Infrared Spectrometry of Polymers
in the Overtone and Combination Regions

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Synopsis

The application of infrared spectrometry in the overtone and combination regions (1.0–2.7 μ wavelengths) for determining chemical groups in polymeric materials was studied. Various groups such as CH_2, NH, and C=O were assigned to spectra of polyethylene, polypropylene, nylon 66, polyisobutylene, polystyrene, polyvinyl acetate, polyvinyl chloride and a polyvinylidene–polyvinyl chloride copolymer. The technique for sample preparation and experimental procedure is given. It is suggested that these spectra assignments in the overtone and combination regions can be used to obtain relative degradation measurements, determine water adsorption, quantitatively measure physical polymer blends, and finally to study polymer reaction kinetics.

Determination of chemical groups in polymeric materials by using infrared spectroscopy has been confined mainly to the fundamental vibration region (2.7–25 μ wavelengths).

Little work has been done in the combination or overtone regions (1.0–2.7 μ wavelengths). This is unfortunate, since certain advantages could be gained by using spectra in these regions. One important advantage would be that many laboratories that are equipped with spectrophotometers that only range up through the combination and overtone regions could carry out meaningful studies of polymer structure. Furthermore, sample preparation could be considerably simplified if the combination and overtone regions were used instead of the fundamental region.

The present investigation was, therefore, undertaken to extend the pioneer work of Glatt and Ellis[1,2] in the area of infrared spectra for polymers in the combination and overtone regions.

Glatt and Ellis, in the course of a study of pleochroism, assigned vibration modes and frequencies of the CH_2, NH, and C=O groups for polyethylene, nylon 66, polyvinyl chloride, polyvinyl alcohol, and polyvinylidene chloride.

The present work considered assignment of CH_2, NH, and C=O groups as well as others for polyethylene, polypropylene, polyisobutylene, nylon 66, polystyrene, polyvinyl acetate, polyvinyl chloride, and a polyvinylidene–polyvinyl chloride copolymer.

| POLYMER | ASSIGNMENT | | REFER-ENCE |
	GROUP	EXPERIMENTAL WAVELENGTH, μ	
NYLON	—CH₂—	1.21	5
	—NH—	1.53, 1.57	1,2
	—CH₂—	1.72, 1.76	2,5
	OH	1.95	2
	—NH—	2.05	2
	C=O	2.18	
	OH	2.18	
	—CH₂—	2.35, 2.49	2
	Free OH	2.75	3
	C=O	2.95	3
	—NH—	3.08	3
	—CH₂—	3.19	
POLYETHYLENE (δ = 0922 g./cc.)	—CH₂—	1.23	2,5
	—CH₂—	1.41	2
	—CH₂—	1.75	2,5
	—CH₂—	2.37, 2.49	2
	Free OH	2.75	3
	C=O	2.97	7
	—CH₃, Vinyl, CH₂ or CH	3.33	6
POLYETHYLENE (δ = 0960 g./cc.)	—CH₂—	1.23	2
	—CH₂—	1.75	2,5
	—CH₂—	2.37, 2.49	2
	Free OH	2.78	3
	C=O	2.98	7
	—CH₂—	3.32	6

Fig. 1. Assignments for nylon and polyethylene.

Sample preparation presented somewhat of a problem in that commonly used solvents were strong absorbers of infrared radiation in the overtone or combination regions.

This difficulty was circumvented by using test samples prepared as films. The technique used was to press its particular resin between polytetrafluoroethylene (Teflon, Du Pont) and FEP (Tedlar, Du Pont) film. The films were formed by using preheated press platens and a pressure of 700 psi.

The only exception was polyisobutylene, which was studied in a carbon tetrachloride solution.

All samples were analyzed with a Beckman DK-2 recording spectrophotometer. Air was used as a reference for the films and carbon tetrachloride for the polyisobutylene solution.

Assignments of frequencies and vibrations of structural groups were made on the following bases: (1) correlating the spectra of the polymers studied with simple aliphatic and aromatic compounds; (2) comparing the test spectra with spectra of polymers published in the literature; (3) relating fundamental vibration frequencies of various structural groups to the frequency position they should occupy as combination and overtone modes.

POLYMER	GROUP	ASSIGNMENT	
		EXPERIMENTAL WAVELENGTH, μ	REFER-ENCE
POLYISOBUTYLENE			
	—CH$_3$	1.20	7
	—CH$_2$—	1.21	7
	—CH$_3$	1.40	7
	—CH$_3$	1.69	7
	—CH$_2$—	1.76	7
	—CH$_3$	2.26	8
	—CH$_2$—	2.31	2
	—CH$_2$—	2.35	2
	—CH$_3$	2.47	
	Free OH	2.75	3
	CH$_3$,CH$_2$OR CH	3.08, 3.11, 3.32	6
POLYPROPYLENE			
	—CH$_3$	1.20	5
	—CH$_3$	1.40	5
	—CH$_3$	1.70	5
	—CH$_2$—	1.75	2,5
	—CH$_3$	2.27	8
	—CH$_2$—	2.31	2
	—CH$_2$—	2.40	2
	—CH$_3$	2.47	
	Free OH	2.75	3
	HOO—	2.92	7,9
	CH$_3$, CH$_2$ or CH	3.14, 3.35	6

Fig. 2. Assignments for polyisobutylene and polypropylene.

POLYMER	GROUP	ASSIGNMENT	
		EXPERIMENTAL WAVELENGTH, μ	REFER-ENCE
POLYSTYRENE			
	=CH—arom	1.15	5
	=CH—arom	1.65	5
	—CH$_2$—	1.75	5
	=CH—arom	2.18	8
	—CH$_2$—	2.31	2
	=CH—arom	2.47	8
	Free OH	2.75	10
	HOO—	2.90	10
	=CH—arom or CH	3.25	11
POLYVINYL CHLORIDE			
	—CH$_2$—	1.20	2
	—CH$_2$—	1.41	5
	—CH$_2$—	1.76	2
	—CH$_2$—	2.30, 2.49	2
	Free OH	2.75	3
	Vinyl, CH$_2$ or CH	2.78, 3.35	6

Fig. 3. Assignments for polystyrene and polyvinyl chloride.

The experimental data and assignments are shown in Figures 1–4. Reference numbers for assignments are indicated.

These data should be useful for fundamental studies of polymer structure. For example, a measurement of the hydroperoxide peak (indicated

for polypropylene, polystyrene and the polyvinylidene chloride–polyvinyl chloride copolymer) could be used for relative degradation measurements. Furthermore, the OH group peak shown for several of the samples could

POLYMER	GROUP	ASSIGNMENT EXPERIMENTAL WAVELENGTH, μ	REFER-ENCE
POLYVINYLIDENE CHLORIDE— VINYL CHLORIDE			
	—CH₂—	1.69, 1.75	2,5
	—CH₂—	2.29, 2.39	2
	Free OH	2.75	8
	HOO—	2.89	9
	Vinyl, CH₂ or CH	3.01, 3.33	6
POLYVINYL ACETATE			
	—CH₃	1.19	5
	—CH₃	1.68	5
	—CH₂—	1.75	5
	C=O	1.91	4
	C=O + OH	2.12	
	—CH₃	2.25	8
	—CH₂—	2.33	2
	—CH₂—	2.49	2
	Free OH	2.75	3
	Bonded OH	2.83	3
	C=O	2.90	4
	Vinyl, CH₃, CH₂ or CH	3.10, 3.32	3

Fig. 4. Assignments for polyvinylidene chloride–vinyl chloride and polyvinyl acetate.

be used as an indicator of the amount of water adsorbed. The near infrared spectra could be also used for quantitative measurement of physical mixtures or blends and copolymers. Finally, the reaction kinetics of certain polymeric systems could be studied.

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Résumé

On a étudié l'application de la spectrométrie infra-rouge dans les régions de recoure-ment et de combinaison (longueurs d'ondes de 1.0 à 2.7 μ), dans le but de déterminer les groupements chimiques de matériaux polymériques. On détermine plusieurs groupe-ments, comme par exemple CH_2, NH et C=O, dans les spectres du polyéthylène, du polypropylène, du nylon 66, du polyisobutylène, de l'acétate de polyvinyle, du chlorure de polyvinyle et du copolymère polyvinylidène-chlorure de polyvinyle. La technique de la préparation des échantillons et les procédés expérimentaux sont décrits. On suggère que ces attributions spectrales dans les régions de recouvrement et de combinaison peuvent servir à des mesures de dégradations relatives à la détermination de l'adsorption d'eau, des mesures physiques quantitatives sur des mélanges polymériques et finalement à l'étude de la cinétique des réactions polymériques.

Zusammenfassung

Es wurde die Verwendbarkeit der Infrarotspektroskopie in den Oberton- und Kom-binationsbereichen (Wellenlänge 1,0 bis 2,7 Mikron) zur Bestimmung chemischer Grup-pen in polymeren Stoffen untersucht. In den Spektren von Polyäthylen, Polypropylen, Nylon-66, Polyisobutylen, Polystyrol, Polyvinylacetat, Polyvinylchlorid und eines Polyvinyliden-Polyvinylchlorid-Copolymeren konnten verschiedene Gruppen wie CH_2, NH und C=O zugeordnet werden. Die Herstellung der Proben und die experimentelle Durchführung der Messungen werden beschrieben. Man nimmt an, dass diese Spek-trenzuordnung in den Oberton- und Kombinationsbereichen zur Messung des relativen Abbaues, zur Bestimmung der Wasseradsorption, zur quantitativen Bestimmung physikalischer Polymermischungen und zur Untersuchung der Polymerisationskinetic verwendet werden kann.