Infrared Determination of the Composition of Copolymers and Terpolymers of Propene and Butene-1 with and without Octene-1

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Synopsis

An infrared spectrophotometer was calibrated for the quantitative determination of butene-1 in copolymers with propene, and of butene-1 and limited concentrations of octene-1 in terpolymers with propene. ^{14}C-tagged standards were used for the butene-1 calibration while standards for the octene-1 calibration were prepared from a homopolymer by blending. Films were pressed from the standards, and the absorbance per mil thickness was correlated with composition. For our instrument, wt-% C_4 = 510 (A/mil) at 766 cm^{-1}, and wt-% C_8 = 539 (A/mil) at 725 cm^{-1}. No special steps were required to eliminate the effects of crystallinity.

INTRODUCTION

A routine method was needed for determining the composition of co- and terpolymers of propene and butene-1 with and without octene-1. The ratios of infrared absorbance bands have been used successfully by Slonaker et al.,[1] Khodzhayeva and Mamedova,[2] and Tosi et al.[3] to determine olefin copolymer compositions. However, such methods became unwieldy when adopted for terpolymers. These methods generally require melting the sample in the spectrophotometer to eliminate the effect of crystallinity, whereas our method requires no heated cell or other attachment.

A different technique, used by Huff et al.[4] and by Turner-Jones,[5] correlates the absorbance per mil thickness with composition at an appropriate wave number. Polymers containing butene-1 have a distinctive absorbance at 766 cm^{-1}, the wave number of the CH_2 stretching vibration in the pendant ethyl group.[1,5] This vibration shifts to lower wave numbers as the length of the pendant group increases. Polymers prepared with n-octene-1 absorb at 725 cm^{-1}, and a minimum wave number of 719 was found for n-decene-1 and higher 1-olefins.[4] Any one of these higher 1-olefins can be measured, but a mixture of them cannot be resolved.

The CH_2 stretch band is essentially independent of monomer sequence and chain conformation.[5] Work by our crystallographers on homopoly-

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butene-1 showed this band to be independent of crystal form. Luongo and Salovey[6] did not find changes in this band when studying the infrared spectra of polybutene-1 single crystals in all three modifications. No change was found in the values of absorbance per mil thickness of our standard sample films when measured four months after preparation. The co- and terpolymer samples had total crystallinities in the range 19% to 54% after annealing. The actual crystallinities of the films prepared for infrared scanning were not determined.

EXPERIMENTAL

A series of Ziegler-Natta-type copolymers were prepared from propene and ^{14}C-labeled butene-1. A homopolymer of the labeled butene-1 was also prepared and blended with polypropylene to make additional compositions available. Blending was accomplished by pressing a film of the mixture, then folding and repressing 15 times.

Standards for the octene-1 analysis were blends of a homopolymer with a propene–butene-1 copolymer. This blending was accomplished by dissolving the components in hot heptane and evaporating the solvent.

Films were pressed between Mylar sheets without spacers at a pressure of 280 psig. The temperature was varied from 250°F for 50% or less C_3 to 350°F for 80% or more C_3. The films were easily released from the Mylar with a few drops of acetone.

Film samples were mounted in stiff paper holders equipped with pressure-sensitive adhesive (The Cedar Tree Press, Wilmington, Del.). They were scanned from 850 to 670 cm^{-1} with a Perkin-Elmer 137B spectrophotometer. Immediately after scanning, the film thickness was measured using a deep throat micrometer with a $3/16$ in. anvil (No. 56212, B.C. Ames Co., Waltham, Mass.). A typical film was 5 mil. A baseline was drawn for each absorbance peak to be used and the absorbance was measured from the baseline to the maximum.

TABLE I

Calibration of Butene-1 Analysis with Tagged Samples

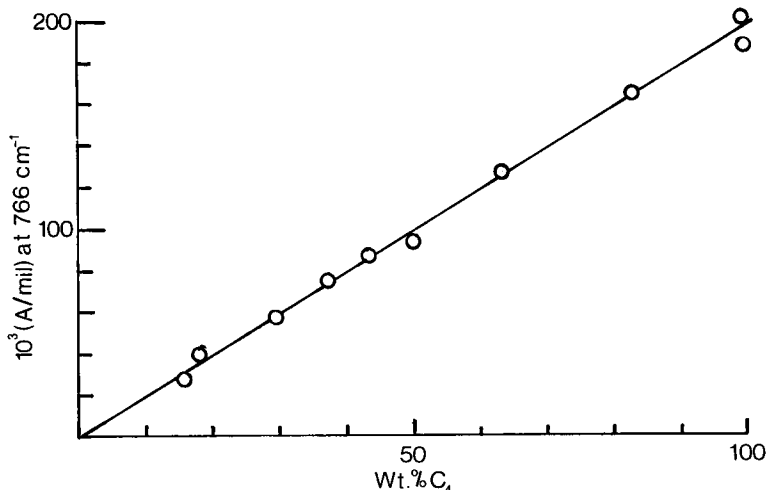| Sample	C_4 by Radio-assay, wt-%	$(A/\text{mil}) \times 10^2$ at 766 cm^{-1}
Blend A	15.8	27
B	62.0	126
C	83.1	163
Copolymer 1	18.3	39
2	29.2	57
3	37.3	74
4	43.6	86
5	49.3	93
6	98.6	187,200

Fig. 1. Calibration of butene-1 analysis with tagged samples.

RESULTS AND DISCUSSION

The radioassays of ^{14}C-labeled samples used to calibrate the butene-1 analysis are listed in Table I, along with the absorbance per mil at 766 cm^{-1}. The same data are presented graphically in Figure 1. A functional expression for the correlation found is

$$\text{wt-}\% \ C_4 = 510 \ (A/\text{mil}) \text{ at } 766 \text{ cm}^{-1}.$$

The standard deviation is 1.94 wt-$\%$ C_4.

This result indicates an absorbance of 77 per cm of butene-1, somewhat lower than the value of 85 reported by Turner-Jones.[5] The difference reflects the variations which require individual calibration of infrared instruments used for quantitative analysis.[7-9]

Data for the calibration of octene-1 analysis are listed in Table II and plotted in Figure 2. No measurements were made above 25 wt-$\%$ C_8 since overlapping of the 725 and 766 cm^{-1} absorption bands occurs at this con-

TABLE II
Calibration of Octene-1 Analysis

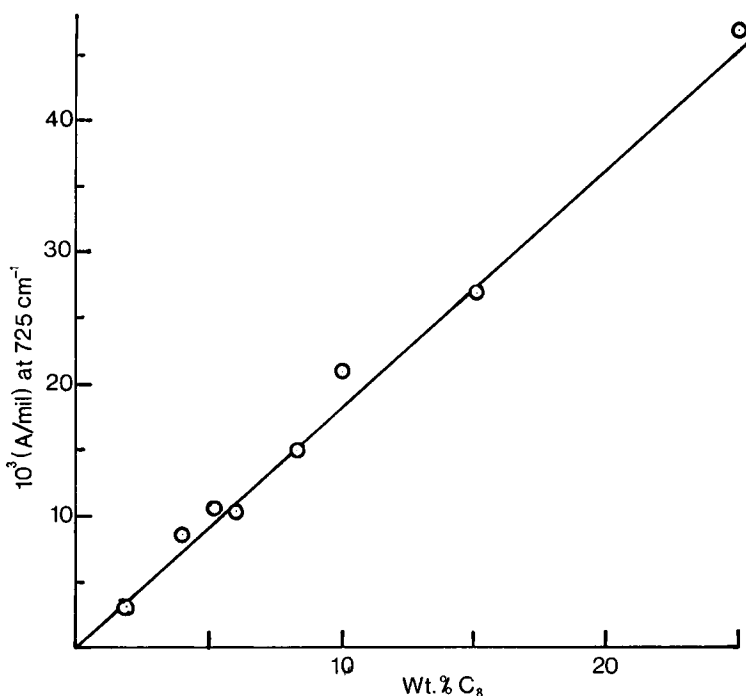| Blend	C_8, wt-$\%$	$(A/\text{mil}) \times 10^3$ at 725 cm^{-1}
A	1.99	3.0
B	4.06	8.5
C	5.29	10.5
D	6.02	10.3
E	8.03	15.0
F	10.0	20.9
G	15.3	26.9
H	25.0	46.9

Fig. 2. Calibration of octene-1 analysis with blends.

centration, causing uncertainty in the placement of baselines. The relationship obtained is

$$\text{wt-}\%\ C_8 = 539\ (A/\text{mil})\ \text{at } 725\ \text{cm}^{-1}$$

with a standard deviation of 0.37 wt-% C_8.

CONCLUSIONS

Butene-1 and octene-1 content of copolymers, terpolymers, or blends can be conveniently measured from pressed film samples by proper calibration of the particular infrared spectrophotometer to be used. The method is applicable to any 1-olefin of four or more carbons, or to butene-1 plus limited concentrations of a higher 1-olefin.

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