

## The Near-Infrared Spectra of Polymers

ELBERT W. CRANDALL and ASHVIN N. JAGTAP, *Kansas State College of Pittsburg, Pittsburg, Kansas 66762*

### Synopsis

A series of step reaction polymers have been prepared and studied as melt films or in solution in the overtone region and the combination region of the near-IR. Systems containing aryl rings show bands in the 2.13- to 2.16- $\mu\text{m}$  region which are not observed in those systems not having aryl rings. Polyester, polyamide, and urea-formaldehyde polymers show carbonyl, hydroxyl, and N—H overtones. Polyurethanes show only the intense band of N—H, in the 2.0- to 2.1- $\mu\text{m}$  region. Urea-formaldehyde and polyamides show this same band. Relative band intensities were compared to the first overtone of C—H which appears at 1.67–1.72  $\mu\text{m}$ . In this way, polymers can be compared in a quantitative manner, both with respect to reaction conditions and effect of heat curing.

### INTRODUCTION

In a recent study in our laboratories, we found that the near-infrared region was very useful in studying a series of polyamic acids.<sup>1</sup> We were able to identify certain overtones of aryl N—H, amide N—H, C—H, and carbonyl bands which proved useful in following the course of polymerization, both the amidization and imidization processes. The process was made more useful by comparing the intensity of various bands with the C—H stretch band whose fundamental vibration lies at 3.3–3.5  $\mu\text{m}$  in the middle-IR and the first overtone appears at 1.7  $\mu\text{m}$  in the near-IR. In this way, by observing the appearance and disappearance of certain overtone bands, the polymerization could be followed in a quantitative manner.

There has been little work done on the near IR spectra of step reaction polymers. Foster et al.<sup>2</sup> looked at various C—H overtones in several vinyl polymers and N—H in nylon. Miller and Willis<sup>3</sup> have used the 2- $\mu\text{m}$  combination region while Goddu and Delker<sup>4</sup> used the 1.65- $\mu\text{m}$  and 2.20- $\mu\text{m}$  bands to follow the terminal epoxy groups in epoxy resins. Glatt and Ellis<sup>5</sup> used polarized near-IR to study pleochroism of some polymers. The presence of hydroxyl content was measured in the near-IR by Hilton,<sup>6</sup> Burns and Muraca,<sup>7</sup> and Miller and Willis.<sup>8</sup>

Because of the success in using near-IR on polyamic acid resins, we have determined the near-IR spectra of a series of step reaction and addition polymers with the expectation that these spectra may be useful in polymer identification and in following polymerization processes. Accordingly, we have prepared anionic polystyrene, a TDI-ethylene glycol polyurethane, nylon 66 from adipic acid and hexamethylenediamine, polyesters from phthalic anhydride and ethylene

glycol, phthalic anhydride and glycerol and adipic acid and ethylene glycol, a phenol-formaldehyde resin, and a urea-formaldehyde resin. Polyethylene, a caprolactone polyester (Niax), and a TDI-polypropylene glycol prepolymer from commercial sources were used.

## EXPERIMENTAL

Sample preparation for use in the near-IR involved melting the polymer and pressing between glass plates to give a transparent film. Nylon did not form a clear film; accordingly, the spectrum of this polymer was obtained in a solution of hexafluoropropanol-2 run against pure hexafluoropropanol-2.

All spectra were run on a Beckman Model DK-2A recording spectrophotometer.

A description of the polymers, prepolymers, and resins used in this study are described below. All polymers were prepared according to methods given in Sorenson and Campbell.<sup>9</sup>

### Samples

1. Polyethylene beads from a commercial source were used, mp 110–113°.
2. Anionic polystyrene was prepared from 10 ml styrene, 50 mg sodium naphthalene<sup>9</sup> catalyst, and 50 ml bis(2-methoxyethyl) ether reacted under nitrogen at -70°C; mp 110–115°;  $\eta_{inh}$  in 0.4% toluene 0.85;  $M_w$  by gel permeation = 12,650.
3. A polyester prepolymer was prepared by reacting dimethyl phthalate (0.08 mole) and ethylene glycol (0.19 mole) in the presence of calcium acetate dihydrate (0.025 g) and 0.006 g antimony trioxide. The reaction was carried out at 197°C for 2 hr. The material was used without further polymerization. The product had a mp 50–53°, a hydroxyl number of 147, acid number 4.5, and  $M_w$  of 769.
4. A polyester was prepared from phthalic anhydride (0.5 mole) and glycerol (0.5 mole). The product had an acid number of 5.1, OH number 186, and  $M_w$  = 588.
5. A sample of polycaprolactone from Union Carbide Corp. (Niax D-510) had a  $M_w$  of 530.
6. A urea-formaldehyde resin prepared from 37% formaldehyde (1.6 moles) and urea (1.0 mole) gave a gel which gave an inherent viscosity (0.4% formic acid) of 0.32.
7. Nylon 66 prepared from 0.013 mole adipoyl chloride and 0.037 mole hexamethylenediamine melted at 240–245° and had an inherent viscosity of 0.46 (0.5% *m*-cresol).
8. A hydroxy-terminated polyurethane was prepared from ethylene glycol (0.5 mole) and 2,4-toluene diisocyanate (0.3 mole). A gel was obtained which showed no free isocyanate in the middle-IR.
9. Sample 9 is an isocyanate-terminated polyurethane from TDI and polypropylene glycol,  $M_w$  = 600, obtained from Allied Chemical.
10. Sample 10 is a typical Novalak prepared from 1.38 moles phenol and 1.14 mole aq. 37% formaldehyde.
11. Sample 11 is a typical resol prepared from 1.5 mole formaldehyde and 1 mole phenol.

## DISCUSSION

All of the polymers studied show the first overtone of the 3.3–3.5  $\mu\text{m}$  C—H stretch of the middle IR in the 1.67  $\mu\text{m}$  to 1.70  $\mu\text{m}$  region of the near-IR. Because this band is characteristic of all compounds containing carbon and hydrogen, we have used this band as an internal standard and measured other band intensities against it, as described by Henniker.<sup>10</sup> The results are shown in Table I.

Polymers containing aryl rings all show a doublet in the 2.13- to 2.16- $\mu\text{m}$  region. Goddu and Delker<sup>11</sup> and Foster, Row, and Griskey<sup>2</sup> assign these bands to aryl C—H. They could also be due to C=C stretching of the aryl ring. However, Wheeler<sup>12</sup> indicates the C=C fundamental gives a very weak overtone below 2  $\mu\text{m}$ . Bands above 2  $\mu\text{m}$  have been considered to be due to combinations of bond vibrations.<sup>12</sup> Benzene shows bands at 2.15 and 2.2  $\mu\text{m}$  which are of the same intensity as the overtone of the 3.4  $\mu\text{m}$  band found at 1.7  $\mu\text{m}$ . Whatever the source of these bands, they are present in all polymers containing aryl rings and absent in polymers containing no aryl rings, i.e., polyethylene, the polyamide from adipic acid and hexamethylenediamine, and urea-formaldehyde polymers.

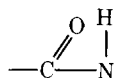
Polymers which contain alkyl chains show three intense bands in the 2.30- to 2.50- $\mu\text{m}$  region. Several workers<sup>1,5,11</sup> have assigned bands in this region to —CH<sub>2</sub>— and —CH<sub>3</sub> overtones. Miller and Willis<sup>3,8</sup> believe these are combination bands of alkyl C—H frequencies.

The presence and intensities of these bands vary from system to system, but are more intense in those systems containing alkyl chains, except for polyamide. In those systems containing a high proportion of aryl rings to alkyl chains, i.e., polystyrene and phenol-formaldehyde, the bands in the 2.30- to 2.35- $\mu\text{m}$  region are less intense than the 2.14- $\mu\text{m}$  aryl band.

Polyesters show the expected<sup>12</sup> carbonyl second overtone at 1.91  $\mu\text{m}$  both for phthalic anhydride and adipic acid esters with intensities varying from 0.2 to 0.3 compared to the C—H stretch band. Terminal hydroxyl groups show up at 1.42  $\mu\text{m}$ . The intensity of this band is dependent on the molar ratios of acid to alcohol. A period of heating causes a decrease in the intensity of this band, as well as a decrease in the intensity of the carbonyl band.

Phenol-formaldehyde resins prepared with no heating or curing time show the presence of unreacted formaldehyde as indicated by the presence of the carbonyl band. A period of heating causes this band to disappear with a corresponding increase in the intensity of the hydroxy band at 1.43  $\mu\text{m}$ . Base-catalyzed (resol) and acid-catalyzed phenol-formaldehyde (Novolak) differ in that the former shows a much higher hydroxyl content.

Those polymers containing the



grouping which is found in polyurethane, urea-formaldehyde, and polyamide resins and polymers should show carbonyl and N—H overtones. The polyamide prepared from adipic acid and hexamethylenediamine (nylon 66) shows the N—H overtone at 1.42  $\mu\text{m}$ , the carbonyl overtone at 1.94  $\mu\text{m}$ , and an intense band at 2.11  $\mu\text{m}$ . A urea-formaldehyde resin shows O—H at 1.34  $\mu\text{m}$ , carbonyl at 1.90  $\mu\text{m}$ , and a strong band at 2.03  $\mu\text{m}$ . These compare favorably to acetamide as a model compound, which has bands at 1.52, 1.96, and 2.16  $\mu\text{m}$ , the latter two

Near-Infrared Bands of Polymers<sup>a</sup>

Polymer	C—H Stretching, $\mu\text{m}$		O—H Stretching $\mu\text{m}$		C=O $\mu\text{m}$		Amide and amine N—H $\mu\text{m}$		Aryl C—H $\mu\text{m}$	
	$\mu\text{m}$	R.I.	$\mu\text{m}$	R.I.	$\mu\text{m}$	R.I.	$\mu\text{m}$	R.I.	$\mu\text{m}$	R.I.
ethylene	1.70									
styrene	1.66								2.13 2.16	1.27 1.27
esters										
thalic anhydride + ethylene glycol	1.66	1.42	0.26	1.91	0.30				2.14 2.16	1.52 0.25
thalic anhydride + ethylene glycol cured at 150° for 13 hr	1.66	1.42	0.23	1.91	0.09				2.14 2.16	1.44 0.50
thalic anhydride + glycerol	1.65	1.41	0.50	1.91	0.69				2.13	0.94
thalic anhydride + glycerol cured at 150° for 13 hr	1.65	1.41	0.33	1.91	0.20				2.16 2.13 2.16	0.20 0.87 0.31

5	Polycaprolactone (Niax D-510) cured at 150° for 13 hr	1.69	1.35	0.58	1.89	0.35					2.29	2.70
6	Urea-formaldehyde resin	1.67	1.34	1.0	1.90	1.33	2.03	1.50			2.46	0.71
6a	Urea-formaldehyde resin-cured at 90° for ½ hr	1.67			1.91	2.85	1.46	0.28			2.24	6.66
	Polyamide (Nylon 66)						2.03	1.67			2.49	4.00
7	Adipic acid + hexamethylenediamine Polyurethanes	1.72			1.94	4.00	1.42	5.80			2.29	7.00
		1.76	1.39				2.11	5.80				
8	TDI + ethylene glycol	1.67	1.42	0.70			1.47	1.10	2.14	0.75	2.26	8.30
8a	TDI + ethylene glycol cured at 150° for 13 hr	1.67	1.42	0.04			2.05	3.07			2.31	5.25
9	TDI-polypropylene glycol (Allied Chemical)	1.65	1.35	0.33	1.90	0.25	1.47	0.25	2.12	0.5	2.49	7.70
9a	TDI + polypropylene glycol-cured at 135° for 2 hr	1.69	1.37	0.20	1.90	0.17	2.04	0.83	2.14	1.0	2.26	10.71
10	Phenol + formaldehyde acid catalyzed (Novalac), no cure time	1.67	1.43	0.43	1.90	1.14	1.47	0.20	2.16	0.7	2.31	6.71
10a	Phenol + formaldehyde acid catalyzed, cured at 150° 13 hr	1.67	1.43	0.55	1.90	0	2.04	1.33	2.14	3.86	2.30	6.0
11	Phenol + formaldehyde base catalyzed (resol)	1.67	1.43	1.29	1.90	2.86			2.16	4.71	2.46	3.29
									2.14	4.7	2.35	1.14
									2.16	4.73	2.46	2.09
									2.14	4.71	2.35	2.00
									2.16	4.42	2.46	2.14

a R.I. = Relative intensity.

being very strong compared to the 1.70- $\mu\text{m}$  C—H band. On heat curing of the urea-formaldehyde resin, several changes occur. The O—H band disappears, and an N—H band appears at 1.46  $\mu\text{m}$  which is not present in the uncured resin. In addition, a large increase occurs in the carbonyl band, while the band at 2.03  $\mu\text{m}$ , which we have associated with the amide grouping, increased slightly. Unlike any of the other systems, the combination band at 2.24  $\mu\text{m}$  of urea-formaldehyde shows a sharp increase on heat curing.

The polyurethane from TDI and ethylene glycol appears to differ from this pattern. This polymer shows the N—H band at 1.47  $\mu\text{m}$ , but a single high-intensity band at 2.05  $\mu\text{m}$ , and no band in the 1.9- $\mu\text{m}$  region. A lower intensity band at 2.14  $\mu\text{m}$  is probably due to the TDI-aryl system. Glatt and Ellis<sup>5</sup> and Foster et al.<sup>2</sup> have assigned a band at 2.05 which they have observed in nylon to N—H of the amide grouping. This band in TDI-ethylene glycol polyurethane undergoes a large increase on heat curing, while the O—H band at 1.42  $\mu\text{m}$  decreases sharply. The polyurethane derived from TDI and polypropylene glycol does show a very weak carbonyl overtone. This system, like the TDI-ethylene glycol system, shows a strong overtone at 2.04  $\mu\text{m}$  which increases on heat curing.

The results from this study indicate that the near-infrared region could be used to identify resins and polymers and give some indication of the state of cure. The overtone bands of carbonyl, amino and amide N—H, and alcoholic O—H are observed along with alkyl and aryl C—H overtones. Of particular interest are the aryl C—H bands which are present for polymers having many aryl units in the polymer backbone and are absent in all alkyl polymers. Bands associated with terminal functional groups tend to decrease on heat curing, while those associated with linkages in the polymer backbone tend to increase or remain constant. Bands in the combination region (2.3–2.5  $\mu\text{m}$ ) vary in number and intensity from system to system and further study of this region may prove to be valuable.

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