(3) Iwatsuki, S.; Shin, Y.; Yamashita, Y. *Makromol. Chem.* **1967**, *102*, 232.

(4) Iwatsuki, S.; Yamashita, Y. *J. Polym. Sci., Part A-1* **1967**, *5*, 1753.

(5) Iwatsuki, S.; Itoh, T. *Makromol. Chem.* **1979**, *180*, 663.

(6) Iwatsuki, S.; Itoh, T.; Horiuchi, K. *Macromolecules* **1978**, *11*, 497.

(7) Iwatsuki, S.; Itoh, T. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2971.

(8) Hauser, C. F.; Zutty, N. L. *Macromolecules* **1971**, *4*, 478.

(9) Iwatsuki, S.; Itoh, T. *Macromolecules* **1980**, *13*, 983.

(10) Iwatsuki, S.; Itoh, T. *Macromolecules* **1982**, *15*, 347.

(11) Iwatsuki, S.; Yamashita, Y. *Makromol. Chem.* **1967**, *104*, 263.

(12) Alfrey, T.; Goldfinger, G. *J. Chem. Phys.* **1946**, *14*, 115.

(13) Chen, E. C. M.; Wentworth, W. E. *J. Chem. Phys.* **1975**, *63*, 3183.

(14) Iwatsuki, S.; Nishio, K.; Yamashita, Y. *Kogyo Kagaku Zasshi* **1967**, *70*, 384.

(15) Kokubo, T.; Iwatsuki, S.; Yamashita, Y. *Macromolecules* **1968**, *1*, 482.

(16) Ham, G. "Copolymerization"; Wiley: New York, 1964; p 421.

(17) Alfrey, T., Jr.; Bohrer, J. J.; Mark, H. "Copolymerization"; Interscience: New York, 1952; p 64.

(18) Young, L. J. "Polymer Handbook"; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975; Vol II, p 364.

(19) Tsuchida, E.; Tomono, T.; Sano, H. *Kogyo Kagaku Zasshi* **1970**, *73*, 2031.

(20) Ledwith, L.; Woods, H. J. *J. Chem. Soc.* **1970**, *13*, 310.

(21) Heublein, H.; Spange, S.; Adler, P. *Faserforsch. Texitiltechn.* **1978**, *29*, 513.

(22) Watanabe, K.; Nakayama, T.; Mottle, J. *Quant. Spectrosc. Radiat. Transfer* **1962**, *2*, 369.

(23) Price, W. C. *Chem. Rev.* **1947**, *41*, 257.

(24) Chemical Society of Japan "Kagaku Binran, Fundamental Edition", 2nd ed.; Maruzen: Tokyo, 1975; p 1276.

(25) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.

(26) Hall, H. K., Jr.; Bentley, J. H. *Polym. Bull.* **1980**, *3*, 203.

(27) Fieser, L. F. "Experiments in Organic Chemistry"; D. C. Heath and Co.: New York, 1955; p 95.

(28) Allen, C. F. H.; Bell, A. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 312.

(29) Cretcher, L. H.; Koch, J. A.; Pittenger, W. H. *J. Am. Chem. Soc.* **1925**, *47*, 1173.

(30) Noller, C. R.; Adam, R. *J. Am. Chem. Soc.* **1924**, *46*, 1889.

(31) Iwai, K.; Furue, M.; Nozakura, S.; Shirota, T.; Mikawa, M. *Polym. J.* **1980**, *12*, 97.

(32) Overberger, C. G.; Saunders, J. H. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 204.

Structure of *p*-Hydroxybenzoate/Ethylene Terephthalate Copolyester Fibers

John Blackwell,*[†] Günter Lieser,[‡] and Genaro A. Gutierrez[§]

Institüt für Makromolekulare Chemie der Universität Freiburg, D-7800 Freiburg, West Germany, and Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106. Received July 12, 1982

ABSTRACT: X-ray methods are used to investigate the structure of melt-spun fibers of *p*-hydroxybenzoate/ethylene terephthalate copolymers, by analogy with the electron diffraction patterns obtained from single crystals of homopoly(*p*-hydroxybenzoate) [systematic name: poly(1,4-oxybenzoyl)]. The fiber diagrams of copolymers containing 60–80% *p*-hydroxybenzoate are very similar to the electron diffraction patterns of homopolymer single crystals that have been heat treated at 360 °C. These observations indicate that the fibers contain oriented, ordered regions with the same basic structure as the high-temperature form of the homopolymer. These regions probably consist of copolymer sequences rich in hydroxybenzoate, in which some ethylene terephthalate units are present as defects. The data also define the orientation of the chains with respect to the homopolymer crystal morphology. Both the X-ray and electron diffraction data show that the poly(*p*-hydroxybenzoate) chain has a stiff, extended 2_1 helical conformation, with two monomer units repeating in $\sim$12.4 ± 0.2 Å, for which a stereochemically acceptable model is presented.

Introduction

Copolymers of *p*-hydroxybenzoate with one or more of a number of aromatic esters are known to form liquid crystalline structures in the melt, and this property can be utilized, e.g., to form high-strength fibers (see, for example, ref 1–8). The homopolymer, poly(*p*-hydroxybenzoate) [systematic name: poly(1,4-oxybenzoyl)], is a crystalline, infusible, intractable polymer,[6,9] and it is necessary to introduce a second component, which is thought to lead to defects in the solid-state structure, thereby lowering the melting point and resulting in a processable material. The present paper describes work by X-ray methods to investigate the structure of copolymers of *p*-hydroxybenzoate and ethylene terephthalate, in which our interpretations are based on electron diffraction studies of poly(*p*-hydroxybenzoate) single crystals. We seek to determine the three-dimensional structure of the copolymer fibers, i.e., how the chains are packed together, and hence to understand why the use of certain copolymerized components leads to better properties.

The *p*-hydroxybenzoate/ethylene terephthalate copolymers are prepared from *p*-acetoxybenzoic acid and poly(ethylene terephthalate) as described by Jackson and Kuhfuss.[5] NMR evidence was presented by these authors in favor of totally random sequences for these copolymers. However, Lenz and Feichtinger[10] have reported the development of blockiness as a result of transesterification in the melt, and Wunderlich and co-workers[11,12] presented optical microscopy and DSC data demonstrating a biphasic structure. We have studied the structure of copolymers containing 60 and 80% *p*-hydroxybenzoate. Jackson and Kuhfuss[5] report an X-ray diffraction maximum at $d = 4.6$ Å for these monomer ratios, which they assign to an ordered poly(*p*-hydroxybenzoate) phase, but no detailed analyses of the structure were made. The structure of the homopolymer, poly(*p*-hydroxybenzoate), is not known at present, although a threefold double-helical conformation has been proposed by Economy et al.,[9] based on limited powder X-ray data for the unoriented polymer. More recently, Hay[13] has performed X-ray and electron diffraction studies for poly(*p*-hydroxybenzoate) and its oriented copolymers and has proposed an orthorhombic unit

---

[†] Visiting Professor at the Institüt für Makromolekulare Chemie der Universität Freiburg, Jan–June 1982.

[‡] Institüt für Makromolekulare Chemie der Universität Freiburg.

[§] Case Western Reserve University.

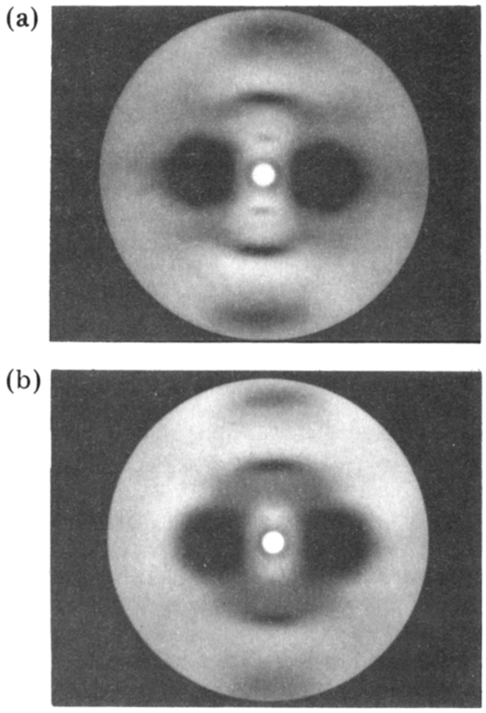

Figure 1. X-ray fiber diagrams of melt-spun fibers of *p*-hydroxybenzoate/ethylene terephthalate copolymers: (a) 80% *p*-hydroxybenzoate; (b) 60% *p*-hydroxybenzoate. The fiber axes are vertical and approximately perpendicular to the beam.

cell with dimensions $a = 7.52$ Å, $b = 5.58$ Å, and $c = 12.51$ Å, with a 2_1 screw axis parallel to *c*. An X-ray analysis of copolymers of *p*-hydroxybenzoic acid, 2,6-dihydroxynaphthalene, and terephthalic acid by Blackwell and Gutierrez[14] showed that the data are compatible with a structure consisting of highly oriented chains of truly random sequence. However, as will be seen below, there are significant differences between the latter data and those for the present *p*-hydroxybenzoate/ethylene terephthalate system.

Experimental Section

Specimens of Kodak X7G fibers containing 60–80% *p*-hydroxybenzoate were generously supplied by Dr. R. G. Seymour of Tennessee Eastman Co. in the form of melt-spun fibers. The polymers had been prepared from *p*-acetoxybenzoic acid and poly(ethylene terephthalate) in the manner described by Jackson and Kuhfuss.[5] X-ray patterns of parallel bundles of these fibers were recorded with a Searle toroidal camera, Kodak No Screen film, and Ni-filtered Cu Kα radiation from a Rigaku Denki rotating-anode source. The *d* spacings were calculated with calcium fluoride.

Poly(*p*-hydroxybenzoate) was generously supplied by Drs. G. Schwarz, and H. R. Kricheldorf of the University of Hamburg and had been synthesized as described in ref 15. The average degree of polymerization ($\overline{DP}$) was determined by NMR end-group analysis of the fully degraded polymer. For the as-polymerized material with acetoxy end groups, $\overline{DP} = 10$. However, the electron diffraction patterns described below were obtained for specimens that had been heat treated in the microscope (in vacuo) at 360–390 °C, giving rise to transesterification. For these specimens, the DP exceeds 100, as was confirmed by NMR analysis of a reference sample of macroscopic size that had been annealed for 4 h at 320 °C.

Electron micrographs and diffraction patterns were obtained with a Philips EM400 HTG electron microscope. Powder X-ray patterns of the heat-treated reference sample were recorded with a Debye–Scherrer camera.

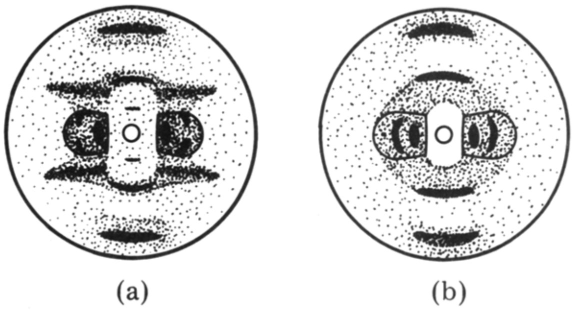

Figure 2. Schematics of the X-ray fiber diagrams shown in Figure 1.

Table I
X-ray Powder Diffraction Data for
Poly(*p*-hydroxybenzoate) Annealed for 4 h at 320 °C
(Reference Sample)

d(obsd), Å	rel int[a]	*d*(obsd), Å	rel int[a]	*d*(obsd), Å	rel int[a]
7.42	w	3.58	s	2.27	m
6.29	w	3.31	w	2.08	s
5.57	s	3.08	vs	1.95	m
5.10	m	2.79	m	1.87	w
4.50	vs	2.66	m	1.25	w
4.24	m	2.51	w		
3.72	vs	2.32	m		

[a] Relative intensities (rel int): vs = very strong, s = strong, m = medium, and w = weak.

Results

X-ray fiber diagrams of the fibers containing 60 and 80% *p*-hydroxybenzoate are shown in Figure 1. In view of the inevitable poor reproduction, schematics of these patterns are shown in Figure 2. The high degree of orientation is apparent from the low extent of arcing of the meridional reflections. The 80% *p*-hydroxybenzoate fiber shows equatorial reflections at $d \simeq 4.4$ Å (very strong) and 2.5 Å (weak), and there is intense diffuse scatter in the 6–3-Å equatorial region. Also, an off-equatorial reflection is seen at $d \simeq 3.2$ Å (medium), and this lies at a layer line spacing of 12–13 Å. Three meridional reflections are seen at $d \simeq 6.2$ Å (weak), 3.15 Å (strong), and 2.1 Å (strong), and there is a diffuse layer line streak at ~4.1 Å, but without meridional intensity. These layer lines correspond to the first, second, third, fourth, and sixth orders of a repeat of 12.4 ± 0.2 Å, and the absence of odd-order meridional indicates a 2_1 screw axis parallel to the fiber axis. The diffuse equatorial scatter and the continuous third layer line show that the lateral packing is relatively disorded, except for the features of the structure responsible for the Bragg reflections. The fiber diagram of the 60% copolymer is much less sharp but has the same general features, and the observed *d* spacings are the same within experimental error. We can conclude that this copolymer contains ordered regions with the same basic structure as those in the 80% copolymer, except that they are smaller and more distorted. Nevertheless there are other differences between the two X-ray patterns, notably the absence of the first meridional reflection for the 60% copolymer, that may indicate differences of detail in the ordered structure, and further work is in progress in this regard.

The powder X-ray diffraction pattern for the reference sample of heat-treated poly(*p*-hydroxybenzoate) shows 19 reflections with *d* spacings and relative intensities as shown in Table I. Similar data have been reported by Economy et al.:[9] the *d* spacings are not exactly the same, but we have seen some variations in the *d* spacings and also the intensities, depending on the DP and the thermal history (see below and ref 16).

Figure 3a shows an electron micrograph of a crystal of poly(*p*-hydroxybenzoate) after thermal treatment on the

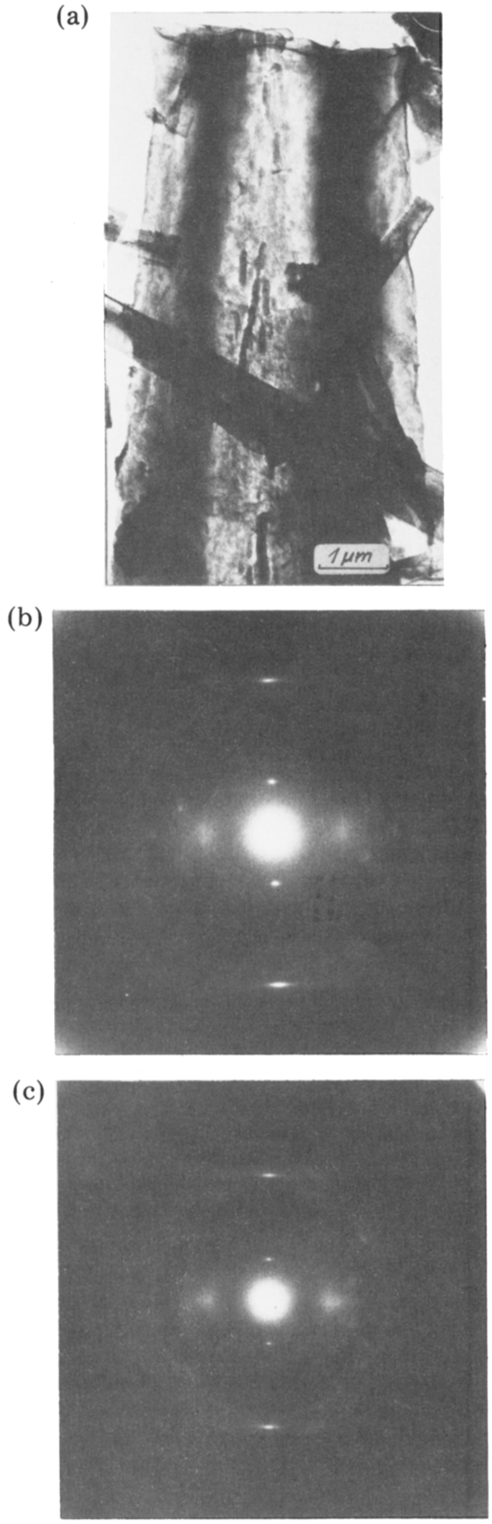

Figure 3. (a) Transmission electron micrograph of a poly(*p*-hydroxybenzoate) crystal after heat treatment at 360 °C. (b) Electron diffraction pattern of the crystal in (a) at 360 ± 5 °C. (c) Electron diffraction pattern of the crystal in (a) after cooling to room temperature. The fiber axis of the diffraction patterns corresponds to the long axis of the crystals. The diffraction patterns were obtained from a 3.9-μm-diameter circular area in the upper part of the crystal, using a selected-area diffraction diaphragm.

hot stage of the electron microscope. The electron diffraction patterns of this specimen at 360 ± 5 °C and after cooling to room temperature are shown in parts b and c of Figure 3, respectively. The patterns have the appearance of fiber diagrams and are similar to the X-ray patterns in Figure 2. Morphologically the specimen is at an intermediate stage between a crystal and a fiber, as is confirmed by the fact that only small changes occur in the diffraction pattern when the specimen is rotated about its long axis.

The electron diffraction pattern obtained at high temperature contains equatorial reflections at d = 4.59 and 2.64 Å and a first layer line reflection at d = 3.31 Å. Meridional reflections are seen on the second, fourth, and sixth layer lines for a repeat of c = 12.34 Å, and the absence of odd-order meridionals indicates a 2_1 screw axis parallel to the fiber axis. The sixth layer line is an extended streak with the appearance of some sampling at a point corresponding to the first equatorial reflection. In addition, there is diffuse scatter in the 6–3-Å equatorial region and a weak continuous off-meridional streak for the third layer line. Some sharp rings are also seen: the one passing through the first equatorial reflection is probably due to the many small unoriented crystals that can be seen in the background of the micrograph; the others are due to the platinum shadowing and the carbon substrate. The diffraction pattern for the same region of the specimen after cooling to room temperature (Figure 3c) is similar except that it is a little sharper and more detailed. The fiber repeat is 12.42 Å, and there is evidence for the ninth and twelfth layer lines. There is only a single reflection on the equator, at d = 4.53 Å, and the equatorial scatter is much less intense; a first layer line reflection is seen at d = 3.11 Å. In addition, there are reflections forming a row line at d = 2.77, 2.59, 2.33, and 2.07 Å, on row lines 1, 2, 3, and 4, respectively. These match d spacings for a low-temperature form, as will be discussed below. The absence of the second equatorial may be due to the development of some preferred orientation in the cooled specimen. It is interesting to note that a fiber repeat of 12.56 Å is seen in regions of the specimen that have not been in the beam during the thermal treatment, and it may be that some of the above differences in the fiber repeat and other d spacings arise from beam damage at high temperature.

Figure 4 shows the electron micrograph and electron diffraction pattern of a second region of the same specimen at 388 ± 5 °C (the difference between 360 and 388 °C is not significant). The reflections in the electron diffraction lie on a hexagonal net, with d = 4.62, 2.64, and 2.30 Å. The first two of these match the equatorial d spacings in Figure 3b and indicate that the data in Figure 3 and 4 arise from projections perpendicular and parallel to the c = 12.4 Å axis. The d spacings on the equator of Figure 3b and in Figure 4 are compatible with a hexagonal unit cell with dimension a (=b) = 5.3 Å. However, in order to index the first layer line reflection at d = 3.31 Å in Figure 3b, it is necessary to use the orthorhombic description of the lattice: a = 9.2 Å, b = 5.3 Å, and c = 12.4 Å, for which d_{200} = 4.6 Å, d_{020} = 2.6$_5$ Å, and d_{211} = 3.3$_4$ Å. Nevertheless, this unit cell should be regarded as tentative in view of the limited data available.

Discussion

The similarity between the X-ray patterns of the copolyester fibers (especially for the 80% copolymer) and the electron diffraction patterns of thermally treated poly(*p*-hydroxybenzoate) is quite striking and leads simultaneously to two conclusions. First, the copolyester fibers contain ordered regions with the same basic physical structure as the high-temperature form of poly(*p*-hydroxybenzoate). This cannot be concluded from the X-ray powder diffraction data, because of the variation in d spacings and relative intensities, depending on the sample history. These variations probably reflect polymor-

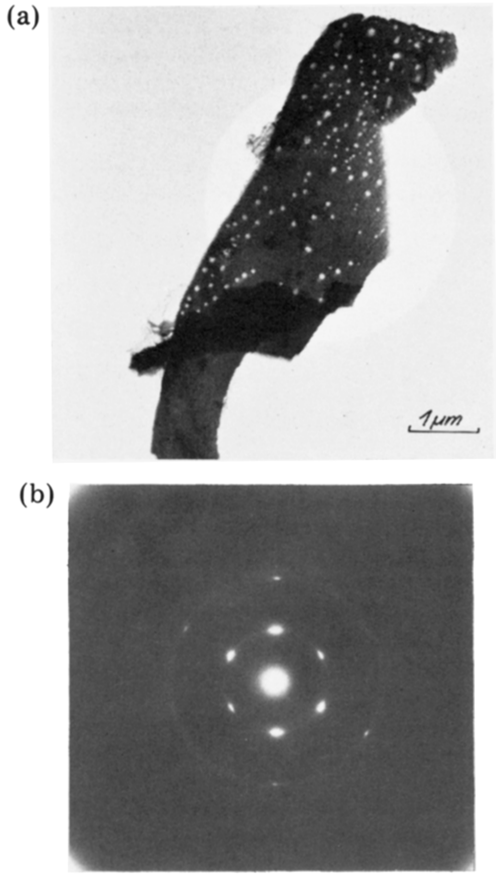

Figure 4. Transmission electron micrograph of a second region of the same EM grid of the specimen giving Figure 3. The pattern was recorded at 388 ± 5 °C. The electron diffraction pattern at that temperature is shown below the micrograph and was obtained for the circular area shown.

phism of the homopolymer and other structural differences (see ref 16). There is no indication of ordered poly(ethylene terephthalate) structure, although as the minor component this would be less easy to detect. Jackson and Kuhfuss[5] report that this is observed in specimens containing higher proportions of ethylene terephthalate.

Second, the match between the fiber and electron diffraction data defines the chain direction in the homopolymer crystals to be parallel to the $c = 12.4$ Å dimension. This repeat and the 2_1 symmetry clearly rule out the threefold double helix proposed by Economy et al.[9] The data suggest a 2_1 helix for the chain conformation, with two *p*-hydroxybenzoate residues repeating in 12.4 Å, similar to that proposed for poly(*p*-benzamide).[17] Using standard bond lengths and angles, we have constructed a 2_1-helical model for poly(*p*-hydroxybenzoate) as shown in Figure 5. Assuming planar carboxyl groups, the only conformational variables are the torsion angles about the phenyl–CO and O–phenyl bonds. These parameters have only a small effect on the axial rise per residue because the linkage bonds are almost parallel to the chain axis. Setting these torsion angles at 30° (see Hummel and Flory[18]) we find a fiber repeat of 12.64 Å, which is in good agreement with the observed repeat, given the allowed ranges for the stereochemistry and the experimental error.

As will be described elsewhere, Lieser[16] has obtained high-quality electron diffraction patterns of non-heat-treated poly(*p*-hydroxybenzoate) that can be indexed by an orthorhombic unit cell with dimensions $a = 7.52$ Å and $b = 5.70$ Å, which are very close to those proposed by Hay.[13] These electron diffraction data contain reflections at $d = 4.52$ and 2.62 Å, which approximately match the

Figure 5. Projections of the chain conformation of poly(*p*-hydroxybenzoate) viewed perpendicular to the chain axis. The chain has a 2_1 screw axis with a fiber repeat of 12.64 Å.

equatorial *d* spacings in Figure 3. However, an orthorhombic unit cell with these *a* and *b* dimensions and $c \simeq 12.4$ Å will not index the $d = 3.31$ Å reflection on the first layer line of the fiber patterns. The reflections on the extra row line for the cooled specimen are indexed by this low-temperature form, and it appears that some of this structure is re-formed on cooling. We conclude therefore that the structure of the non-heat-treated specimen is different from that of both the heat-treated and fiber copolymer specimens. Significantly, the unit cell for the latter group of specimens, $a = 9.2$ Å, $b = 5.3$ Å, and $c = 12.4$ Å, is approximately 13% larger than that for the non-heat-treated specimen. This is a large decrease in density, greater than that expected due to a polymorphic change without a major change in chain conformations. In this regard it is significant that Economy et al.[9] report a crystal–crystal transition for higher molecular weight poly(*p*-hydroxybenzoate) in the range 325–360 °C and suggest from dielectric measurements that above the transition the carboxyl groups have greater rotational freedom. Thus it could be that the fibers and heat-treated homopolymer contain a structure in which the stiff chains are oriented parallel to the *c* axis but are arranged more irregularly in the perpendicular directions due to axial and/or torsional rotations. The latter defects would lead to a cylindrical cross section for the chains and hence to the pseudohexagonal packing with a lower density than the low-temperature forms of the homopolymer. It is possible that this corresponds to some sort of liquid crystalline structure. However, the structure is not nematic: the first layer line reflection is definite evidence for a specific or preferred axial register of adjacent chains.

The observed data for the copolymers could be explained by segregation of homopoly(*p*-hydroxybenzoate) sequences, as might be expected if there is extensive blockiness. This explanation of electron diffraction data for the copolymers has been given in a recent paper by Zachariades et al.[19] However, if this is the case it is surprising that the ordered structures have the high-temperature form of the homopolymer. It seems more likely that the ordered regions contain sequences *rich* in *p*-hydroxybenzoate, in which some ethylene terephthalate units are present as defects. Such defects could probably be tolerated in the open high-temperature form of the homopolymer but could prevent adoption of the more compact low-temperature crystalline structure. The ordered structures are only a fraction of the total fiber, and the disordered regions responsible for the diffuse equatorial sections probably contain higher proportions of ethylene terephthalate. This view is supported by the thermal analyses of Meesiri et al.,[12] which demonstrate the existence of two phases in the copolymers. The melting behavior of the higher melting phase, which is probably the ordered region seen here, suggests that this consists of segregated copolymer rich in *p*-hydroxybenzoate rather than homopolymer blocks. For the 80% copolymer, even a fully random structure will contain extensive sequences rich in *p*-hydroxybenzoate, and thus it is not surprising that this composition is more ordered than the 60% copolymer.

Acknowledgment. This work has been supported by grants from the Deutsche Forschungsgemeinschaft and from the United States National Science Foundation (DMR78-24150 and DMR81-07130). A visiting professorship to John Blackwell from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References and Notes

(1) Jin, J. I.; Antoun, S.; Ober, C.; Lenz, R. W. *Br. Polym. J.* **1980**, *12*, 132–146.

(2) Calundann, G. W.; Davis, H. C.; Gorman, Z. J.; Mininni, R. M. *U.S. Pat.* 4 083 829, 1978 (Celanese).

(3) Calundann, G. W. *U.S. Pat.* 4 067 852, 1978; 4 130 545, 1978, (Celanese).

(4) Kuhfuss, H. F.; Jackson, W. T. *U.S. Pat.* 3 804 805, 1974 (Tennessee Eastman).

(5) Jackson, W. J.; Kuhfuss, H. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2043–2058.

(6) Cottis, S. G.; Economy, J.; Nowak, B. E. *U.S. Pat.* 3 637 595, 1972 (Carborundum).

(7) Schaefgen, J. R. *U.S. Pat.* 4 118 372, 1978 (du Pont).

(8) Goodman, I.; McIntyre, J. E.; Stimpson, J. W. *U.S. Pat.* 3 321 437, 1967 (I.C.I.).

(9) Economy, J.; Storm, R. S.; Markovich, V. I.; Cottis, G. G.; Nowak, B. E. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *14*, 2207–2224.

(10) Lenz, R. W.; Feichtinger, K. A. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20*, 114–117.

(11) Menczel, J.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1433–1438.

(12) Meesiri, W.; Menczel, J.; Gaur, U.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 719–728.

(13) Hay, I. Abstracts of the 39th Pittsburgh Diffraction Conference, Cleveland, Ohio, Nov 1981.

(14) Blackwell, J.; Gutierrez, G. A. *Polymer* **1982**, *23*, 671–675.

(15) Schwarz, G.; Kricheldorf, H. R., submitted to *Makromol. Chem.*

(16) Lieser, G., submitted to *J. Polym. Sci., Polym. Phys. Ed.*

(17) Tadokoro, H. In "Structure of Crystallin Polymers"; Wiley: New York, 1979; p 398.

(18) Hummel, J. P.; Flory, P. J. *Macromolecules* **1980**, *13*, 479–484.

(19) Zachariades, A. E.; Economy, J.; Logan, J. A. *J. Appl. Polym. Sci.* **1982**, *27*, 2009–2014.

Structure and Degradation of an Intractable Polymeric System: Melamine Formaldehyde Cross-Linked Acrylic Coatings[†]

A. D. English* and D. B. Chase

Central Research and Development Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

H. J. Spinelli

Finishes and Fabricated Products Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.

Received October 27, 1982

ABSTRACT: Curing and degradation chemistry at the primary cross-linking site in pigmented melamine formaldehyde cross-linked acrylic copolymer coatings have been characterized as a function of depth by using the complementary techniques of diffuse reflectance infrared spectroscopy and solid-state ^{13}C NMR. The curing of an acid-catalyzed coating is shown to go to completion under the conditions used with no significant concurrent melamine self-condensation reactions. Degradation is promoted by the presence of heat and/or light, residual acid, and atmospheric water; the degradative pathway invokes irreversible acid-catalyzed hydrolysis of (i) unreacted melamine methoxymethyl moieties throughout the coating and (ii) primary cross-links only at the very surface.

Introduction

The cross-linking and degradation chemistry of melamine formaldehyde–acrylic copolymer coatings have been a field of renewed interest recently.[1–4] One aspect of these coatings that makes them difficult to study is the intractability of the system to conventional physical techniques. In the cured state the system consists of a highly cross-linked polymeric network in which a large amount of finely dispersed pigment, metallic flake, and other additives are present. The system is not amenable to conventional transmission infrared spectroscopic studies due to the high scattering power of the additives. Also, solution NMR techniques are not of use since the act of dissolution greatly perturbs, if not destroys, the primary melamine–acrylic cross-linking sites. An additional complication with this system is often the poorly defined nature of the melamine formaldehyde cross-linking agent and the acrylic

---

[†] Contribution No. 3086.

0024-9297/83/2216-1422$01.50/0