

The Near Infrared Spectra of Some Polyamic Acid Resins

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Synopsis

The absorption spectra of a series of polyamic acids prepared using various reaction conditions were studied using the ultraviolet (UV), visible, and near-infrared (IR) ranges. The near-IR proved most valuable; the amidization and imidization processes could be followed by observing the change of intensities of the 1950-nm combination amine band and a band at 2300 nm assumed to be a function of the amide group.

INTRODUCTION

In conjunction with a study carried out at The Bendix Corporation, Kansas City Division, and the Kansas State College of Pittsburg on a series of polyamic acids and polyimides, it was felt that it would be valuable to follow the imidization processes of these systems.¹ Therefore, the ultraviolet (UV), visible, and near-infrared (IR) spectra of polyamic acids prepared under various reaction conditions were studied. The study was an attempt to correlate the effects of concentration and reaction temperature with the positions of absorption bands in the UV and visible regions and the intensities of C-H, amine, and amide overtones in the near-IR region.

The polyamic acids of interest are products of the reaction of diamines with tetrabasic acid dianhydrides in a polar solvent such as *N,N*-dimethylacetamide. The system reported here involved the reaction of bis(4-aminophenyl)methane with 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride. The first step in the reaction, amidization, occurs under very mild conditions in aprotic solvents to form the polyamic acid.^{1,2} Imidization is reported to occur on heating to temperatures of 120° to 140°C.

EXPERIMENTAL

The polyamic acids were prepared in equipment described in an earlier report.¹ However, for the sake of continuity, a typical procedure for the preparation of a 23.1% solute resin system is given here.

3,3',4,4'-Benzophenonetetracarboxylic acid dianhydride (BTDA), 162.70 pbw; bis(4-aminophenyl)methane (MDA), 100.10 pbw; *N,N*-dimethylacetamide (DMAc), 612.95 pbw. The BTDA and MDA were thoroughly blended

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together. After stabilizing 90% of the DMAc at $40 \pm 2^\circ\text{C}$ in a nitrogen atmosphere, the blended components were added to the solvent at a rate of 5.0 ± 1.0 g/min. The temperature of the reaction mixture was maintained at $40 \pm 2^\circ\text{C}$ throughout the synthesis. The reaction temperature was held at $40 \pm 2^\circ\text{C}$ for an additional 20.0 min after all reactants and the remaining 10% of the solvent were added. The reaction mixture was allowed to cool to room temperature and was then stored in a sealed glass jar.

Spectra were determined approximately one month after preparation of the resins and again after four months storage at 2°C . Measurements in the ultraviolet region were carried out using 1.0- to 1.5-mg samples dissolved in 1.0-ml N,N-dimethylacetamide diluted to 25 ml with propanol-2. Absorption in the visible region was measured using concentrations of 2.5 mg/ml in N,N-dimethylacetamide. UV and visible data were obtained using a Bausch and Lomb Model 505 spectrophotometer.

A Beckman Model DK-2A recording spectrophotometer was used to cover the near-IR region, 1000 to 2850 nm. Samples were run as films between potassium bromide plates.

DISCUSSION

The Ultraviolet and Visible Regions

A study of absorption in the ultraviolet region was difficult to carry out because of the insolubility of the polyamic acids in solvents used for UV measurements. Spectra were obtained by dissolving the polymers in a small amount of N,N-dimethylacetamide and diluting with propanol-2. All of the systems showed a high-intensity band in the 210- to 220-nm region which is probably the 1L_a benzene band.³ In addition, a very low-intensity, very broad band appeared sometimes in the 250- to 270-nm region and sometimes at 320 to 340 nm. Interpretation of the UV data was considered to be of questionable value because the high-intensity, short-wavelength band lies below the UV cutoff point for most solvents, and the longer-wavelength bands are so broad that precise λ_{max} values could not be obtained.

TABLE I
Summary of Visible Wavelength Spectral Analyses for Polyamic Acid Resins

Sample no.	Maximum wavelength, nm	Reaction temp., $^\circ\text{C}$	Solute, %
1	785	10	23.1
2	786	25	23.1
3	789	40	23.1
4	795	60	23.1
5	791	80	23.1
6	789	100	23.1
12	795	40	6.6
13	791	40	10.0
14	778	40	20.0
15	...	40	30.0
16	...	40	40.0

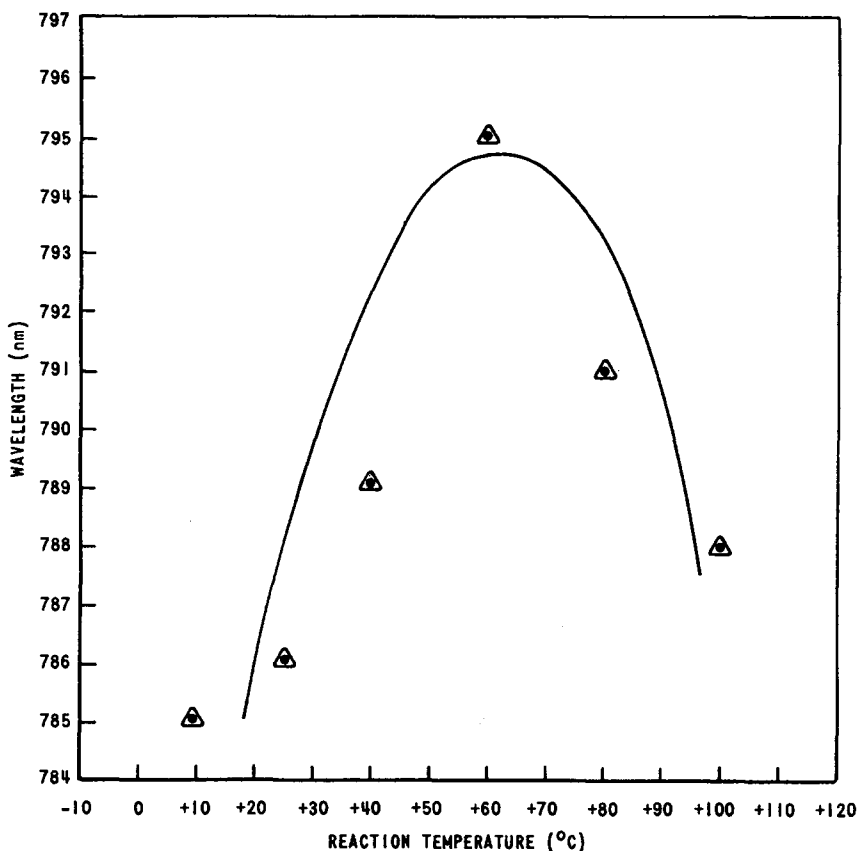


Fig. 1. Visible wavelength absorption maximum as a function of reaction temperature.

Studies of visible wavelength absorption, carried out using the *N,N*-dimethylacetamide diluent, showed a single absorption in the 770- to 790-nm region (Table I). There appears to be a correlation between the wavelengths of absorption of samples 1 through 6 and reaction temperature (Fig. 1). The wavelength shifts to the red as particle size increases to a maximum at 60°C. In addition, as shown in Figure 2, some correlation appears to exist (samples 12 through 14) between the visible wavelength absorption and the concentration of the sample. These relationships suggest that both the reaction temperature employed in the preparation of polyamic acid resins and the per cent solute of such material can be monitored using spectroscopy techniques in the visible wavelength region.

The Near-Infrared Region

The near-IR region, 1000 to 2850 nm, proved to be the most fruitful area of study (Table II). All of the polyamic acid systems showed the same bands, but these bands varied in intensity from system to system. Starting with shorter wavelengths, all the polyamic acids studied show the first overtone of the 2.86- μm stretching band of amine N—H at 1400 nm. This band is usually very weak.⁴ The first overtone of the 3.3- to 3.5- μm C—H stretching band lies at 1700 nm and is a medium to strong band.⁵ In addition, a weak band at 2160 nm is probably the second overtone of the C—H bending vibration at 6.9 μm in the middle IR.

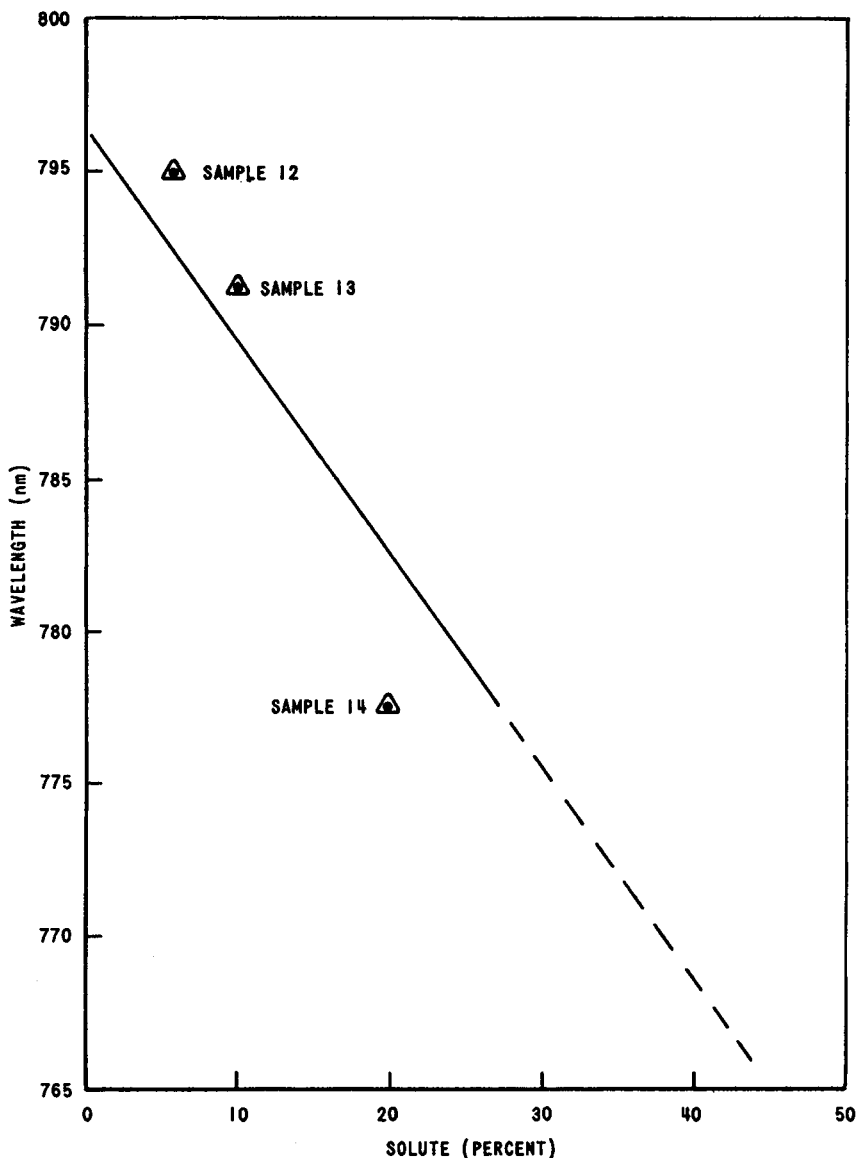


Fig. 2. Visible wavelength absorption maximum as a function of per cent solute.

A band at 1950 nm could be either the first carbonyl overtone or the combination stretching, bending band of aromatic N—H.^{4,6} Acetone shows a strong band at 1980 nm and acetophenone a weaker band at 1920 nm, but benzophenone shows nothing in the 1900- to 2000-nm region. However, aniline shows an intense band at 1975 nm; therefore, the 1950-nm band has been assigned to the stretching and bending overtones of unreacted amino groups.⁷ This band tends to decrease when the resins are heated, suggesting that further reaction is occurring.

A very intense band occurs at 2300 nm in every system. No reference to this band was found in the literature. Benzanilide shows a medium band at 2040 nm which could be the second overtone of the 6.14- μ m carbonyl stretching vibration

TABLE II
Infrared Analysis of Polyamic Acid Resins

Sample no.	Solute, %	Reaction temp., °C	Storage temp., °C ^a	Band ratios			Viscosity at 25°C, cps
				Amide/C-H	Amine/C-H	Amide/Amine	
1	23.1	10	27	6.16	0.72	8.54	127.5
				5.93 ^a	0.73 ^a	8.09 ^b	125
2	23.1	25	27	6.16	0.68	9.00	264
				6.22	0.72	8.61	400
3	23.1	40	27	6.33	0.83	7.6	252
				5.66	0.58	9.71	400
4	23.1	60	27	7.0	1.50	4.67	105
				6.4	0.73	8.72	168
5	23.1	80	27	5.84	0.71	8.23	159
				6.13	0.53	11.50	
6	23.1	100	27	6.91	0.54	12.76	134
				5.46	0.60	9.1	265
7	23.1	40	27	6.13	0.97	6.32	61
				5.50	0.75	7.34	75
8	23.1	40	27	6.07	0.69	8.82	2,860
				6.00	0.43	14.00	2,960
9	23.1	40	27	7.00	0.75	9.34	1,000
				4.66	1.07	4.38	1,020
9A	film heated for 3 hr at 250°C			0.19	0.75	0.22	
9B	film heated for 3 hr at 50°C			0.23	0.77	0.30	
10	30	40	5	6.20	0.44	14.15	33,250
10A	film heated for 12 hr at 150°C			0.21	0.83	2.5	
11	30	40	5	6.3	1.2	5.25	
				5.74	0.47	12.3	
12	6	40	27	5.00	1.00	5.00	4.7
				0.17	0.85	0.20	4.6
12A	film at R.T. for 3 days			3.11	0.56	5.60	
13	10	40	27	6.14	1.14	5.38	5.9
				0.56	0.69	0.81	5.9
14	20	40	27	6.22	1.04	6.00	48
				6.33	0.50	12.67	45
14A	film at R.T. for 3 days			4.72	0.64	7.43	
14B	film heated for 12 hr at 50°C			4.26	0.41	10.35	
14C	film heated for 12 hr at 70°C			1.50	0.36	4.13	
15	30	40	27	6.92	2.07	3.0	1,650
				3.85	1.15	3.34	1,450
16	40	40	27	4.54	1.82	2.5	50,000
				0.44	1.33	0.33	...
17	25	40	5	5.85	1.21	4.82	5,400
				5.10	1.00	5.10	4,900

^a Prior to testing schedule.

^b After 4 months of storage at 2°C.

or the second overtone of the $6.6\text{-}\mu\text{m}$ N—H bend of secondary amides. Middle-IR spectra of polyamic acids show a strong band at $6.14\ \mu\text{m}$ and a medium band at $6.6\ \mu\text{m}$. The 2300-nm band has, therefore, been interpreted as being due to either the second overtone of the carbonyl or the N—H of secondary amides of the polyamic acid. Model compounds prepared from aniline and BTDA show a band at $2040\ \text{nm}$. Upon heating of the samples to temperatures above 50°C , the 2300-nm band tends to disappear (samples 10 and 15). In some cases, gelling occurred as the sample was heated, and the 2300-nm band also decreases in these cases.

In order to follow the polymerization process using the near-IR data, the changes in band intensities were followed using the technique of Henniker.⁸ The first overtone of the C—H band at $1700\ \text{nm}$ was chosen as the internal standard. Baselines were chosen that remained constant from system to system, and the 2300-nm amide band and the 1950-nm amine band were compared to the C—H band (Table II). In order to determine the effects of storage, near-IR absorption values were determined four months after the first measurements. These values are given just below the original determinations for each sample in Table II.

The amide/C—H, amine/C—H, and amide/amine ratios can be used as a measure of the degree of polymerization and the amount of imidization. For example, a large amine/C—H ratio indicates a relatively low molecular weight polymer, while a low amide/amine ratio indicates a higher average molecular weight.

A study of Table II shows that reaction parameters determine particle size, chain length, and storage life. The effects of temperature can be seen in samples 1 through 6. For reaction temperatures of 10° , 25° , and 40°C , the ratios remain fairly constant and indicate a long chain. At 60°C , the lower amine/C—H and amide/amine ratios suggest shorter chains are forming. At 80° and 100°C , decreasing amine/C—H and increasing amide/amine ratios indicate increasing chain lengths.

In a series of reactions involving variations in concentration (samples 13 through 17), little change is observed up through a total concentration of 20%. At concentrations of 30% and 40%, a decrease occurs in the amide/C—H and amide/amine ratios, with a corresponding increase in the amine/C—H ratio, suggesting the formation of relatively short chains. It is interesting to note that three systems having concentrations of 28% or greater gelled after the first determination. These three (samples 15, 16, and 17) had amide/amine ratios of 3.0 or less and high amine/C—H ratios. Since these samples were stored originally at 27°C , it is possible some imidization was occurring even at this low temperature.

After four months of storage at 2°C , it was evident that some changes occurred in the resins. In several cases, chain lengthening processes (amidization) apparently continued, and in at least one case (sample 9) hydrolysis appeared to occur. A large change in the amide/amine ratio with a slight decrease in the amine/C—H ratio suggests imidization. This occurred (samples 12, 13, 16, and 17) where the total concentrations were 6%, 10%, 30%, and 40%, respectively. Sample 14, in which the concentration was 20%, showed no change after storage. The effect of temperature on the imidization process was seen when samples 9, 10, and 14 were heated as films at temperatures of 25° , 50° , 70° , and 150°C ; both the 2300-nm amide band and the 1950-nm amine band decreased in intensity, with the 2300-nm band being most affected. When this occurs, other bands such

as the 2160-nm and 2480-nm C—H bands of benzene and the 1920-nm C=O band begin to appear.

The near-IR data indicate that reaction temperatures up to 60°C cause the formation of long chains. Chain length decreases at 60°C and increases again at 80°C. The effects of concentration are similar, the longer chains being formed at 20% concentration. Samples with very low and very high concentrations show the greatest change after storage, and samples stored at temperatures of 5°C show less change over a four month period than do samples stored at 27°C.

CONCLUSIONS

The results of this study indicate that the visible and the near-IR regions of the electromagnetic spectrum are useful in the spectrographic characterization of polyamic acids. It was found that the visible absorption maxima observed for the various resins studied varied directly with the reaction temperature employed in the preparation of the resin and indirectly with the per cent solute of the resin. It was also shown that the near-IR spectral region was the most important for characterizing polyamic acid resins. This is due to the attribution to the absorption of the amide N—H group in the polymer of the band appearing at 2300 nm which disappears as the curing progresses and imidization takes place. In addition, it was noted that the UV region was of little value in the spectrographic characterization of the resins studied in this investigation.

Using the near-IR region, the effects of reaction and storage temperatures and of concentration can be observed by comparing the amine and amide overtones against the first C—H overtone. A concentration of approximately 20%, a reaction temperature below 40°C and storage temperatures of 5°C or less appear to give optimum results for the polyamic acid resins studied.

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