Macromolecules 1993, *26*, 6749–6755 **6749**

Morphological Characterization of Bioerodible Polymers. 2. Characterization of Polyanhydrides by Fourier-Transform Infrared Spectroscopy

Edith Mathiowitz,* Mark Kreitz, and Kathleen Pekarek

Division of Biology and Medicine, Brown University, Providence, Rhode Island 02912

Received May 24, 1993; Revised Manuscript Received September 14, 1993®

ABSTRACT: This paper describes the Fourier-transform infrared (FTIR) spectroscopy of a series of polyanhydrides made of the following diacids: sebacic acid (SA); 1,3-bis(*p*-carboxyphenoxy)propane (CPP); 1,6-bis(*p*-carboxyphenoxy)hexane (CPH); (carboxyphenoxy)methane (CPM); fumaric acid (FA); 5-(*p*-carboxyphenoxy)valeric acid (CPV). All the polymers revealed typical anhydride peaks corresponding to aliphatic–aliphatic, aliphatic–aromatic, and aromatic–aromatic diads in the wavenumber range 1820–1710 cm^{-1}. Additional paired peaks corresponding to SA–SA diads were identified in the fingerprint region at 1382, 1360 and 1307, 1286 cm^{-1}. The second pair was assigned to the crystalline regions of the copolymers. This information allows easy identification of bond distribution in a variety of polyanhydrides, and correlates well with information previously presented using nuclear magnetic resonance (NMR) spectroscopy and X-ray powder diffraction.

Introduction

This is the second paper in a series of publications dealing with morphological characterization of polyanhydride copolymers.[1–4] In previous publications, we discussed the NMR[2] as well as X-ray diffraction[1] of polyanhydrides. NMR studies permit determination of the degree of randomness and frequency of specific comonomer sequences. X-ray powder diffraction combined with differential scanning calorimetry (DSC)[1] studies enable the calculation of the degree of crystallinity for a series of polyanhydride copolymers. In future publications, we will address the morphological changes that occur in these polyanhydrides after degradation using scanning electron microscopy (SEM),[3] and a combination of FTIR and DSC.[4] Since one of the methods that we use to characterize the degradation is FTIR, we describe in this paper the analysis of the different characteristic absorption patterns for this series of polyanhydrides made of the following diacids: sebacic acid (SA), fumaric acid (FA), 1,3-bis(*p*-carboxyphenoxy)propane (CPP), 1,6-bis(*p*-carboxyphenoxy)hexane (CPH), bis(*p*-carboxyphenoxy)methane (CPM), and 5-(*p*-carboxyphenoxy)valeric acid (CPV). FTIR is a useful tool as it allows analysis of solid materials which are not soluble in organic solvents, making it a more practical tool to study sequence distribution than NMR.

Experimental Section

Polymer Synthesis. Sebacic acid, fumaric acid, 4-hydroxybenzoic acid, 1,3-dibromopropane, and 5-bromovaleric acid were all purchased from Aldrich Chemicals. The polyanhydrides were synthesized by melt polycondensation of mixed anhydrides of diacids and acetic acid. Poly(sebacic anhydride) (PSA), poly[1,3-bis(*p*-carboxyphenoxy)propane] (PCPP), and their copolymer P(CPP–SA), poly[1,3-bis(*p*-carboxyphenoxy)hexane] (P(CPH)) and its copolymer with sebacic acid anhyride P(CPH–SA), poly(fumaric anhydride) (PFA) and its corresponding copolymer P(FA–SA), poly(*p*-carboxyphenoxy)methane) (PCPM) and copolymer P(CPM–SA), and poly(5-(*p*-carboxyphenoxy)valeric anhydride) (PCPV) were prepared according to the literature.[5,6] All the polyanhydrides were analyzed by GPC and had a weight-average molecular weight ($\bar{M}_{\mathrm{w}}$) between 20 000 and 40 000, except the poly(fumaric-*co*-sebacic) anhydrides which had molecular weights between 5000 and 20 000. NMR studies showed that all the polymers studies were random copolymers with the sequence length distribution determined by the comonomer ratio.[2]

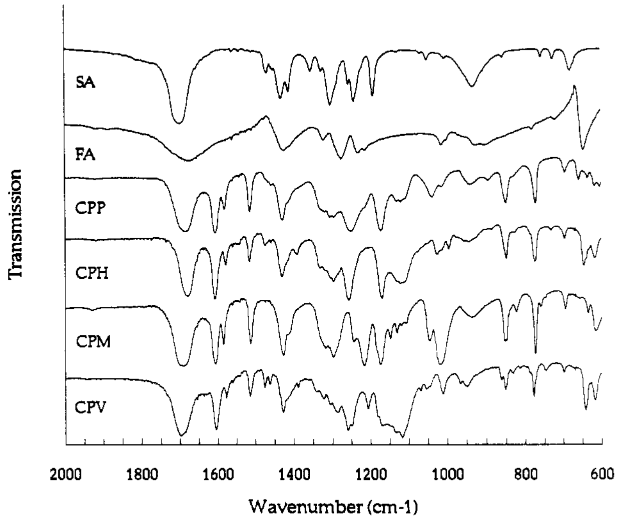


Figure 1. FTIR spectra of the various monomers.

Instrumentation. All FTIR spectra were obtained using a Model 1725 spectrophotometer (Perkin-Elmer). Polymer samples were cast onto NaCl crystals from a solution of polymer in methylene chloride or compressed into pellets with KBr (Aldrich). The molecular weight of the polymers was estimated on a gel permeation chromatography (GPC) system (Perkin-Elmer) consisting of the Series 10 pump and the 3600 data station with the LKB 214-rapid spectral detector at a wavelength of 254 nm. Samples were eluted in alcohol free chloroform through a PL gel 5-mm mixed column (Polymer Laboratories) at a flow rate of 1.0 mL/min and a +23 °C. Molecular weights of polymers were determined relative to polystyrene standards (Polysciences, molecular weight between 500 and 160 000) using CHROM 2 and GPC 4 computer programs (Perkin-Elmer).

Results and Discussion

Characterization of Polymer Microstructure by FTIR. Figure 1 displays the FTIR spectra of the various monomers that were used to prepare the polymers. Note that these are not the prepolymers but the acid form of each monomer. All are characterized by a strong absorp-

---

* To whom all correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts,* November 1, 1993.

0024-9297/93/2226-6749$04.00/0

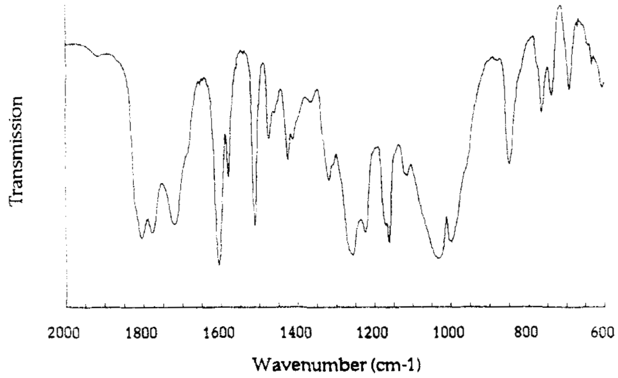


Figure 2. FTIR spectra of PCPV.

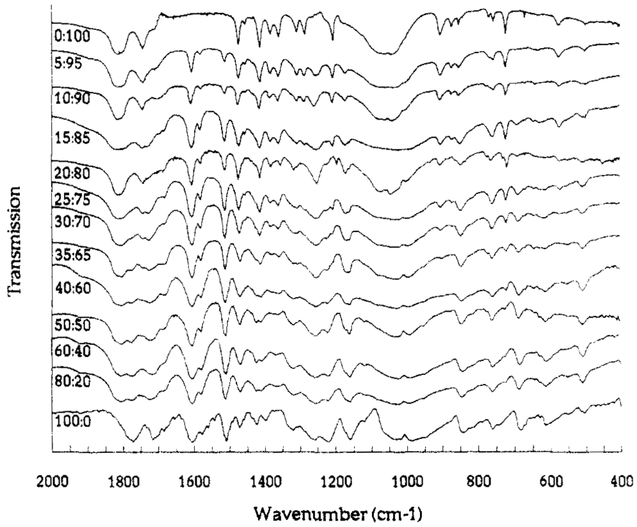


Figure 3. FTIR spectra of the P(CPP–SA) series.

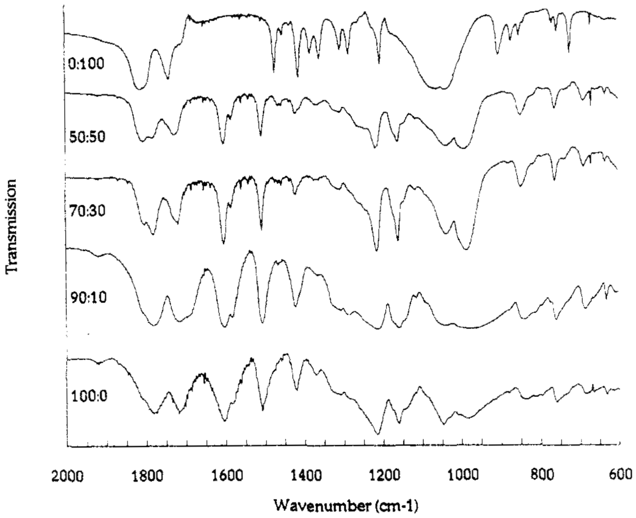


Figure 4. FTIR spectra of the P(CPM–SA) series.

tion due to the carbonyl group of the carboxylic acid near 1700 cm^{-1}. Anhydrides generally display two stretching bands in the carbonyl region, bands from asymmetrical and symmetrical C═O stretching modes, explaining why the anhydride bonds appear in pairs. Saturated noncyclic anhydrides absorb near 1818 and 1750 cm^{-1}.[7] Conjugated noncyclic anhydrides show absorptions near 1775 and 1720 cm^{-1} with the higher frequency band being more intense. Unconjugated straight chain anhydrides absorb near 1047 cm^{-1}. Other strong bands appear in the spectra of anhydrides as a result of C–C(O)–O–C(O)–C stretching vibrations.

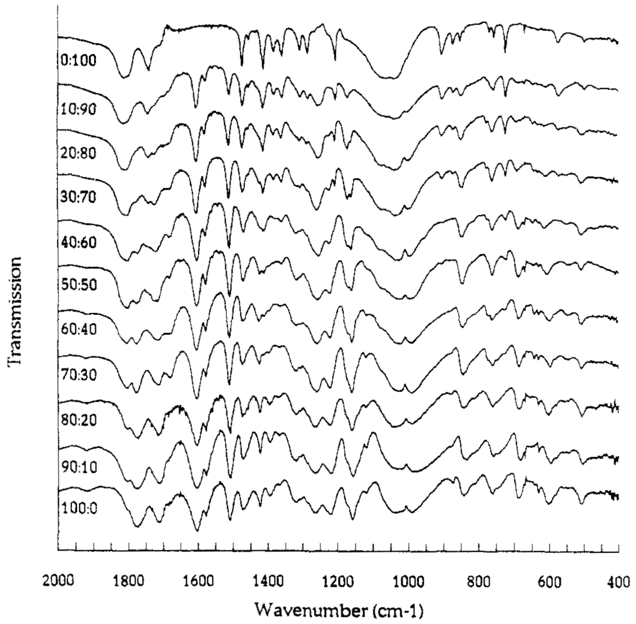


Figure 5. FTIR spectra of the P(CPH–SA) series.

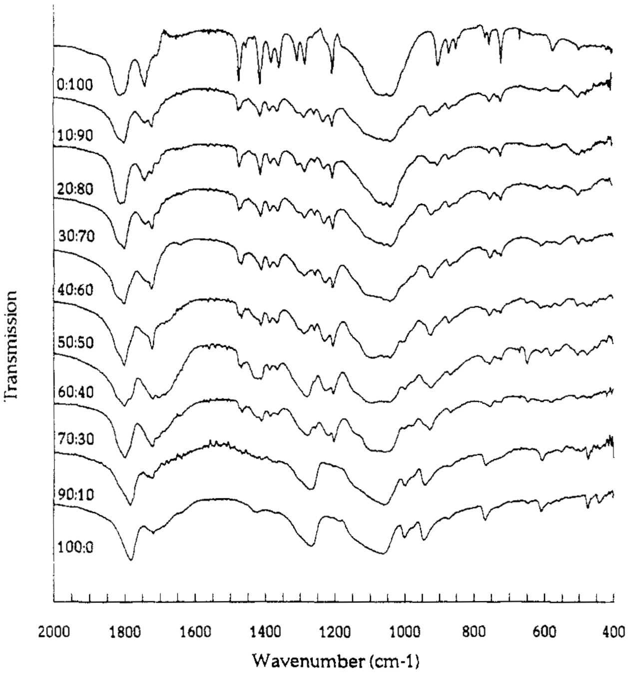


Figure 6. FTIR spectra of the P(FA–SA) series.

Figures 2–6 display the FTIR spectra of the various polyanhydride copolymer series of PCPV, P(CPP–SA), P(CPM–SA), P(CPH–SA), and P(FA–SA), respectively. Table I lists the peak maxima for each of the above series. We expect to see absorption bands which correspond to aliphatic–aliphatic, aromatic–aromatic, and aliphatic–aromatic bonds in each of the copolymers. We have listed the exact location of the important peaks in Table I, but throughout the text we refer only to the general range in which the peaks appear, since the peaks tend to drift 1–2 cm^{-1}. In each group of polyanhydrides, we first studied the spectra of the homopolymers, because by identifying the absorptions in the homopolymers, determination of the origin of the various bands in the copolymers was simplified.

(a) PCPV. Figure 2 displays the spectra of PCPV—a homopolymer made of a monomer containing both aliphatic and aromatic units. The anhydride C═O region is characterized by three main pairs of peaks, with each

Table I[a]

composition	ALI–ALI	ALI–ARO	ARO–ARO	ALI–ALI	ALI–ARO	ARO–ARO						
PSA 100	1813			1741					1383	1359	1305	1286
CPP-SA 5:95	1815			1742			1709	1605	1382	1360	1307	1286
CPP-SA 10:90	1814	1806		1742			1702	1606	1383	1360	1307	1286
CPP-SA 15:85	1814	1810		1744	1731			1605	1383	1360	1307	1286
CPP-SA 20:80	1812	1808		1741	1730		1697	1605	1381	1364	1307	1288
CPP-SA 25:75	1816	1806		1742	1727		1681	1605	1383	1360	1307	
CPP-SA 30:70	1814	1806	1777	1742	1725			1605	1382	1360		
CPP-SA 35:65		1805	1777	1742	1725		1693	1605	1381	1360		
CPP-SA 40:60		1805	1775		1724	1714	1686	1605	1381	1361		
CPP-SA 50:50		1803	1773		1724	1715	1693	1604				
CPP-SA 60:40		1805	1775		1723	1714		1604				
CPP-SA 80:20		1804	1775		1724	1714		1605				
CPP 100			1771			1715	1683	1604				
PSA 100	1813			1741					1383	1359	1305	1286
CPM-SA 50:50		1806	1782		1726			1603				
CPM-SA 70:30		1802	1782			1718		1603			1308	
CPM-SA 90:10			1781			1716		1602			1308	1287
CPM 100			1782			1719		1603			1309	
PSA 100	1813				1741				1383	1359	1305	1286
CPH-SA 10:90	1815		1742					1605	1383	1360	1308	1286
CPH-SA 20:80	1812	1807		1741	1726			1604	1382	1360	1307	1286
CPH-SA 30:70	1813	1806		1741	1725		1706	1605	1382	1360		
CPH-SA 40:60		1805	1773	1741		1717		1605	1381	1361		
CPH-SA 50:50		1806	1773	1738	1724	1717		1605				
CPH-SA 60:40		1806	1777			1715		1604				
CPH-SA 70:30		1803	1777			1713		1605				
CPH-SA 80:20		1803	1773			1715		1605				
CPH-SA 90:10		1804	1773			1711		1604				
PCPH 100			1774			1712		1604				
PSA 100	1813			1741					1383	1359	1307	1285
FA-SA 10:90	1810	1802		1742	1723				1385	1363	1304	1288
FA-SA 20:80	1812	1806		1742	1723				1384	1361	1304	1286
FA-SA 30:70	1811	1802		1742	1723				1386	1363		1287
FA-SA 40:60	1812	1801		1741	1723				1386	1364		1288
FA-SA 50:50		1802			1722				1386	1365		1288
FA-SA 60:40		1802			1721				1387	1364		1279
FA-SA 70:30		1802			1723				1386	1364		1280
FA-SA 90:10			1785			1721			1389			1273
FA 100			1783			1719						1266

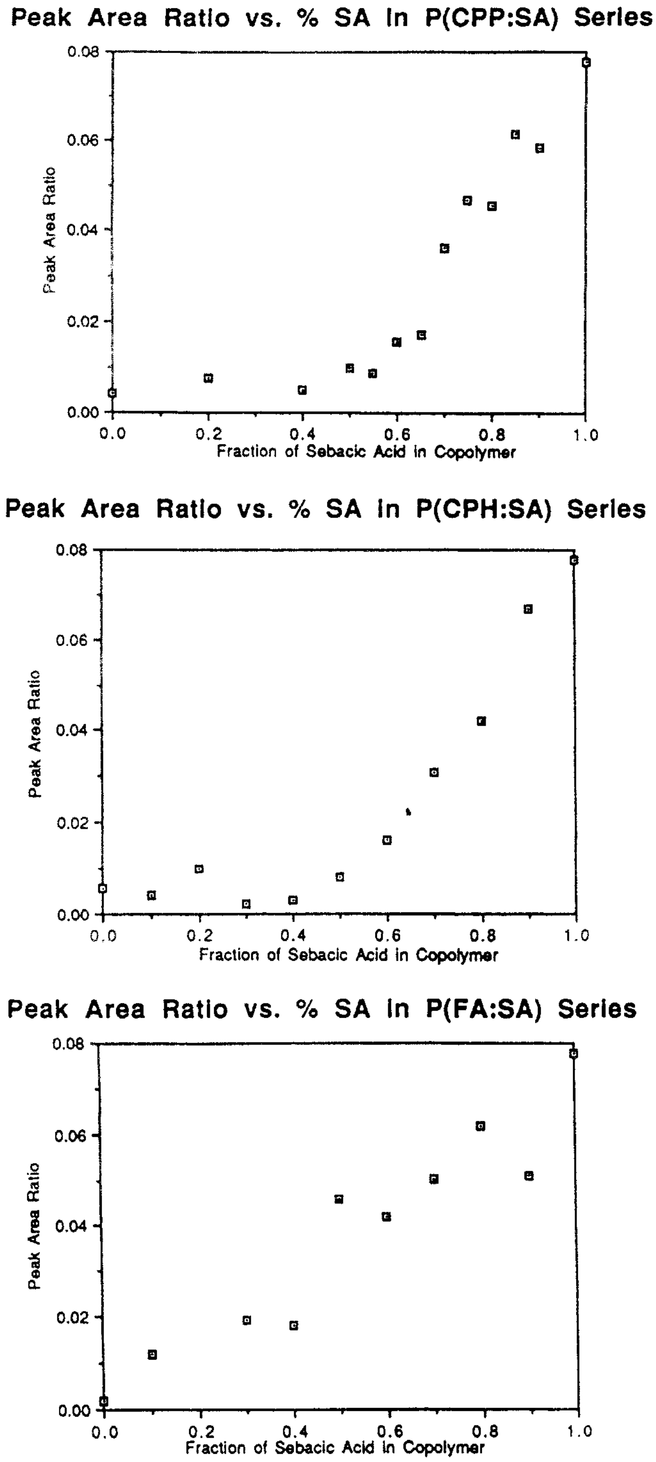
[a] ALI–ALI = aliphatic–aliphatic anhydride bond. ALI–ARO = aliphatic–aromatic anhydride bond (in the case of P(FA–SA), the FA–SA bond). ARO–ARO = aromatic–aromatic anhydride bond (in the case of P(FA–SA), the FA–FA bond).

pair representing one particular type of anhydride bond occurring in the polymer. The aliphatic–aliphatic anhydride bonds absorb at 1820 and 1743 cm^{-1}, the aliphatic–aromatic bonds absorb at 1804 and 1742 cm^{-1}, and the aromatic–aromatic bond absorbs at 1776 and 1719 cm^{-1}. In the first two pairs, the second peak listed appears as a shoulder only.

(b) P(CPP–SA) Series. For the P(CPP–SA) series (Figure 3) we could identify two characteristic anhydride peaks at 1813 and 1741 cm^{-1} in pure PSA polymer, representing the SA–SA diads. For the pure PCPP polymer, the characteristic anhydride peaks appear at 1771 and 1715 cm^{-1}. For the various copolymers made of different CPP–SA ratios we expect absorptions corresponding to the following diads: SA–SA, CPP–CPP, and SA–CPP. In a previous publication[2] we have shown the existence of and calculated the probability of finding these diads in CPP–SA polymers, and here we provide further support for these calculations.

The introduction of a small amount of CPP in the copolymer P(CPP–SA) 5:95 shifts the SA–SA anhydride absorption to 1815 and 1742 cm^{-1}, and as the amount of CPP is increased, a new peak appears and increases in intensity at 1806 cm^{-1}. In the P(CPP–SA) 10:90 copolymer, three peaks appear at 1814, 1806, and 1742 cm^{-1}. In this copolymer, as in the 5:95 copolymer, the most dominant diads are SA–SA and SA–CPP, since the concentration of CPP monomer is low. In the P(CPP–SA) 15:85 copolymer there are four distinct peaks at 1814, 1744, and 1810, 1731 cm^{-1}. In the P(CPP–SA) 20:80 copolymer the peak at 1812 cm^{-1} is broad, but the 1808-cm^{-1} peak is seen clearly. Additional peaks, which are the second stretching pairs of the higher frequency bands, appear at 1741 and 1730 cm^{-1}. We thus conclude that the 1808- and 1731-cm^{-1} peaks correspond to the SA–CPP diads.

In the next four copolymers we again expect to see three peaks of absorption due to SA–SA, SA–CPP, and CPP–CPP diads. This is the case, although in some spectra the peaks overlap, making them difficult to distinguish. In the P(CPP–SA) 25:75 copolymer, the peaks at 1816, 1742 and 1806, 1727 cm^{-1} are evident, but the peaks at 1727 and 1742 cm^{-1} also appear with equal intensity, which is explained by the existence of a higher concentration of CPP–SA diads. In the P(CPP–SA) 30:70 copolymer, the intensities of the 1806- and 1725-cm^{-1} peaks are higher than those of the 1814- and 1742-cm^{-1} peaks, again indicating an increased concentration of the CPP–SA diad as the concentration of the CPP monomer increases. In the P(CPP–SA) 35:65 copolymer, the 1814-cm^{-1} peak appears only as a shoulder and its partner at 1742 cm^{-1} is apparent but reduced in intensity, indicating the decreasing concentration of SA–SA diads. There are sharp peaks at 1805 and 1725 cm^{-1} due to the CPP–SA diad and a peak at 1777 cm^{-1} which is characteristic of the CPP–CPP diads. The second peak that should appear around 1714 cm^{-1} is not seen distinctly but rather appears as a shoulder in the P(CPP–SA) 40:60 copolymer. The intensity of the anhydride peak of the P(CPP–SA) 50:50 copolymer at 1814 cm^{-1} is very low and its corresponding peak at 1742 cm^{-1} is not seen at all, indicating a low concentration of SA–SA diads. There is a sharp peak at 1803 cm^{-1} and a small but well defined peak at 1724 cm^{-1},


Peak Area Ratio vs. % SA in P(CPP:SA) Series

Peak Area Ratio vs. % SA in P(CPH:SA) Series

Peak Area Ratio vs. % SA in P(FA:SA) Series

Figure 7. Ratio between the 1383- and 1360-cm^{-1} peaks to the area under the anhydride peaks from 1800 to 1650 cm^{-1}, as a function of SA concentration for the (a, top) P(CPP-SA) series, (b, middle) P(CPH-SA) series, and (c, bottom) P(FA-SA) series.

indicating high concentrations of SA-CPP diads. The strong peaks at 1773 and 1715 cm^{-1} are indicative of high concentrations of the CPP-CPP diad. For this copolymer, the two main peaks corresponding to the CPP-SA and CPP-CPP diads (1803 and 1773 cm^{-1}) have roughly the same intensity, indicating almost the same ratio between the two diads. The next two copolymers display spectra similar to the 50:50 copolymer, with the only difference being the increased intensities of the CPP-CPP peaks (1775, 1714 cm^{-1}) compared to the CPP-SA peaks (1805, 1723 cm^{-1}), while the SA-SA peaks (1814, 1846 cm^{-1}) no longer appear.

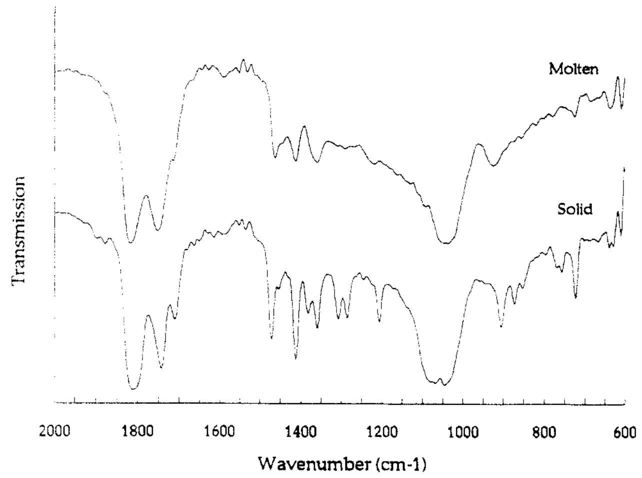


Figure 8. FTIR spectra of molten and solid PSA.

There are several more peaks that are of great importance which are found in the fingerprint region of the FTIR spectra. The first is a peak at 1604 cm^{-1} corresponding to the aromatic ring of the CPP monomer. There are four additional peaks (at 1382, 1360, 1307, and 1286 cm^{-1}) which appear only in the pure PSA polymer and the copolymers consisting mostly of SA, and as such are very useful in understanding microstructure during degradation. These peaks do not appear in the monomer IR spectra (Figure 1), so they could be only attributed to the polymer structure. In addition, as the concentration of the CPP increases, the intensity of these peaks decrease. In the P(CPP-SA) 30:70 copolymer, the two peaks at 1307 and 1286 cm^{-1} disappear, and in the P(CPP-SA) 50:50 copolymers, the peaks at 1382 and 1360 cm^{-1} are hardly seen. Therefore, we consider these peaks to be specific to the SA-SA sequence. This information is valuable later in determining the nature of the degradation of these polymers.[4]

In order to obtain quantitative information, we calculated the ratio of the area under the 1383- and 1360-cm^{-1} peaks to the area under the entire anhydride peaks at 1800-1650 cm^{-1}, as a function of the SA concentration in the copolymers. Clearly, Figure 7a demonstrates that the ratio increases as the concentration of the SA increases, again strengthening the conclusion that these peaks correspond to the SA-SA bonds. In order to further identify the origin of the 1382, 1360 and 1307, 1286 cm^{-1} peaks, we compared spectra of solid and molten PSA (Figure 8). These results reveal that the peaks at 1382 and 1360 cm^{-1} as well as the peaks at 1307 and 1286 cm^{-1} disappear in the molten state. This strongly indicates that both peaks are more characteristic of the solid state or more specifically the crystalline regions of the solid polymer. The two peaks at 1307 and 1286 cm^{-1} were also found to disappear in the FTIR spectra of the P(CPP-SA) copolymers with monomer ratios higher than 30:70 of CPP to SA which further suggests that they are characteristic of the crystalline SA-SA region.

Additional support for the last conclusion is found in our previous publication where X-ray studies were performed on the same series of copolymers (Figure 9).[1] In that paper, we have shown that for up to a ratio of 25:75 CPP to SA, the X-ray diffraction of the copolymers displays patterns which are typical of the PSA polymer. Above that concentration, although there are still high probabilities of having short sequences of SA close to each other, the diffraction is more amorphous and completely different in structure. Our conclusion is that the peaks at 1307 and 1286 cm^{-1} are characteristic of the crystalline

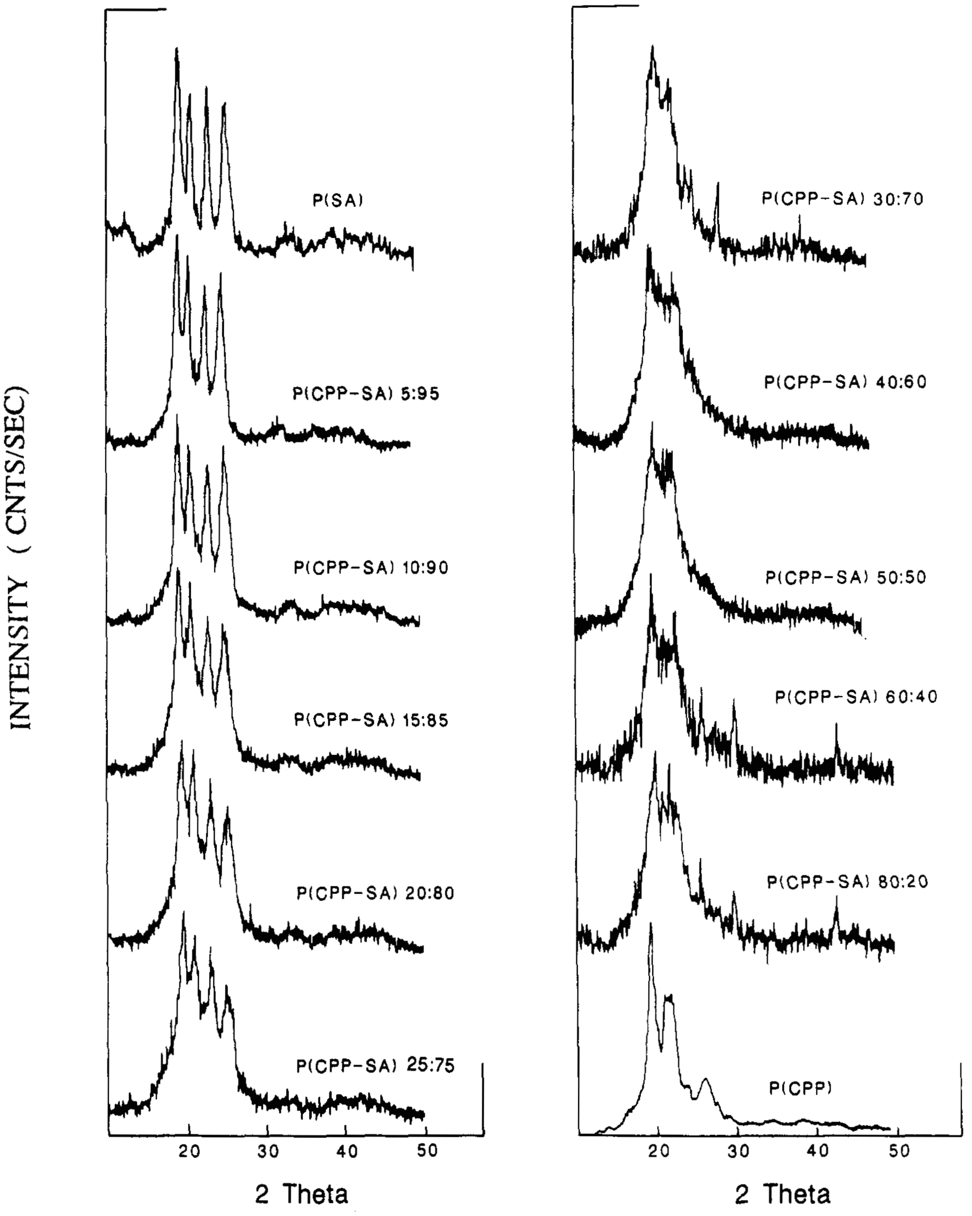


Figure 9. X-ray powder diffraction of the P(CPP–SA) series.[1]

regions of the SA–SA diads while the peaks at 1382 and 1360 cm^{-1} are more characteristic of the SA–SA diads in both amorphous and crystalline regions. The last two peaks can thus be used to estimate the real concentration of the SA monomer in any copolymer, provided that the curve shown in Figure 7a is known.

(c) P(CPM–SA) Series. Figure 4 displays the spectra of PSA, PCPM, and copolymers. For the PSA, two characteristic anhydride peaks at 1813 and 1741 cm^{-1} are again identified. The anhydride peaks of the pure PCPM polymers appear at 1782 and 1719 cm^{-1}. The characteristic anhydride bond absorbances are similar to what was found with the P(CPP–SA) copolymers. There are two main peaks typical for the CPM–SA diad that absorbed at 1806 and 1726 cm^{-1} (shoulder) as the concentration of the CPM is increased. The peaks are sharp, indicating a high degree of order. The P(CPM–SA) 50:50 copolymer displays a simpler structure than the P(CPP–SA) 50:50 copolymer. The absorptions are characteristic of CPM–SA and CPM–CPM diads, and their sharpness again indicates a higher degree of order compared to the (CPP–SA) 50:50 copolymer which is known to be amorphous.[1] The same is true for the P(CPM–SA) 70:30 copolymer. Interestingly, the P(CPM–SA) 90:10 copolymer displays much broader anhydride absorptions, indicating a lower degree of crystallinity.

(d) P(CPH–SA) Series. Figure 5 summarizes the results obtained from the P(CPH–SA) series. This series of polymers displays the main characteristic absorptions of the CPP–SA series, but with some very interesting differences. For PSA we again identify the two characteristic anhydride peaks at 1813 and 1741 cm^{-1}. Pure PCPH displays two peaks at 1774 and 1712 cm^{-1}. The anhydride peaks of the P(CPH–SA) 10:90 copolymer are similar to the PSA spectrum, and the absorptions correspond to the SA–SA diad, by far the most probable diad. In the P(CPH–SA) 20:80 copolymer, it was possible to identify the typical anhydride absorptions corresponding to the SA–SA and CPH–SA diads. Each pair was assigned the following wavenumbers: 1813 and 1741 cm^{-1} for SA–SA and 1807 and 1726 cm^{-1} for CPH–SA. The four SA–SA peaks of the fingerprint region at 1382, 1360 and 1307, 1286 cm^{-1} are apparent (as discussed in the P(CPP–SA) series), but the intensities of the last two are much lower, describing a less crystalline polymer. The P(CPH–SA) 30:70 copolymer displays only four characteristic anhydrides peaks, corresponding to SA–SA and CPH–SA bonds. The absorptions corresponding to the CPH–CPH

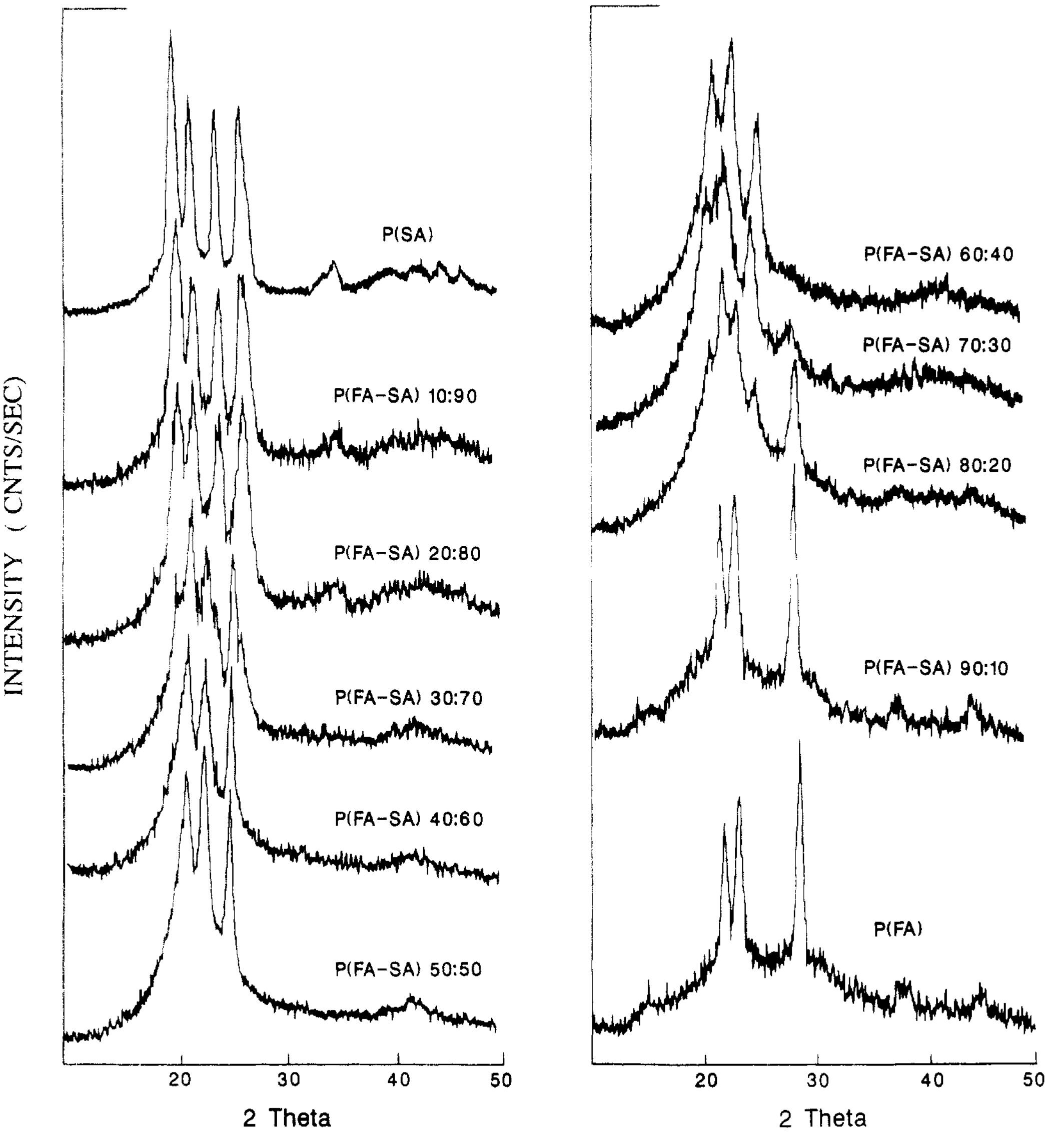


Figure 10. X-ray powder diffraction of the P(FA-SA) series.[1]

diad (at 1773 and 1715 cm^{-1}) are not seen but are suggested by the broadness of the peaks. The existence of the SA-SA diads in the fingerprint region is also evident from the two peaks at 1382 and 1360 cm^{-1}, while the two peaks at 1307 and 1286 cm^{-1} are not apparent. This fact indicates that the 30:70 polymer is less crystalline than the 20:80 copolymer. The P(CPH-SA) 40:60 copolymer displays different absorptions than the 30:70 copolymers. The intensity of the 1813- and 1741-cm^{-1} peaks decreases, and the stronger absorptions of the CPH-CPH diad, at 1773 and 1717 cm^{-1}, are clearly seen. In both cases (30:70 and 40:60), the peaks are sharp, indicating a high degree of order. The anhydride absorption of the P(CPH-SA) 50:50 copolymer is similar to that of the 40:60 copolymer, with the only difference being that the SA-SA peaks at 1381 and 1361 cm^{-1} are no longer seen. The 60:40 and 70:30 copolymers show higher absorption of the CPH-CPH diad, and the sharpness of the peaks continues to indicate a high degree of order. Overall, the series seems to develop a high degree of order. X-ray diffraction of the series shows a low degree of crystallinity but a high degree of longitudinal order. These polymers display liquid crystalline properties.[3] Using similar methodology as for the P(CPP-SA) series, we calculated the ratio of the area of the peaks at 1307 and 1286 cm^{-1} to the area of the anhydride peaks at 1800-1650 cm^{-1}. The results (Figure 7b) indicate that the increase in the ratio directly correlates to the concentration of the SA units. The peaks at 1382 and 1360 cm^{-1}, which are attributed to the crystalline region, disappear and actually merge into one peak at ratios above 70:30. X-ray diffraction[1] indicates that at ratios above CPH-SA ratios of 60:40 the typical PSA structure disappears. In the P(CPH-SA) series, the 1308- and 1286-cm^{-1} peaks could be attributed to the crystalline regions, and the peaks that appear at higher concentrations (which seemed to merge to one peak) could be more characteristic of a liquid crystalline state. This last hypothesis will be further investigated in the future.

(e) P(FA-SA) Series. The P(FA-SA) copolymers are also characterized by a high degree of crystallinity, as shown by X-ray diffraction (Figure 10).[1] This property was further demonstrated in the FTIR spectra. Figure 6 shows that all the copolymers display very sharp peaks. In addition, the FTIR spectra of the P(FA-SA) series are simpler, with the homopolymers having very similar anhydride peak absorptions. In the PSA homopolymer, again the absorptions are at 1813 and 1741 cm^{-1}. For PFA, the absorptions are found at 1783 and 1719 cm^{-1}. The P(FA-SA) 10:90 copolymer displays these four peaks, with the 1819-cm^{-1} peak appearing only as a shoulder. Even at that low concentration of FA (10%), the anhydride peak at 1723 cm^{-1} is well pronounced. This peak is atttributed to the FA-SA diad, but it could also be that the FA-FA peak overlaps with that absorption since the copolymers starting with 30:70 have increasing absorptions of this peak. The following copolymers have similar absorptions, with the intensities of the peaks at 1802 and 1723 cm^{-1} becoming more pronounced. The P(FA–SA) 50:50 copolymer has only two peaks at 1802 and 1722 cm^{-1}, as do the other copolymers (P(FA–SA) 60:40 through P(FA–SA) 70:30). Thus, the peaks at 1802 and 1722 cm^{-1} are due to the FA–SA diads which exist in high concentrations throughout the copolymer series. Analysis of the absorption peaks at 1383 and 1360 cm^{-1} reveals that there is almost a linear relation between the ratio of the area of the peaks at 1383 and 1360 cm^{-1} to the area of the anhydride peaks between 1800 and 1650 cm^{-1} and the concentration of SA in the copolymer (Figure 7c). Indeed, Figure 6 reveals that the two SA–SA peaks at 1383–1360 cm^{-1} appear in the entire series up to a FA–SA ratio of 70:30. Since we attribute these absorptions to the SA–SA diads and since at high concentrations of FA the probability of having two SA units next to each other is low, the existence of these two absorption peaks indicates the presence of at least one SA–SA diad in any copolymer with an FA concentration higher than 50%. This was not found in the previous series. The peaks at 1305 and 1286 cm^{-1} appear only in the first three copolymers (10:90, 20:80, and 30:70). For copolymers with FA–SA ratios of 40:60 up to 70:30, there is a new peak at 1280 cm^{-1} that is not seen in the P(FA–SA) 90:10 and PFA polymers. Comparing the results in this paper to results obtained from X-ray diffraction patterns of the same copolymers[1] reveals a very interesting and important observation (Figure 10). The powder diffraction of the P(FA–SA) series up to P(FA–SA) 20:80 has the typical diffraction of a PSA polymer. From P(FA–SA) 40:60 up to P(FA–SA) 70:30 there is a new diffraction pattern (different from the PFA and PSA diffractions). Thus the absorption at 1280 cm^{-1} is characteristic of this particular crystalline state. Figure 11 compares the spectra of the P(FA–SA) 20:80 copolymer slowly crystallized from melt. As found before, the peaks at 1383 and 1360 cm^{-1} as well as the peaks at 1307 and 1287 cm^{-1} disappear in the molten state. This indicates that they are representative of the solid and crystalline regions corresponding to SA–SA sequences.

The entire study of the fumaric copolymers strongly supports the assumption that the peaks at 1383 and 1360 cm^{-1} are characteristic of the amorphous and the crystalline states of the sebacic segments, while the 1307- and 1287-cm^{-1} peaks are characteristic of only the crystalline region of the sebacic segments. In addition, the peak at 1280 cm^{-1} is characteristic of a different crystalline state typical of the P(FA–SA) 30:70 to 70:30 copolymers.

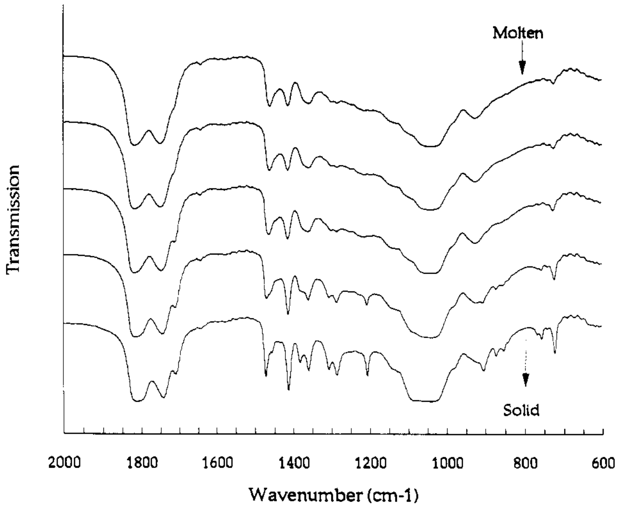


Figure 11. FTIR spectra of P(FA–SA) 20:80 copolymer slowly crystallized from melt.

To summarize, the work in this paper was directed toward understanding the microstructure of polyanhydrides using FTIR. Specifically, five series of polyanhydride copolymers were studied: PCPV, P(CPP–SA), P(CPM–SA), P(CPH–SA), and P(FA–SA). Knowing the absorptions for the aliphatic–aliphatic and aromatic–aromatic diads, we were able to determine the absorptions for aliphatic–aromatic diads. We also discovered four peaks in the fingerprint region which are specific to the sebacic acid segment of the polyanhydrides, with two of them corresponding specifically to the crystalline sebacic acid regions. These peaks allowed calculation of the sequence distribution in each copolymer of the series. The FTIR analysis presented here will be utilized for the characterization of degradation for this group of polyanhydrides.

References and Notes

(1) Mathiowitz, E.; Ron, E.; Mathiowitz, G.; Langer, R. *Macromolecules* **1990**, *23*, 3212.

(2) Ron, E.; Mathiowitz, E.; Mathiowitz, G.; Langer, R. *Macromolecules* **1991**, *24*, 2278.

(3) Mathiowitz, E.; Jacob, J.; Chickering, D.; Pekarek, K. *Macromolecules*, following article in this issue.

(4) Mathiowitz, E.; Bernstein, H.; Pekarek, K.; Kreitz, M. Submitted to *Macromolecules*.

(5) Domb, A.; Langer, R. *J. Polym. Sci.* **1987**, *25*, 3373.

(6) Domb, A.; Mathiowitz, E.; Ron, E.; Giannos, S.; Langer, R. *J. Polym. Sci.* **1991**, *29*, 571.

(7) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1981; pp 1–442.