Direct Evidence for Sequence Ordering of Random Semicrystalline Copolyesters during High-Temperature Annealing

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Received December 26, 1996; Revised Manuscript Received March 24, 1997[⊗]

ABSTRACT: In an effort to study sequence ordering during annealing in semicrystalline copolyesters, the carbonyl carbon of *p*-hydroxybenzoic acid was ^{13}C tagged and then solution polymerized with 2-hydroxy-6-naphthoic acid to form a low molecular weight, 50/50, random copolyester. The random copolyester was annealed at 40 deg below the crystal nematic transition temperature (T_{cn}). DSC results indicated a large increase in crystallinity; however ^{13}C NMR analysis showed no change in the benzoic−naphthoic (BN) and benzoic−benzoic (BB) diad sequence peak ratios. When the random copolyester was annealed near the T_{cn}, DSC results indicated a large increase in the transition temperature, no increase in crystallinity, and a shift in the BN:BB peak ratio indicating a significant increase in alternating sequences. On the basis of these results, the dramatic increase in transition temperature during annealing near T_{cn} is best interpreted as sequence ordering via interchain transesterification reactions within the existing crystalline regions.

Introduction

Over the past 25 years, considerable effort has been expended on the synthesis of rodlike aromatic copolyesters for commercial development. On the other hand, far less progress has been made in characterizing the nature of the microstructure in these copolyesters. It is reasonably well accepted that melt-polymerized copolyesters such as *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) possess a random sequence distribution.[1−3] In the case of copolymers prepared in the solid state, such as HBA with terephthalic acid and biphenol (BPT), preliminary evidence suggests that they are blocky in nature, although the evidence is not as definitive.[4] In the melt polymerization of 60/40 acetoxybenzoic acid/poly(ethylene terephthalate) (PET), there is evidence of a broad compositional distribution in which the phase rich in PET is more blocky.[5]

These issues become even more complicated upon annealing the copolyesters near their crystal nematic transition (T_{cn}). Typically, the melting point, as determined by DSC, increases by 40−75 °C,[6−8] and this is accompanied by a change in crystal structure (hexagonal to orthorhombic).[7] This unusual increase in melting point has led to several sharply different interpretations including (1) sequence ordering occurring within the existing crystallites,[9−11] (2) melting and recrystallization of longer ordered sequences,[6] (3) a sharp increase in molecular weight due to continued polymerization,[12] and (4) physical ordering[13] in a paracrystalline lattice (pcl).[14,15] It should be noted that similar increases in the melting transition temperature have been observed with other kinds of copolyesters.[11,16]

Several years ago, we took an initial step to identify the nature of the increase in melting point by preparing a low molecular weight copolyester of 50/50 HBA/HNA. The advantage of this system was that one could, for the first time, dissolve the higher melting point product after annealing. However, the results from characterization of the higher melting copolyester versus the as-prepared copolyester were not sufficiently conclusive.[11]

In this paper we report, for the first time, direct evidence from ^{13}C NMR analysis proving that sequence ordering is occurring in these copolyesters during high-temperature annealing. This was accomplished by preparing a 50/50 HBA/HNA copolyester with a ^{13}C tag in the carbonyl carbon of the HBA. This permitted us to follow changes in sequence distribution of the random copolyester through changes in the concentration of the tagged diad sequences.

Experimental Section

Materials. Magnesium turnings, acetic anhydride, boron tribromide, 4-bromoanisole, $^{13}CO_2$, and anhydrous diethyl ether were used as-received from Aldrich Co. 2-Hydroxy-6-naphthoic acid was kindly supplied by Hoechst-Celanese Co., Summit, NJ. 2-Acetoxy-6-naphthoic acid was prepared as reported elsewhere.[17] Therminol-66, a high-boiling aromatic hydrocarbon from Monsanto, was used as a solvent for solution polymerization of poly(*p*-hydroxy[carboxy-^{13}C]benzoic acid-*co*-2-hydroxy-6-naphthoic acid).

Preparation of 4-Methoxy[carboxy-^{13}C]benzoic acid. Magnesium turnings (0.44 g, 18 mmol) were added to 40 mL of anhydrous ether under a nitrogen atmosphere. 4-Bromoanisole (5.1 mL, 18 mmol) was slowly added, and the resulting mixture was refluxed for 20 h. This solution was chilled to −10 °C, and $^{13}CO_2$ was slowly bubbled through. The product was extracted with base (1 M NaOH), acidified to precipitate the carboxylic acid, and extracted with ethyl acetate and the solvent evaporated. The resulting powder was purified by recrystallization from acetone and water. Yield: 72%.

Preparation of 4-Acetoxy[carboxy-^{13}C]benzoic acid. 4-Methoxy[carboxy-^{13}C]benzoic acid (2 g, 13 mmol) was dissolved in 65 mL of anhydrous dichloromethane. To this solution was slowly added 2 equiv of 1 M BBr_3 (in dichloromethane), and then the solution was refluxed for 12 h. The solution was cooled and quenched with deionized water. 4-Hydroxy[carboxy-^{13}C]benzoic acid was first extracted with base (1 M NaOH), acidified, extracted with ether, and finally dried. Without further purification, this was dissolved in 5 mL of acetic anhydride at 115 °C and cooled to ~70 °C. After addition of a few drops of sulfuric acid, the solution was held at 70 °C for 2.5 h, at which point the solution was quenched with deionized water. The product was extracted with ether and purified by silica chromatography (10% ethanol/chloroform). Yield: 39%.

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

S0024-9297(96)01900-6 CCC: $14.00

Preparation of Poly(*p*-hydroxy[carboxy-^{13}C]benzoic acid-*co*-*p*-2-hydroxy-6-naphthoic acid). 4-Acetoxy[carboxy-^{13}C]benzoic acid, 2-acetoxy-6-naphthoic acid, and isophthalic acid (added to control molecular weight) in a 15:15:1 molar ratio were dissolved in Therminol-66 to make a 10% by weight solution. The temperature of the solution was raised to 300 °C and held for 50 min. The temperature was then raised to 325 °C and held for 60 min. The solution was then cooled to room temperature and filtered. The product was rinsed with ethanol, ground, and rinsed again, mp 241 °C ($\Delta H = 2.3$ J/g).

Annealing. All samples were annealed under dry nitrogen in a Thermal Analysis (TA) Instruments differential scanning calorimeter (DSC) 2910. Each sample was heated to 350 °C at 20 °C/min and cooled to 100 °C before annealing. Samples were annealed at 190 °C for 24 h followed by 230 °C for 24 h. Other samples were annealed at 190 °C for 48 h followed by 230 °C for 48 h.

Instrumentation. DSC experiments were performed on a TA Instruments DSC 2910. Both temperature and heat flow scales were calibrated with high-purity indium and zinc standards. Heating rates were fixed at 20 °C/min. All thermal analyses were run under an atmosphere of dry nitrogen. The transition temperatures were taken to be the maxima of the endotherm peaks.

^{13}C NMR spectra were taken on a Varian Unity 500 spectrometer. The copolymer was dissolved in 10% toluene-d_8–pentafluorophenol at 80 °C.

Spectra were referenced to the toluene solvent. Acquisition parameters were adjusted to the carbonyl carbon of the polymer to maximize signal and ensure accurate integrations. The 90° pulse width was determined to be 12.3 μs and was used throughout. The T1 was first estimated with a pulse saturation experiment to be approximately 3 s. Later, we confirmed this surprisingly short T1 with a standard inversion recovery experiment. Throughout the experiments, a delay of 15 s was used to ensure complete relaxation between transients. Approximately 1920 transients were collected for each sample, giving a signal to noise ratio of ~100. Integration of the diad peaks was performed on standard intervals to ensure consistency (BB, 164.5–164.9 ppm; BN, 165.2–165.7 ppm).

Results and Discussion

High-Temperature Processes in the LC Copolyesters. There appear to be several distinct processes that occur upon heating random copolyesters at elevated temperatures. Annealing at 40–70 °C below the melting point (T_{cn}) leads to a significant increase in transition enthalpy with little change in the melting temperature. Diffusion processes dominate under these conditions, and it is well accepted that ordering occurs by a physical process.[6–8,18,19] ^{13}C NMR analyses of 50/50 HBA/HNA[20] and 73/27 HBA/HNA[10] copolyesters annealed well below the T_{cn} do not indicate any change in diad sequence distribution.

There has been some confusion in the literature as to what happens upon heating the liquid crystalline copolyesters above their T_{cn}. Some workers have claimed that there is no evidence for interchain transesterification reactions (ITR), while others have argued that ITR does occur.[6,12,13] Support for the latter interpretation comes from the work of Kugler et al. who determined by small angle neutron scattering that a mixture of deuterated and protonated PET chains completely randomized after annealing for 1 h at 300 °C.[21] The kinetics of the ester interchange reactions were found to follow an Arrhenius process and calculations reveal that at 280 °C there are 10 transesterification reactions occurring per chain per minute.

More pertinent to the aromatic copolyesters, we reported several years ago that compression molding a 1:1 mixture of the two homopolymers HBA and HNA at 450 °C for 10–15 s yielded a new material melting at ~260 °C, which is near the T_{cn} of a 50/50 random copolymer of HBA/HNA.[20] The ^{13}C NMR spectrum of the compression-molded polymer showed the presence of a random sequence that closely matched the ^{13}C NMR spectrum of the solution-polymerized 50/50 HBA/HNA. It was estimated that at 450 °C the rate of ITR was approximately 1000 interchanges per chain per second. Additional evidence for ITR occurring at lower temperatures was obtained from the polymerization of ^{13}C-tagged HBA with the dimer of HBA/HNA.[9] In this experiment, it was shown that 14% of the ^{13}C-tagged HBA inserted between the HBA/HNA unit during polymerization at 245 °C. From the above results, it is clear that the preponderance of evidence supports the idea of ITR in the nematic melt of a copolyester resulting in a random copolyester.

Additionally, ITR has been shown to facilitate adhesive bond formation between two LCP coatings.[22,23] For coatings of stiff extended chain polymers, good adhesion requires chain diffusion of 2000 Å across the interface between coatings.[24] Chain penetration to this degree is unrealistic in LCP systems. Very recent adhesion studies using neutron reflection measurements of the diffusion of deuterated and nondeuterated cross-linked polyester films show penetration depths of only 125 Å are required to achieve excellent adhesive bonding.[25] ITR must be responsible for adhesion since the necessary chain penetration via diffusion cannot occur.

Possible Interpretations for the 40–75 °C Increase in Melting Point due to Annealing near T_{cn}. Turning now to the nature of the annealing process that leads to a 40–75 deg increase in the melting point of the random copolyesters, it is useful to consider the competing interpretations put forth.

Winter proposes that ordering is due to a physical process that involves the melting of crystallites when annealing near T_{cn}.[6] Melting is followed by nucleation and crystallization of longer ordered sequences already present within the random copolyester. From a simple statistical analysis, we have found that the probability for pre-existing long sequences of ordered units within a two-dimensional array is less than 1%. Hence, this proposal can be ruled out since the long ordered sequences necessary to explain the relatively large transition enthalpies observed for nucleation and growth of crystals are inprobable.[11,26]

Geil suggests that an increase in crystal size and perfection via a physical process is occurring and that the pcl model[14,15] (a two-dimensional model stating that crystallites form as close-packed, random, rodlike chains without identical matching sequences between adjacent chains) is the “appropriate description of the crystalline state of these copolymers”.[13] Contrary experimental evidence includes results that show there is no difference in the DSC traces of annealed samples slow cooled (1 °C/min) from the annealing temperature versus quenched.[26] One would expect crystalline domains with increased size and perfection formed from a physical process would be sensitive to heating conditions, thus slow cooling should result in a larger endotherm.

Yoon argues that the increase in melting temperature during annealing near the T_{cn} is a result of molecular weight increases because of the long annealing times.[12] However, a recent report by Windle shows that when the molecular weight of a 75/25 HBA/HNA copolyester increases from 8600 to 30 000, the increase in melting point is only 12 °C (from 283 to 295 °C).[27] It is

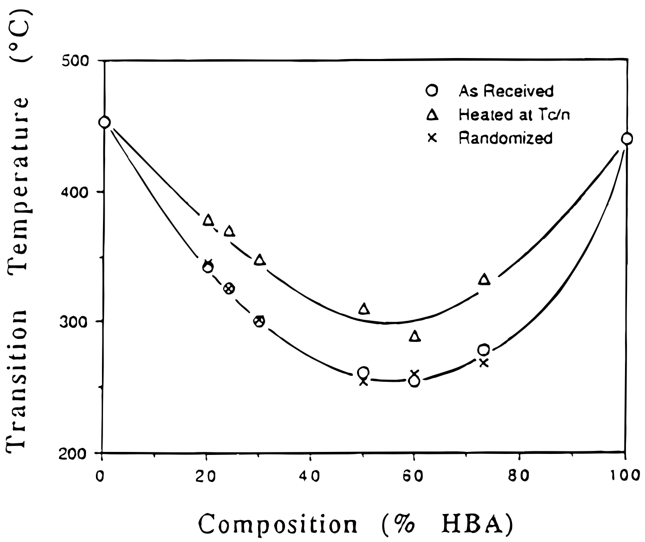

Figure 1. Transition temperatures as a function of composition of HBA/HNA copolyesters.

unrealistic then to attribute changes of 40 °C or more to an increase in molecular weight.

In contrast to the above arguments, one can enumerate several key features that distinguish the random structure from that of the annealed. Annealing HBA/HNA copolyesters near the T_{cn} dramatically increases the transition temperature throughout the entire compositional range, as illustrated in Figure 1.[26] Along with a T_{cn} increase, the microstructure converts from hexagonal to the more ordered orthorhombic.[7] Yoon has noted that the melting transition of the annealed copolymer is best described as a smectic C.[28] In addition, there is a density increase of 6%[29] and a sharp decrease in solubility.[26] All of these points are more consistent with sequence ordering; however, they cannot be considered conclusive.

The ordering mechanism that we propose is limited to the existing crystallites present in the copolyester. Thus, near T_{cn} the end groups have sufficient mobility within the crystallites to facilitate ordering of the microstructure through ITR. These reactions can only occur in the existing crystallites, since in the coexisting nematic melt, randomizing reactions are occurring.[20] The driving force for chemical ordering reactions arise from the improved packing and correspondingly higher density associated with a more ordered structure. ITR allows for improved ordering of sequences, but not necessarily complete ordering. Mobility within the crystallites should drop significantly as the transition temperature begins to increase, limiting the ability of ITR to further order the structure.

It is important to note that these kinds of ordering processes are common to many copolyesters that we have examined. For example, these ordering reactions were found to occur in HBA/BPT copolyesters. Annealing an as-received 2:1 HBA/BPT copolyester ($T_{cn} = 409$ °C) for 5 h at 400 °C increased the transition to 456 °C (Figure 2).[11] Subsequent heating to 460 °C for 10 h followed by annealing at 270 °C for 5 h yielded a randomized structure with a T_{cn} of 359 °C. This structure could be re-ordered by annealing just below the T_{cn}.

Ordering processes are also observed in a non-liquid crystalline copolyester derived from sebacic acid, biphenol, and hydroquinone,[11] as well as a thermoplastic elastomer based on copolyester units.[16]

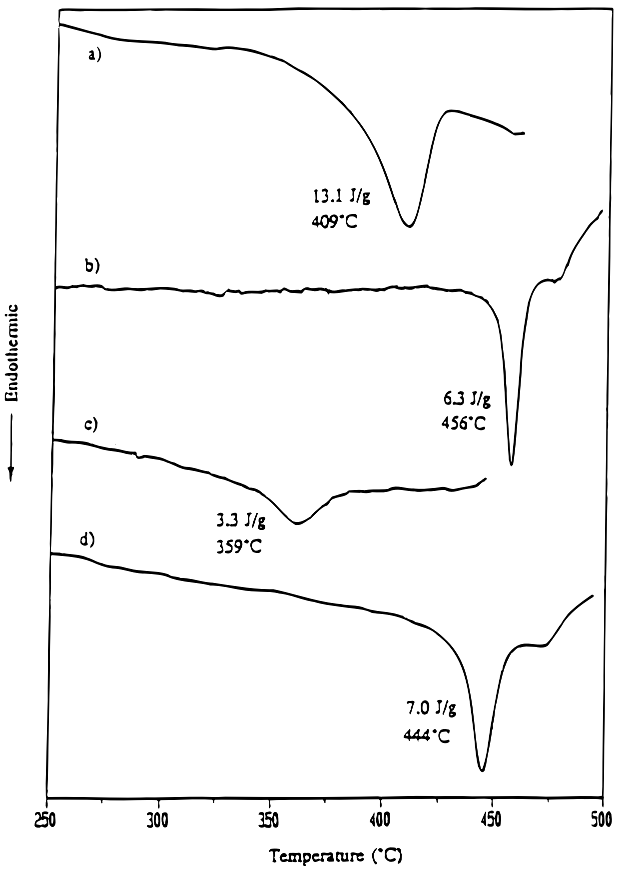

Figure 2. (a) As-received, (b) (a) annealed 5 h at 400 °C, (c) (b) heated to 460 °C for 10 min, followed by annealing 5 h at 270 °C, and (d) (c) annealed 20 h at 349 °C.

Strategy for Proving the Existence of Sequence Ordering. The use of X-ray diffraction techniques to determine the formation of ordered sequences has not proven effective, especially with the HBA/HNA system, due to the relatively low degree of crystallinity in this family of copolyesters. From the transition enthalpies of the annealed random copolyesters examined, the degree of crystallinity is estimated to range from 15 to 20%. Use of ^{13}C NMR techniques with these copolyesters is not easily done because of their low solubility. However, preparing a low molecular weight 50/50 HBA/HNA copolyester in the range of 5000 g/mol increases the solubility dramatically. Our strategy was to prepare the low molecular weight copolyester with the HBA containing a ^{13}C carbonyl carbon. Using ^{13}C NMR, one could then follow the sequence ordering as the concentration of diad sequences changes during annealing.

The as-prepared 50/50 HBA/HNA copolyester had a crystal nematic transition temperature of 241 °C and a transition enthalpy of 2.3 J/g, as shown in Figure 3. The enthalpy peak corresponds to 5% crystallinity based on a highly crystalline homopolymer of HBA ($\Delta H = 46$ J/g).[30] Annealing the copolyester 50 deg below the T_{cn} (190 °C) for 24 h increased the crystallinity from 5% to 16% with little change in T_{cn}. As noted earlier, this increase in crystallinity is due to physical diffusion of the chains. Additional annealing at 230 °C (near the T_{cn}) for 24 h increases the T_{cn} to 264 °C, while the crystallinity decreased from 16% to 9%. Increasing this second anneal temperature closer to the T_{cn} (from 230 to 233 °C) increased the T_{cn} to 276 °C. The effect of increasing the anneal time from 24 to 48 h was also evaluated. DSC results from all of the annealing cycles are shown in Table 1.

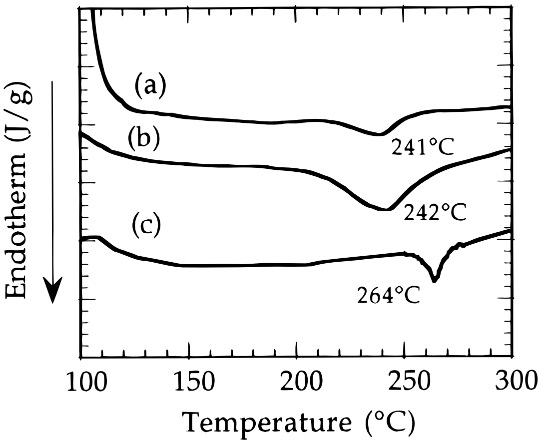

Figure 3. DSC of (a) as-prepared, ΔH = 2.3 J/g; (b) (a) annealed 190 °C for 24 h, ΔH = 7.3 J/g; and (c) (b) annealed 230 °C for 24 h, ΔH = 4.0 J/g.

Table 1. DSC Results of Annealed Samples

sample	T_{cn} (°C)	ΔH (J/g)	% crystallinity[a]
as-prepared	241	2.3	5
(a) 190 °C/24 h	242	7.3	16
(b) (a) + 230 °C/24 h	264	4.0	9
(c) 190 °C/48 h	244	5.7	12
(d) (c) + 230 °C/48 h	268	3.6	8
(e) (c) + 233 °C/ 48 h	276	2.4	5

[a] Based on a fully crystalline homopolymer of HBA (ΔH = 46 J/g).[30]

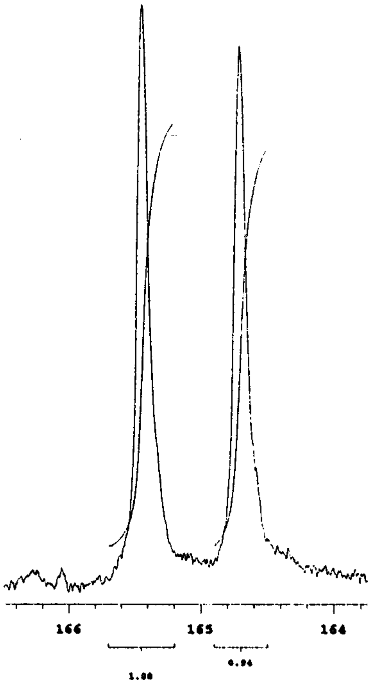

Figure 4. ^{13}C NMR of as-prepared 50/50 HBA/HNA copolyester.

^{13}C NMR of samples annealed at 190 °C for 24 and 48 h (to build up crystallinity) revealed no changes in the benzoic−naphthoic (BN) and benzoic−benzoic (BB) diad ratios. However, the ratio of BN to BB does change upon annealing near the T_{cn}. Figure 4 shows the ^{13}C NMR BB and BN peaks of the as-prepared random copolyester. Table 2 lists the changes which occur upon ordering. The fraction of BN and BB diads initially is 0.515 and 0.485, respectively. Upon annealing near the T_{cn} for 24 h, there is a 1.7% increase in BN diads. This evidence indicates that the sequences are changing from random to alternating during annealing. Since we are only measuring the differences in diad sequences in the crystalline regions (only 9% in this sample), the 1.7% change is significant. Increasing the anneal time from 24 to 48 h further increases the ordering from random to alternating (2.1% increase in BN diads). This evidence proves conclusively that interchain transesterification reactions occur, leading to sequence ordering. It should be noted that these percentages have a range of error of ±0.2, hence the conclusions that have been made are justified.

Table 2. ^{13}C NMR Results

sample	f_{BN}	f_{BB}	% change
as-prepared	0.515	0.485	
190 °C/24 h + 230 °C/24 h	0.524	0.476	1.7
190 °C/48 h + 230 °C/48 h	0.526	0.474	2.1

Table 3. DSC Results of Heating in Nematic Melt and Rebuilding Crystallinity

sample	T_{cn} (°C)	ΔH (J/g)	% crystallinity[a]
(a) 190 °C/24 h	242	7.3	16
(b) (a) + 230 °C/24 h	264	4.0	9
(c) (b) + 400 °C/0.5 min	236	1.8	4
(d) (c) + 190 °C/24 h	234	2.8	6

[a] Based on a fully crystalline homopolymer of HBA (ΔH = 46 J/g).[30]

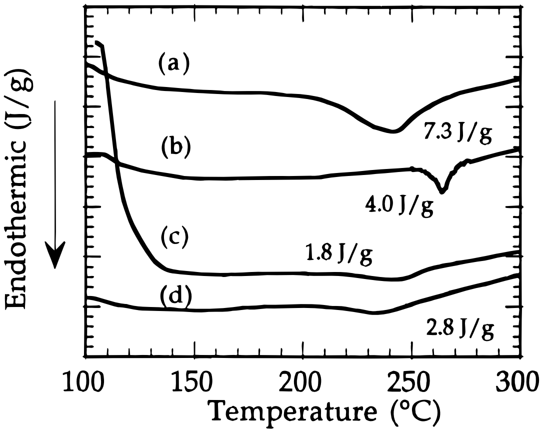

Figure 5. DSC of (a) HBA/HNA annealed 190 °C for 24 h, T_{cn} = 242 °C; (b) (a) annealed 230 °C for 24 h, T_{cn} = 264 °C; (c) (b) heated at 400 °C for 0.5 min, T_{cn} = 236 °C; and (d) (c) annealed at 190 °C for 24 h and 230 °C for 24 h, T_{cn} = 234 °C.

Experiments were also run to confirm that the ordered structure could be randomized upon heating in the nematic melt. The DSC results are listed in Table 3. After heating the ordered copolyester to 400 °C for 0.5 min, we observed a T_{cn} close to its original value (Figure 5). Subsequently, the sample was annealed 50 °C below the T_{cn} to rebuild the crystallinity. The enthalpy peak increased to only 2.8 J/g, much smaller than the enthalpy peak after the initial anneal at 190 °C (7.3 J/g). We partially attribute this inability to rebuild crystallinity to degradation reactions that occur when heating sequence-ordered HBA/HNA copolyesters to 400 °C. Also, we have previously reported that degradation reactions can occur upon further annealing of the ordered HBA/HNA structures near their new transition temperature.[10,11]

Conclusions

^{13}C NMR analysis of the low molecular weight, 50/50, random copolyester of HBA/HNA annealed near the T_{cn} conclusively shows that sequence ordering is occurring. The 2.1% increase in alternating sequences via ITR, which is limited to the crystalline regions, accounts for the dramatic increase in the melting temperature. The change in microstructure from hexagonal to orthorhombic, the increase in density, and the decrease in solubility are all consistent with the proposed mechanism.

Acknowledgment. We thank Dr. Vera Mainz of the Molecular Spectroscopy Laboratory at the University of Illinois at Urbana-Champaign for her advice on ^{13}C NMR experiment setup and analysis.

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MA961900W