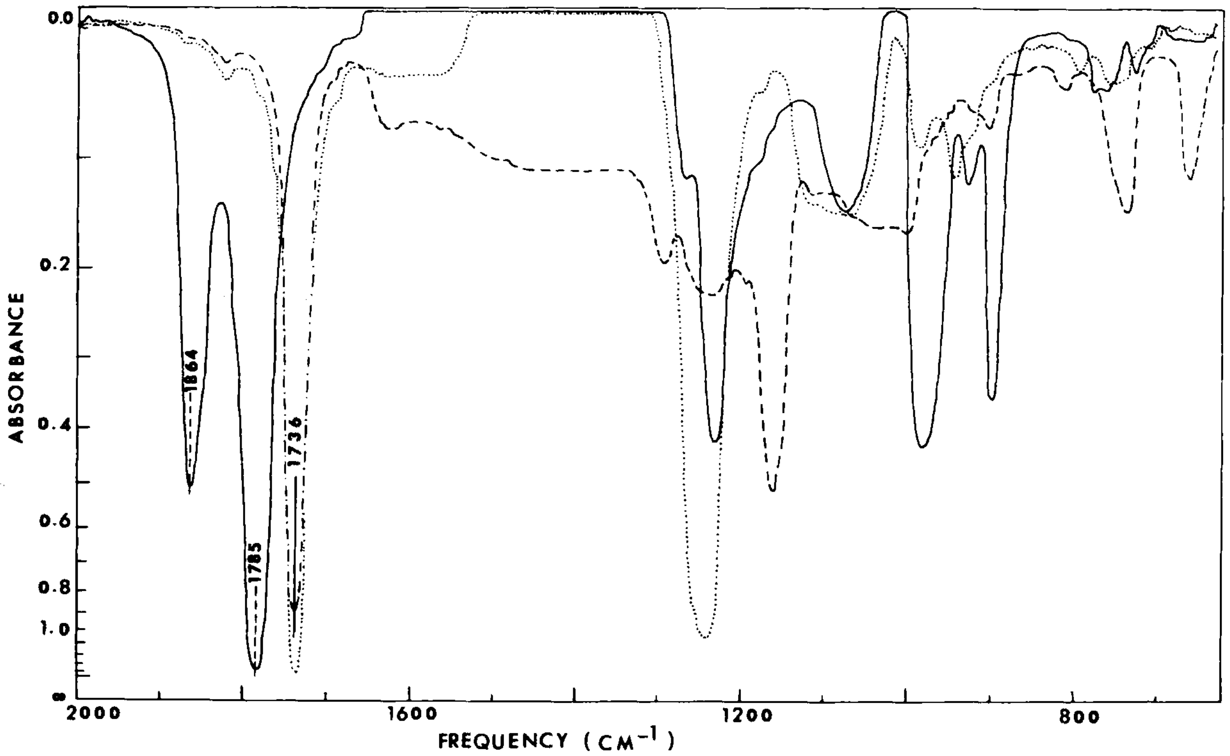

FIG. 1. Infrared spectra of (—) poly(itaconic anhydride), (· · ·) poly(vinyl acetate), and (- -) poly(2-chloroethyl acrylate).

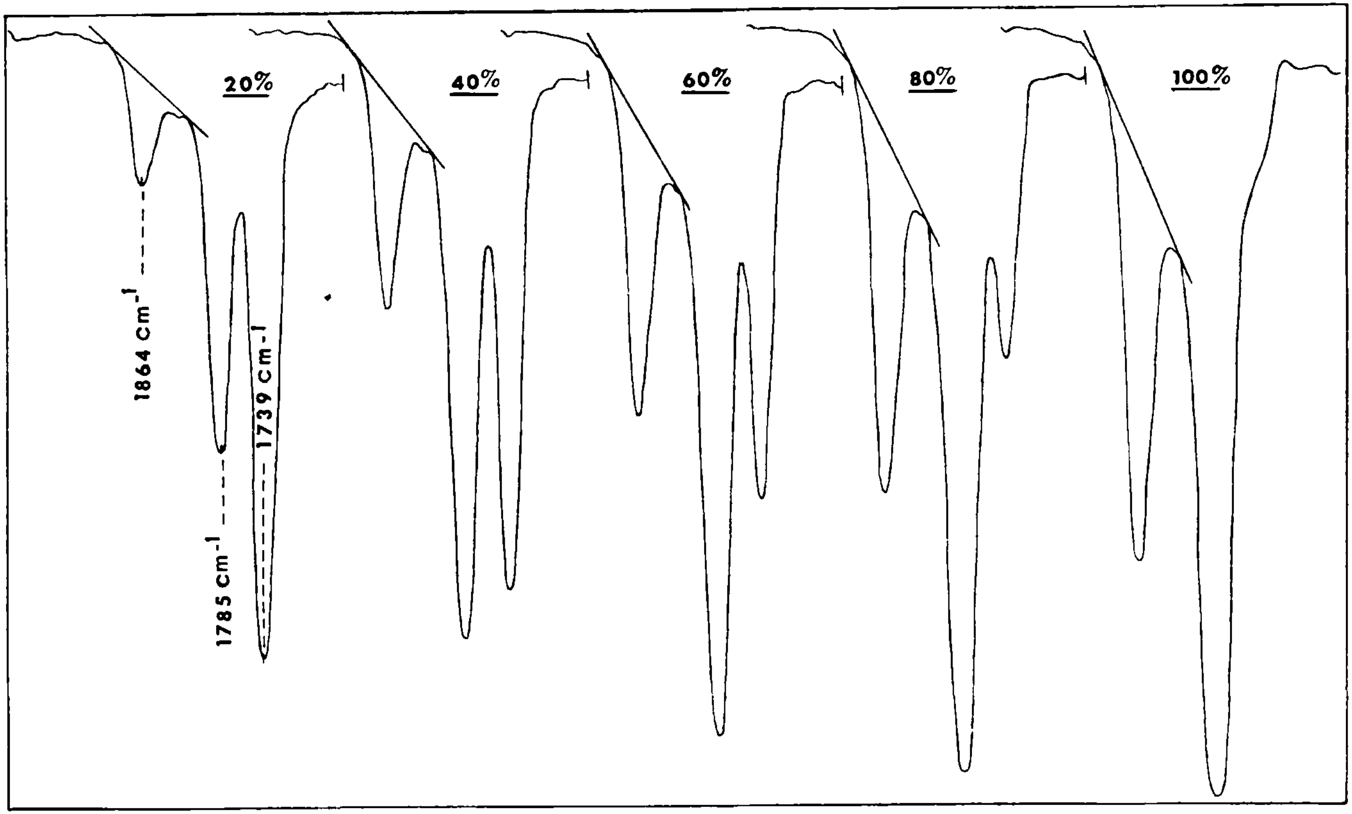

FIG. 2. Infrared absorbances of mixtures of poly(itaconic anhydride) and poly(2-chloroethyl acrylate) of varying anhydride content.

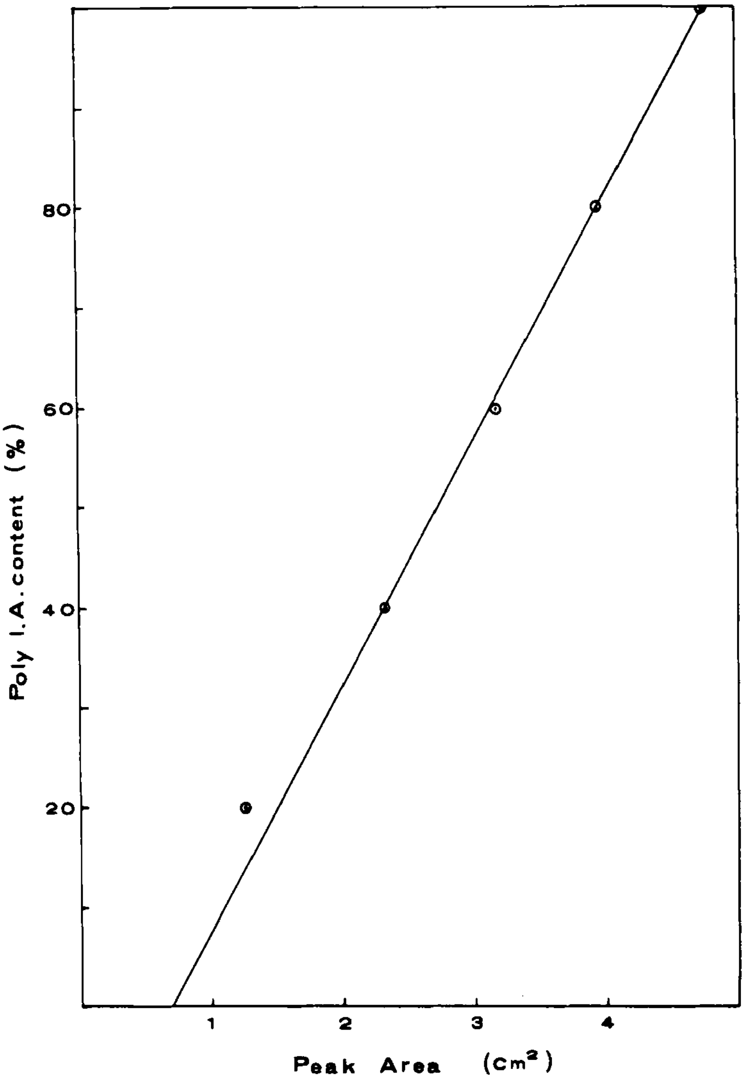

FIG. 3. Graph of the area of the carbonyl peak at 1864 cm^{-1} against the anhydride content in mixtures of poly(itaconic anhydride) and poly(2-chloroethyl acrylate).

TABLE 1. Copolymer Composition of Itaconic Anhydride–2-Chloroethyl Acrylate Polymers

	Infrared spectra		Elemental analysis	
Copolymer	Anhydride moiety content (%)	Anhydride moiety (mole fraction)	Chlorine content (%)	Anhydride moiety (mole fraction)
1	46.0	0.506	14.94	0.48
2	59.0	0.633	11.00	0.620
3	66.0	0.700	9.05	0.690
4	70.0	0.737	9.02	0.700
5	76.0	0.792	7.60	0.750
6	81.0	0.847	6.60	0.785
7	84.0	0.863	4.50	0.855
8	89.0	0.908	3.17	0.920
9	95.0	0.945	1.90	0.945

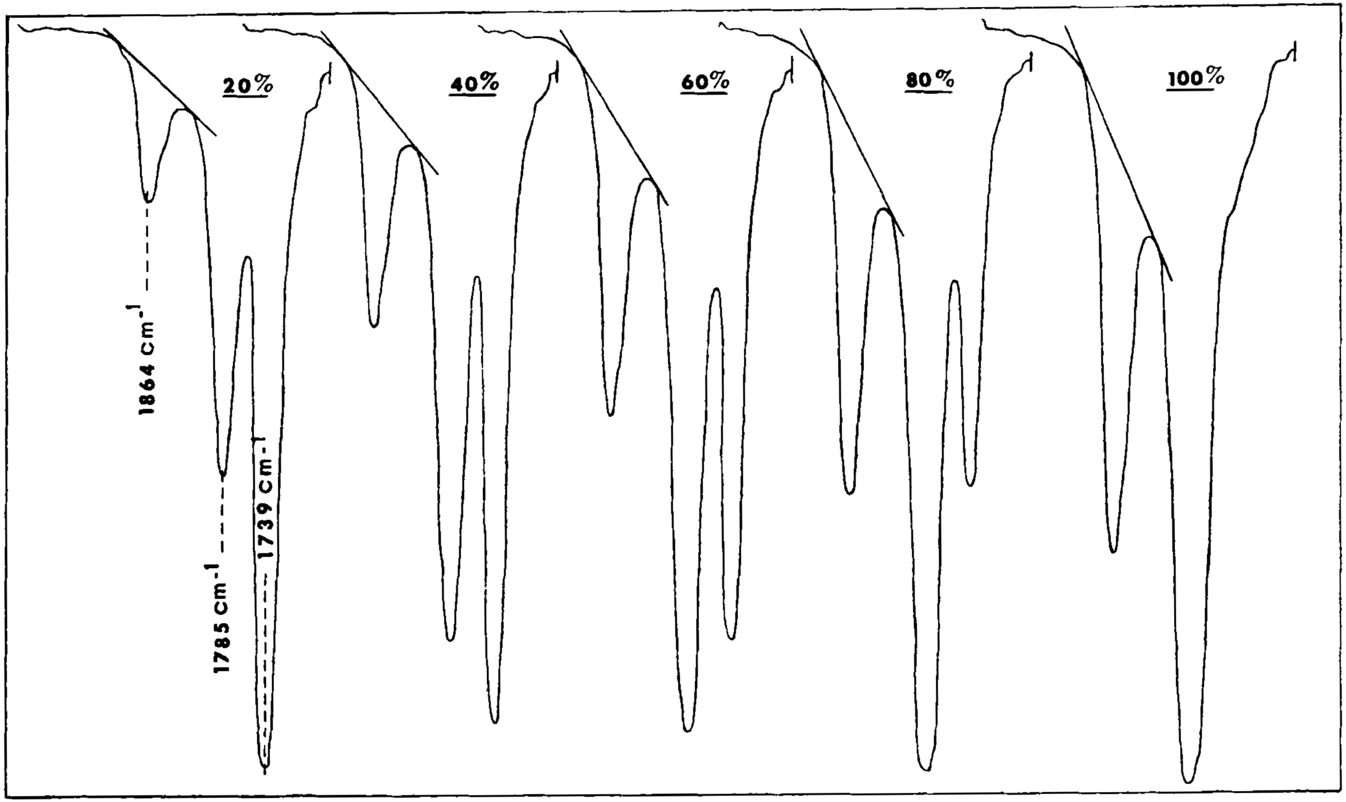

FIG. 4. Infrared carbonyl absorbances of mixtures of poly(itaconic anhydride) and poly(vinyl acetate) of varying anhydride content.

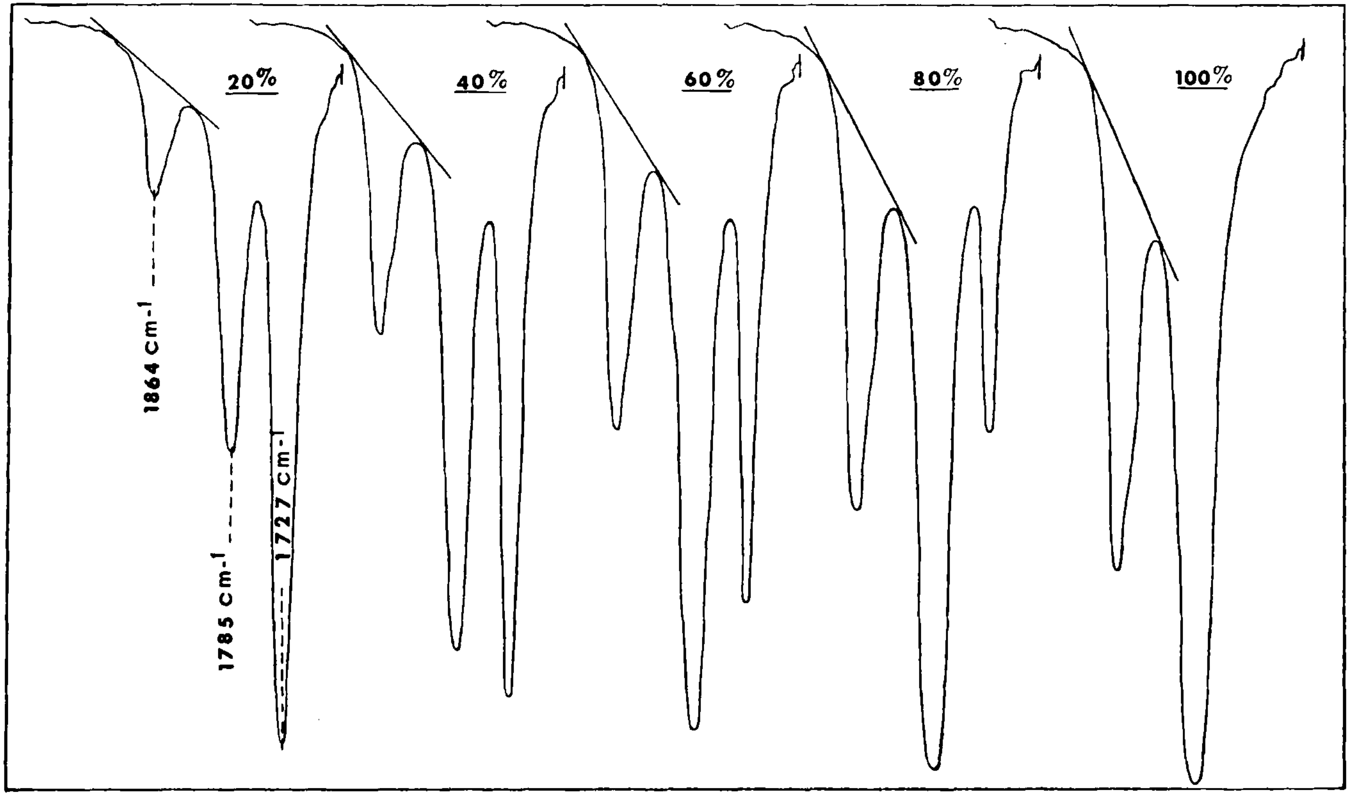

FIG. 5. Infrared carbonyl absorbances of mixtures of poly(itaconic anhydride) and sec-butyl acetate of varying anhydride content.

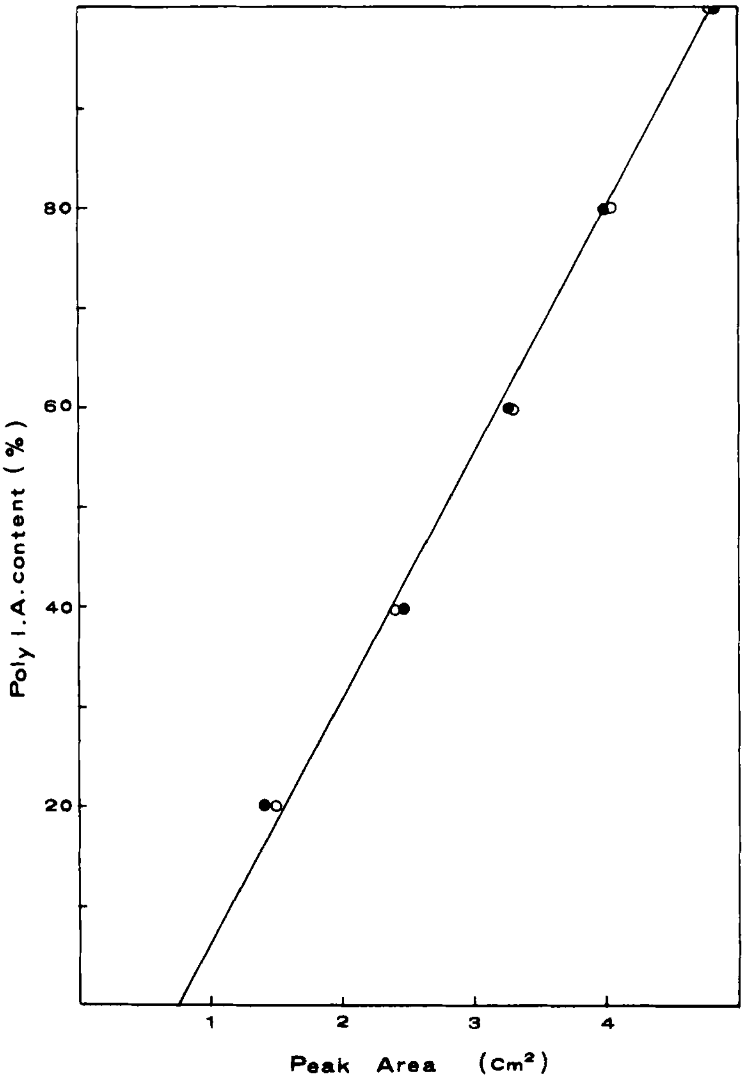

FIG. 6. Graph of the area of the carbonyl peak at 1864 cm^{-1} against the anhydride content in (○) mixtures of poly(itaconic anhydride) and poly(vinyl acetate) and (●) mixtures of poly(itaconic anhydride) and sec-butyl acetate.

TABLE 2. Copolymer Composition of Itaconic Anhydride–Vinyl Acetate Polymers

Copolymer	Anhydride moiety content (%)	Anhydride moiety (mole fraction)
1	60.0	0.535
2	71.0	0.652
3	77.0	0.720
4	81.0	0.775
5	84.5	0.807
6	89.0	0.863
7	91.0	0.882
8	94.0	0.923
9	97.0	0.960

mixtures of varying anhydride content, while Fig. 10 is the plot of the peak area against the anhydride content. Table 4 gives the copolymer composition of the different itaconic anhydride–p-methoxystyrene copolymers determined by both elemental analysis for carbon and infrared analysis.

DISCUSSION

The spectrum for poly(itaconic anhydride) showed two strong peaks at 1785 and 1864 cm^{-1}. The change in the area of the peak at 1864 cm^{-1} with concentration was used to construct the standard curves, since it was not affected by the presence of any other type of carbonyl groups in the mixtures. The peak at 1785 cm^{-1}, although stronger, it showed an overlap with the ester carbonyl peak. The standard curves of the poly(itaconic anhydride) mixtures with either poly(vinyl acetate) or poly(2-chloroethyl acrylate) were practically superimposable. Another standard curve obtained by mixing solutions of poly(itaconic anhydride) and sec-butyl acetate (model compound for the vinyl acetate moiety) was similar to that obtained by using poly(vinyl acetate) in the mixtures. This points out that the carbonyl peak at 1864 cm^{-1} was not affected either by other carbonyls present in the mixture or by the nature of the other component of the mixture (i.e., polymeric or monomeric), and that it is possible to obtain the same anhydride

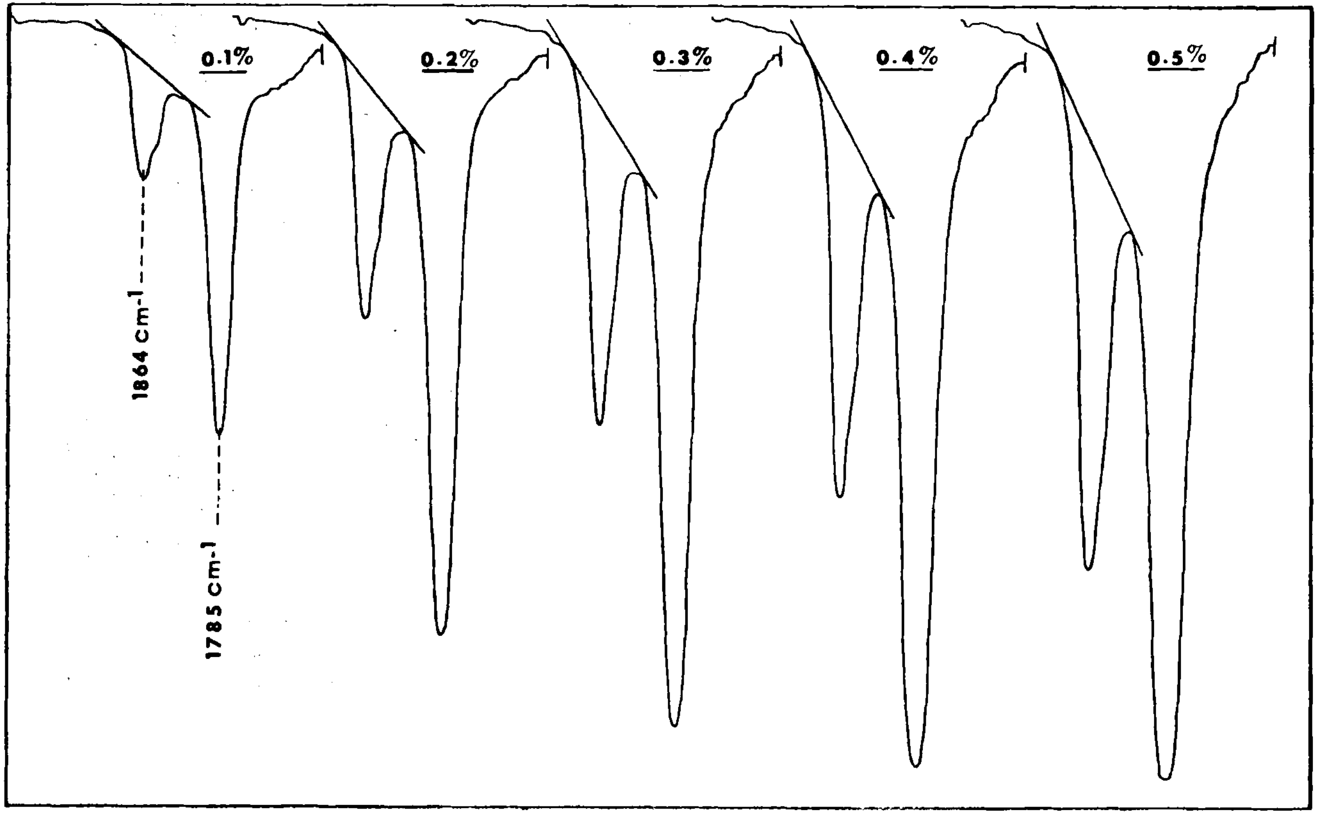

FIG. 7. Infrared carbonyl absorbances of solutions of poly(itaconic anhydride) of varying concentration.

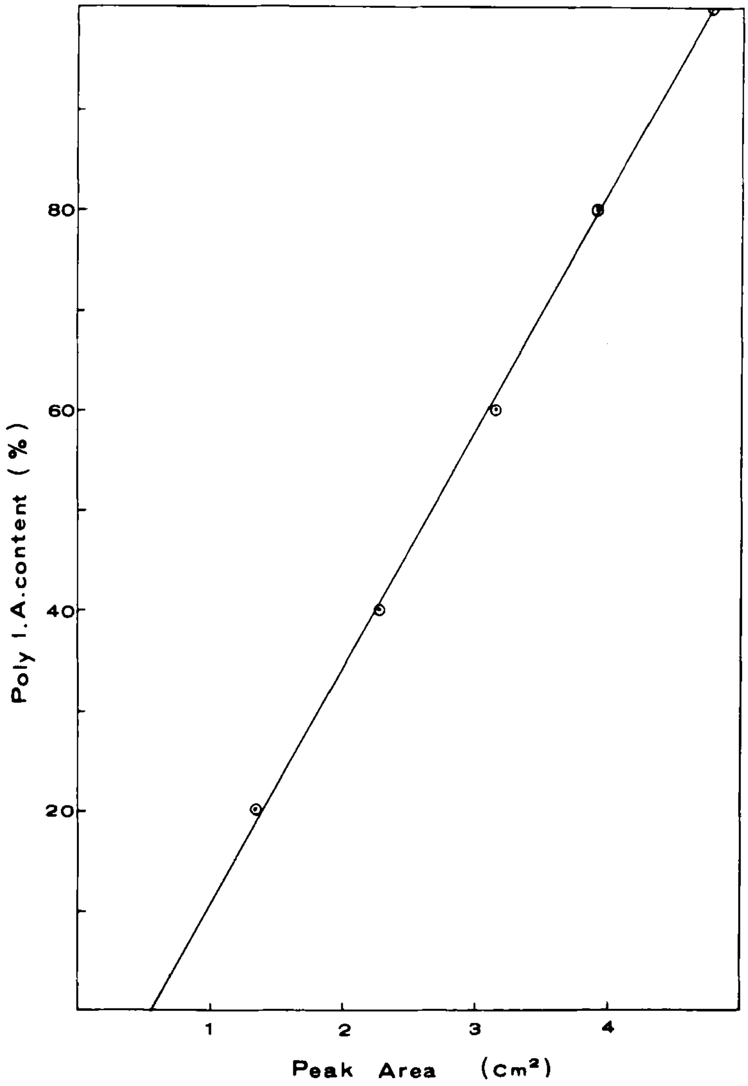

FIG. 8. Graph of the area of the carbonyl peak at 1864 cm^{-1} against the anhydride content. The 0.5% solutions represent the 100% point on the graph.

TABLE 3. Copolymer Composition of Itaconic Anhydride–Styrene Polymers

Copolymer	Infrared spectra		Elemental analysis	
	Anhydride moiety content (%)	Anhydride moiety (mole fraction)	Chlorine content (%)	Anhydride moiety (mole fraction)
1	49.50	0.476	73.00	0.480
2	52.00	0.500	71.61	0.520
3	54.50	0.527	70.23	0.550
4	56.50	0.547	69.72	0.565
5	61.50	0.597	67.83	0.615
6	66.00	0.643	66.31	0.650
7	68.00	0.664	65.32	0.700
8	71.00	0.694	61.60	0.780

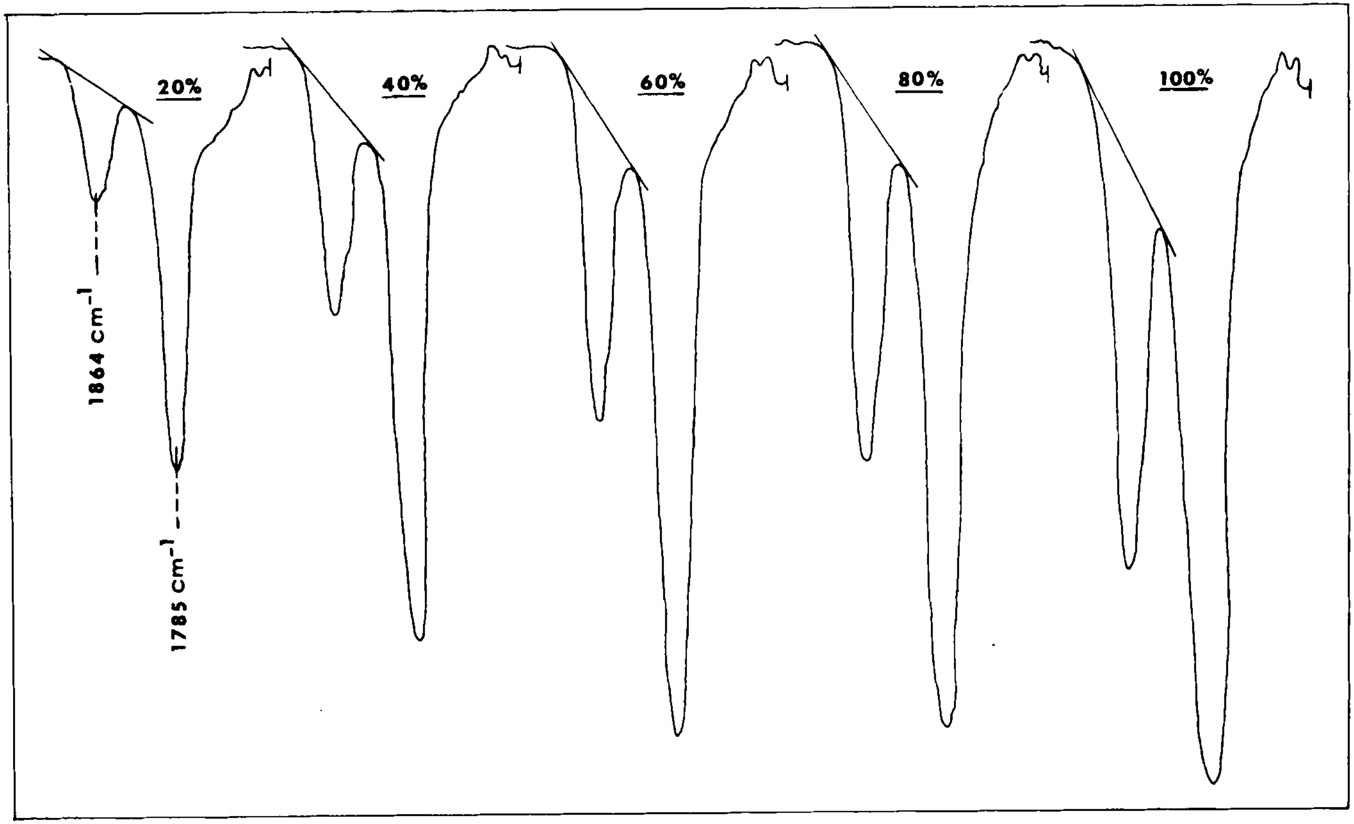

FIG. 9. Infrared carbonyl absorbances of mixtures of poly(itaconic anhydride) and p-(sec-butyl)anisole of varying anhydride content.

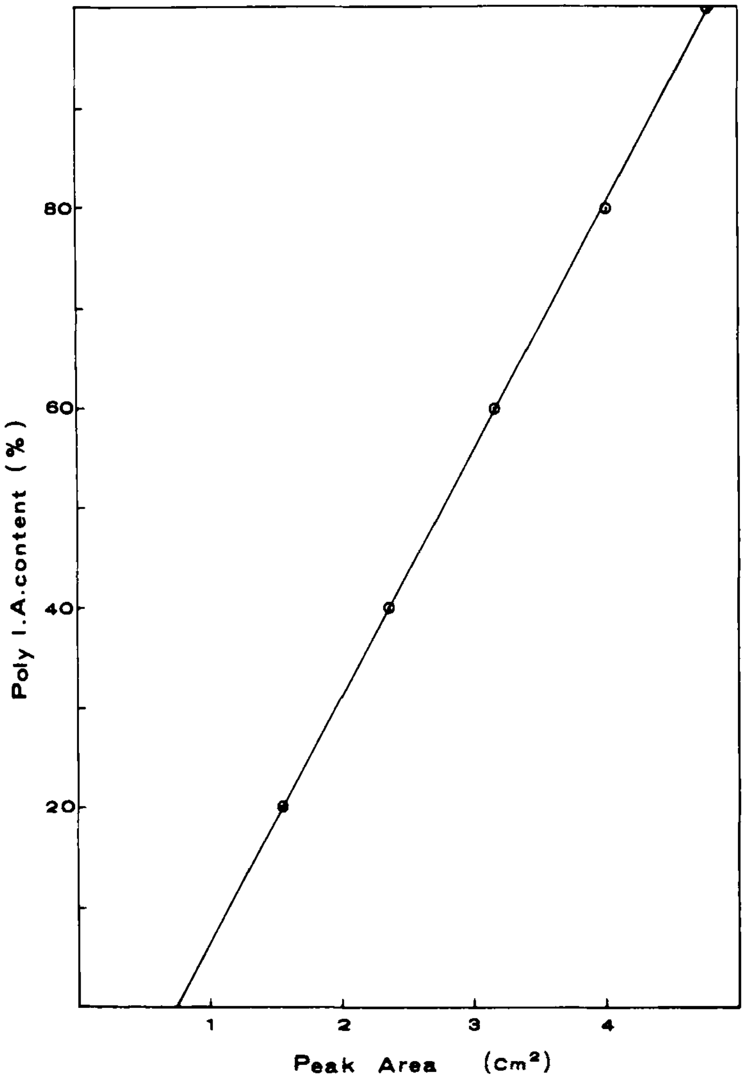

FIG. 10. Graph of the area of the carbonyl peak at 1864 cm^{-1} against the anhydride content in mixtures of poly(itaconic anhydride) and p-(sec-butyl)anisole.

TABLE 4. Copolymer Composition of Itaconic Anhydride–p-Methoxystyrene Polymers

	Infrared spectra		Elemental analysis	
Copolymer	Anhydride moiety content (%)	Anhydride moiety (mole fraction)	Chlorine content (%)	Anhydride moiety (mole fraction)
1	43.50	0.479	68.81	0.485
2	46.50	0.509	68.07	0.515
3	49.00	0.535	67.50	0.530
4	52.00	0.564	-	-
5	54.50	0.590	66.60	0.560
6	57.00	0.613	65.60	0.590
7	60.00	0.643	65.10	0.618
8	62.00	0.661	65.00	0.623
9	73.00	0.764	60.10	0.759

concentrations as the mixtures used without the need for mixing the homopolymer of the comonomer or even a model compound. Figure 8 shows such a curve which is again almost superimposable on the other standard curves obtained.

The data in Tables 1, 3, and 4 clearly show the reliability of the infrared analysis as compared with elemental analysis. Moreover, using infrared analysis, one can detect hydrolysis of the anhydride rings in the polymer which cannot be detected by elemental analysis and which may lead to errors in determinations of composition.

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