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The Degradation Process Observed during Step Annealing of 73/27 HBA/HNA Copolyester

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ABSTRACT: Stepwise annealing near the crystal−liquid crystal transition temperature was applied to a 73/27 4-hydroxybenzoic acid (HBA)/2-hydroxy-6-naphthoic acid (HNA) copolyester to increase the melting transition from 281 to 316 °C. An unexpected degradation process was observed when further annealing was applied at 305 °C. An irreversible loss of crystallinity was confirmed by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). The melt rheology of the step ordered 73/27 HBA/HNA copolyester was investigated using a dynamic rheometer. In contrast to the untreated and ordered sample, the degraded material exhibited an increase in melt viscosity (0.3 orders) after heating at 370 °C for 1 min, indicating some form of irreversible reaction. Furthermore, a plot of storage modulus versus loss modulus showed a completely different pattern for the degraded material. These observations suggest that a small amount of branching or cross-linking has occurred in the 73/27 HBA/HNA copolyester during step annealing at 305 °C. An attempt was made to simulate this process by adding 1 wt % of a cross-linkable oligomer to the 73/27 HBA/HNA copolyester. From the melt viscosity, it could be concluded that a small amount of branching (below 0.5 wt %) has occurred most likely in the crystalline regions of the ordered copolyester.

Introduction

Owing to their excellent thermomechanical properties and high chemical stabilities, a number of applications have emerged for the thermotropic liquid crystalline (TLC) polyesters. The present study on high-temperature annealing was undertaken to provide insight into long-term use of these polymers and to determine whether the sequence distribution in the copolyesters based on HBA/HNA could be further ordered by annealing at higher temperature. In the past decade, considerable efforts[1−4] have been made to understand the effect on the transition behavior of TLC copolyesters. Thus, when HBA/HNA copolyesters are annealed near their transition temperature, the melting point increases by 40−50 °C, and this is accompanied by a change in crystal structure from hexagonal to orthorhombic.[5] This change has been successfully interpreted as a fractional sequence ordering via interchain transesterification reactions (ITR) within existing crystalline regions.[6] As the melting point of the annealed material increased, the rate of ordering due to ester interchain reactions decreased due to increasing immobilization of the chains and end groups.

To further increase the transition temperature, the effect of stepwise annealing near the new crystal−liquid crystal transition temperature was investigated.[7] In fact, the step ordering process has been clearly observed in the HBA/biphenol terephthalate (BPT) series leading to increase in transition temperature of 100 °C.[7]

In contrast to the HBA/BPT copolyesters, the HBA/HNA series displayed an unexpected degradation process. The fact that this degradation process occurred only with HBA/HNA copolyesters suggested that the naphthalene unit might be implicated. One interpretation is that a thermal Fries rearrangement followed by cross-linking at the newly formed phenolic hydroxyl is occurring.[7] These processes would be facilitated by the closer packing of the polyester chains in the orthorhombic structure as compared to that in the hexagonal structure. One should remember that the HBA/HNA copolyester is stable at much higher temperature since it is reportedly prepared with a final polymerization step at 350 °C for 18 h.[8] The closer placement of the adjacent chains in the orthorhombic versus hexagonal or nematic structure would explain the relative instability of the orthorhombic structure at 305 °C versus the stability of these structures during synthesis at 350 °C.

Branching or cross-linking has been demonstrated to have significant effects on the rheological properties of flexible polymers.[9−14] It is well-known that a structural change with very low branching levels can alter the rheological properties in their molten state. Thus, we undertook to examine possible changes in melt rheology to estimate small structural changes due to branching and cross-linking.[15−17]

In this paper evidence is presented proving that some branching and cross-linking are occurring during the step ordering process. The possibility of a thermal Fries reaction proposed by Potter et al.[7] was ruled out in favor of a coupling reaction of naphthalene rings by high-temperature dehydrogenation.

Experimental Section

Materials and Sample Preparation. HBA/HNA (73/27) Vectra A900 (Hoechst-Celanese Corp.) was used in this study. The as-received polymer showed a peak in the DSC at about 282 °C. The polymer pellets were ground into powder and then dried in a vacuum oven at 120 °C for 12 h. The samples were molded into disks ($d = 25$ mm, $h = 1.2$ mm) at 320 °C in a hydraulic vacuum press. These disk-shaped samples were used to measure the transition temperature, wide-angle X-diffraction, and the rheological properties. To magnify the peak

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Table 1. Thermal Properties of the Synthesized 73/27 HBA/HNA Copolyesters Including Oligomer

sample	T_{cn} (°C)	ΔH (J/g)	crystallinity[a] (%)
73/27 HBA/HNA	268	0.89	1.92
73/27 HBA/HNA including 1 wt % oligomer	270	0.31	0.67

[a] Based on a fully crystalline homopolymer of HBA ($\Delta H = 46$ J/g).[19]

intensity of ^{13}C NMR, 50/50 HBA/HNA copolyester was synthesized with ^{13}C-tagged carbonyl in the HBA.[6] The 73/27 HBA/HNA copolyester including 1 wt % of a cross-linkable oligomer[18] was synthesized by melt polymerization. The same procedure was used to produce carboxylic acid (C_1)- and acetoxy (A_1)-terminated thermosetting oligomers. On the basis of the feed ratio, calculated molecular weights, and degree of functionality for oligomers C_1 and C_2, a stoichiometric ratio of reactive end groups could be achieved by mixing 1.1 parts by weight of C_1 with 1 part A_1. This is a reasonable estimate for the production of a stoichiometrically balanced resin mixture based on the NMR characterization of the oligomers discussed.[19] The oligomeric mixture was mixed for at least 1 min in an electric coffee grinder to get adequate mixing and dispersion of the oligomer types. The chemical structures are given in the previous paper.[19] To produce the aromatic copolyesters with and without the thermosetting oligomers, the reactor flask was equipped with a nitrogen gas inlet, a mechanical stirring bar, and a condenser to allow for the collection of acetic acid produced as the byproduct of the condensation reaction between the acetoxy and carboxylic acid end groups. The reactor was purged with nitrogen for 30 min prior to the onset of the reaction. After purging, the reactor was immersed in a salt bath preheated to 300 °C with stirring. After approximately 10 min, acetic acid began to evolve. The reaction continued at 300 °C for 5 h, and then the temperature was raised to 325 °C and held for 10 h. The product was dried in a vacuum oven at 120 °C for 24 h. The thermal properties of the synthesized copolyester are summarized in Table 1.

Annealing. The copolyester disks were annealed in a hydraulic vacuum press under nitrogen atmosphere after extracting the air with vacuum for 10 min. Annealing was carried out at 230 °C for 24 h to increase the amount of crystallinity. Further annealing was carried out at 260 °C for 24 h and 305 °C for 12 h to step order the copolyester crystallites. For the ^{13}C-tagged 50/50 HBA/HNA copolyester, annealing was carried out at 200 °C for 24 h to increase the amount of crystallinity, and further annealing was carried out at 230 °C for 24 h, 260 °C for 24 h, and 290 °C for 12 h.

Hydrolysis. Owing to their limited solubility, the ^{13}C-tagged 50/50 HBA/HNA copolyesters[6] were hydrolyzed in a solution of deuterated methanol, deuterium oxide, and sodium deuterioxide in a ratio of 12:3:1 (CD_3OD:D_2O:NaOD).[20] The polymer concentration was at 3 wt %. The hydrolysis was continued at 70 °C until the sample was entirely dissolved.

Instrumentation. DSC measurements were performed on a TA Instruments DSC 10. Heating rates were fixed at 20 °C/min. All thermal analyses were run under an atmosphere of dry nitrogen.

Wide-angle X-ray diffraction was measured by an X-ray generator (Rigaku Co.). The point focus beam was monochromatized by using Cu Kα target with a graphite crystal. The scan speed was fixed at 5°/min. The conditions were room temperature, 40 kV, and 40 mA. The *d* spacings were calibrated with silicon powder (325 mesh size).

^{13}C NMR measurements were carried out with a General Electric GN500 spectrometer. All spectra, based on 200 acquisitions, were internally referenced relative to methanol.

The oscillatory rheological properties of the HBA/HNA copolyester were measured using a viscometer (Physica, Rheo-Lab MC 120) in a parallel plate type of geometry (12.5 mm in radius and 1.0 mm in gap size) at 320 °C.

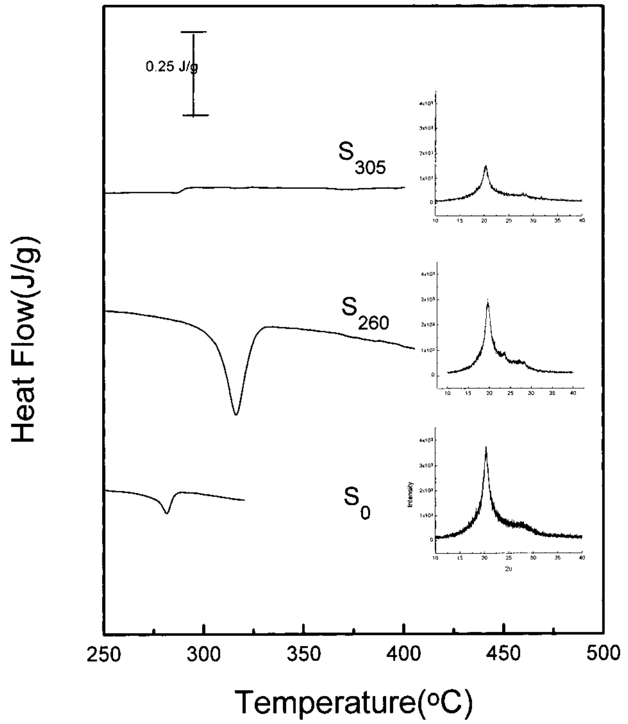

Figure 1. DSC thermograms and WAXD patterns of 73/27 HBA/HNA copolyesters.

Table 2. Summary of DSC and WAXD Results for Annealed Samples

	DSC		WAXD *d* spacing (Å) (2θ)			
sample	T_{cn} (°C)	ΔH (J/g)				
S_0[a]	282	1.05		4.45 (19.90)	3.80 (23.32)	3.15 (28.24)
S_{260}[b]	316	9.13	5.45 (16.10)	4.53 (19.52)	3.90 (22.74)	3.11 (28.62)
S_{305}[c]				4.42 (20.02)		

[a] Untreated sample. [b] Annealed at 230 and 260 °C for 24 h. [c] Annealed at 230, 260 °C for 24 h and 305 °C for 12 h.

Results and Discussion

The Degradation Observed during Sequential Annealing. One of the surprising features for the step ordered HBA/HNA copolyesters is the sharp loss of crystallinity. This kind of process has been observed with the 73/27, 50/50, and 24/76 HBA/HNA copolyesters. DSC thermograms and WAXD patterns of step ordered 73/27 HBA/HNA copolyester are shown in Figure 1. WAXD patterns illustrated the loss of crystallinity in the sample upon further anneal of the ordered materials at 305 °C for 12 h even if the material is not fully amorphous. Scheggenburger[21] reported that the amount of crystallinity in the tested sample had a great effect on the rate of loss of crystallinity. Several 73/27 HBA/HNA films which have different crystallinity were annealed at 305 °C for 12 h. The enthalpy peak of the most crystalline sample decreased to zero while the other samples did not completely lose their crystallinity. The characteristics of the new amorphous 73/27 HBA/HNA copolyester include reduced flow, a decreased solubility in pentafluorophenol, and discoloration.[7] DSC and WAXD results from all of the annealing cycles are shown in Table 2. Possible interpretations of the nature of the thermal degradation process include a thermal Fries rearrangement followed by ITR[7] or a dimerization

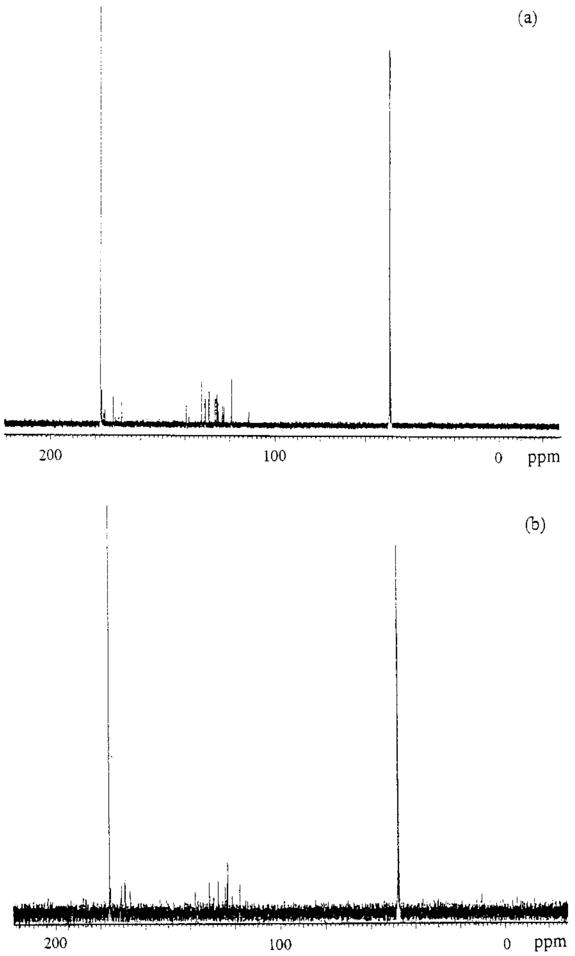

Figure 2. ^{13}C NMR spectra of ^{13}C-tagged 50/50 HBA/HNA copolyester after hydrolyzing: untreated sample (a) and degraded sample (b).

reaction of two adjacent naphthalene rings through hydrogen abstraction.

Since this degradation reaction is only observed with further annealing of the ordered HBA/HNA, it is useful to look at the structure of the ordered phase. Thus, it displays closer chain packing with a change from hexagonal to orthorhombic packing (7% increase in density). The closer chain packing could facilitate intermolecular reactions such as a thermal Fries rearrangement followed by ester interchain reactions of the phenolic hydroxyl with an ester in an adjacent chain. Similarly, the closer chain packing could promote a thermal dehydrogenation reaction of naphthalene rings which would cause branching and cross-linking between chains. Naphthalene is reported to dimerize on heating at 450 °C.[22,23]

In case of the thermal Fries rearrangement, a ketone would form which would be visible at 200−210 ppm. ^{13}C NMR was used to examine the chemical composition of the hydrolyzed ^{13}C-tagged 50/50 HBA/HNA copolyesters before and after step ordering at 290 °C. For the annealed sample at 290 °C the ketone peak was not observed as shown in Figure 2b. This result suggests that no thermal Fries rearrangement has occurred. Potter reported on the ^{1}H NMR spectra for the untreated and degraded samples.[24] It was obvious that changes in the monomer pattern have caused peak splitting in the spectra for the degraded sample. It could also be seen that a decrease in proton peaks within the aromatic ring has occurred. On the basis of the decrease in proton peaks, it seems more reasonable that a coupling reaction through hydrogen abstraction has occurred in the HBA/HNA copolyesters. However, from ^{13}C and ^{1}H NMR results, it was not possible to arrive at an exact placement of the sites on the naphthalene which are more sensitive to dehydrogenation and coupling.

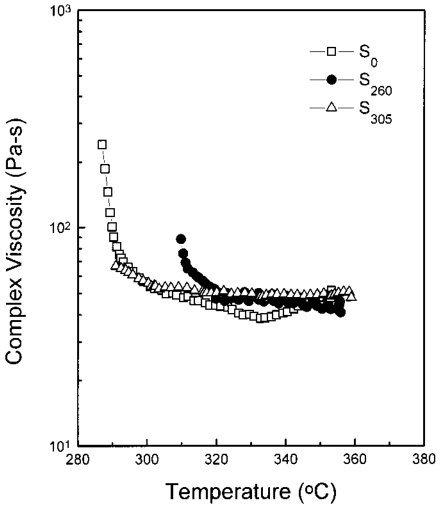

Figure 3. Temperature dependence of complex viscosity at $\omega = 1$ s^{-1}. Scan rate is 20 °C/min.

Rheological Properties of Degraded 73/27 HBA/HNA. Since it is well-known that the rheological properties are very sensitive to structural changes in polymeric materials, the rheological properties of the step ordered HBA/HNA copolyesters were measured using a dynamic viscometer.

On the basis of a recent rheological study,[17] the HBA/HNA copolyesters showed a linear viscoelasticity below strain (γ_0) = 0.1. In this study the strain was fixed at 0.05. Figure 3 shows the temperature dependence of complex viscosity at $\omega = 1$ s^{-1}. The untreated sample (S_0) displayed a melting transition at about 283 °C. For the sample S_{260}, the melting transition increased to 324 °C. Finally, after annealing at 305 °C, there is no melting transition in the heating scan which is in agreement with the DSC results.

Figure 4 shows complex viscosities of the 73/27 HBA/HNA copolyesters. The step ordered sample (S_{260}) displayed a slightly increased complex viscosity. An increase in complex viscosity indicates that the orthorhombic structure formed by annealing near transition temperature is present in the molten state during the measuring period at 320 °C. In addition to an increase in complex viscosity, the degraded material (S_{305}) displayed high shear thinning behavior.

Lin and Winter[3] reported that the rheological properties of the annealed samples display a thermoreversible process which returns to its original state after heating the annealed samples above the crystal−liquid crystal transition temperature. To investigate the thermoreversibility of the degraded HBA/HNA copolyester using rheological properties, measurements were performed for the samples after heating at 370 °C well above crystal−liquid crystal transition temperature. Figure 5 shows the complex viscosities of step ordered 73/27 HBA/HNA copolyesters after heating at 370 °C for 1 min. The randomized sample (S_{260}) displayed a return to the original value. This process can be

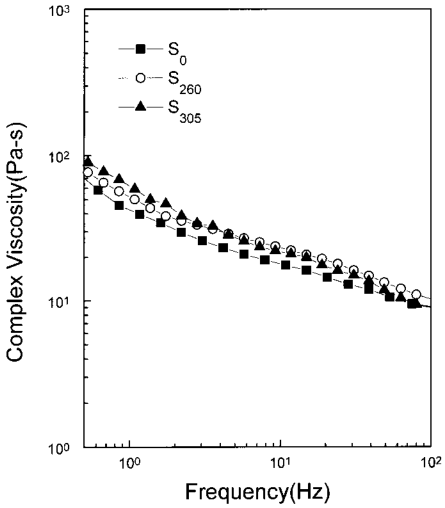

Figure 4. Complex viscosity of 73/27 HBA/HNA copolyesters at 320 °C.

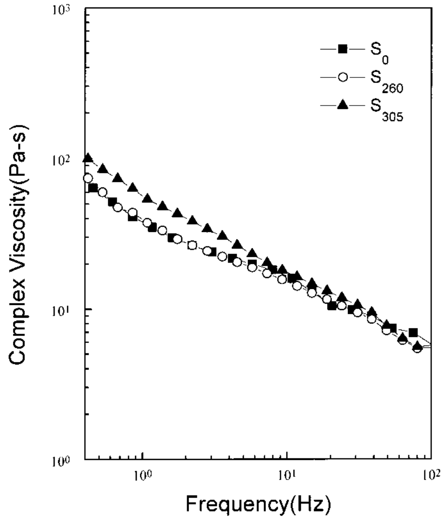

Figure 5. Complex viscosity of 73/27 HBA/HNA copolyesters at 320 °C after heating at 370 °C for 1 min.

described as thermoreversible process; that is, the structure returns to its original random state after heating at 370 °C. After heating the degraded material (S_{305}), however, the copolyester exhibited a slight increase in the complex viscosity in the low-frequency region, suggesting a small thermoirreversible phenomenon. The DSC thermogram of degraded copolyester also shows evidence for a thermoirreversible process (see Figure 6). The fact that the degraded material shows a higher complex viscosity and shear thinning behavior than that of the untreated sample suggests that the step ordering process might lead to a more branchlike structure inducing an increase in entanglement density.

These changes in rheological properties have led to several different interpretations, including an increase in molecular weight due to continued polymerization[9,17,25] and a change in chemical structure**.** Kim and Han[9] reported on the effect of molecular weight on the rheological properties of a thermotropic liquid crystalline polymer with side group and flexible units. The plots of log storage modulus (*G* ′) versus log loss modulus (*G* ″) in the nematic region were seen to lie on a single correlation, independent of molecular weight.

To investigate the effect of molecular weight on rheological properties, the plot of log *G* ′ against log *G* ″ was made for the step ordered HBA/HNA copolyesters as shown in Figure 7. There was a completely different pattern (shift toward left) for the degraded material formed by step annealing at 305 °C. This result indicates that the increase of molecular weight by linear chain growth can be ruled out as the interpretation of the degraded material formed by the step ordering process. Moving toward the left, of course, indicates an increase in elasticity. The elastic property strongly depends on molecular structure properties such as chain branching and cross-linking between chains, and the increase of branching and of the cross-linked portion would explain the increase in elasticity. The influence of molecular weight on the linear viscoelastic properties of the 73/27 HBA/HNA copolyester has been investigated by Rome-Uribe et al.[17] When the dynamic moduli are replotted as storage against loss modulus, the plots of log *G* ′ versus log *G* ″ in the nematic region were seen to lie on a single correlation for two 75/25 HBA/HNA copolyesters having different molecular weights (14 400 and 30 000 g/mol). To further investigate the molecular weight effect, low molecular weight 73/27 HBA/HNA copolyester was synthesized by melt polymerization.

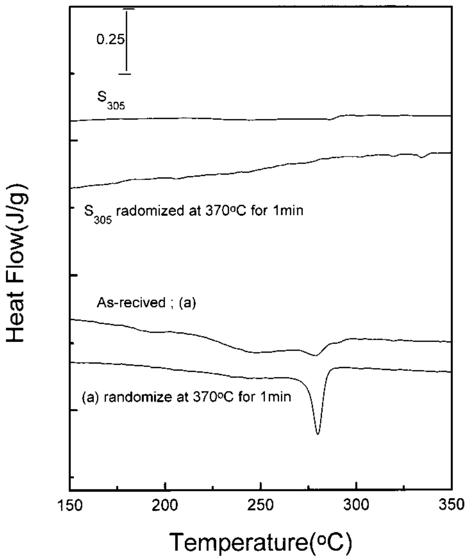

Figure 6. DSC thermograms of untreated sample and degraded sample after heating at 370 °C for 1 min.

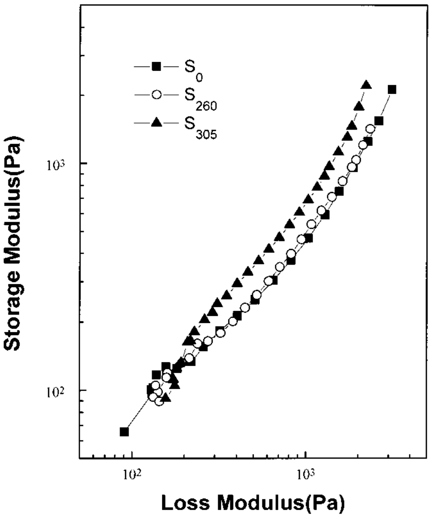

Figure 7. Plots of log G' versus log G'' of 73/27 HBA/HNA copolyesters at 320 °C after heating at 370 °C for 1 min.

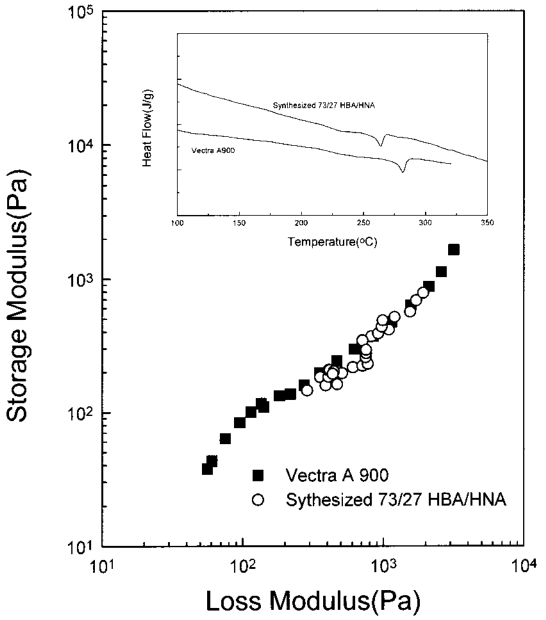

Figure 8. DSC thermograms and dynamic moduli of Vectra A900 and synthesized 73/27 HBA/HNA.

Figure 8 shows DSC thermograms and complex viscosity of commercialized 73/27 HBA/HNA (Vectra A900) and synthesized 73/27 HBA/HNA. The decrease in transition temperature obviously results from the reduction in molecular weight. On the other hand, there is no detectable change in plot of storage versus loss modulus. These results indicate that the increase of molecular weight by linear chain growth can be ruled out as an interpretation of the degraded material formed by the step ordering process.

Unfortunately, because of their insolubility, little progress has been made in characterizing the molecular structure such as long chain branching and cross-linking. On the other hand, the dependence of molecular weight distribution, chain branching, and cross-linking on the rheological properties of flexible polymers has been examined by many researchers.[12–14,26] It is well-known that a branched structure will be produced by dehydrogenation and oxidation when polyethylene is processed at high temperature. Bersted[26] reported that the linear low-density polyethylene (LLDPE) with low branching formed by thermal degradation reaction had a higher complex viscosity compared to that of LLDPE resin without branching. Sheroff et al.[12] reported that, in the case of a different molecular weight distribution (chain branching), a plot of log G' versus log G'' showed a completely different pattern in rheological properties of linear polyethylene. Rheological behavior of flexible polymers provides additional evidence for our interpretation of the degradation mechanism involving chain branching and cross-linking during the step ordering process.

The degraded material that is observed arises from the fact that the degradation reactions can only occur within the orthorhombic crystalline structure. To further investigate this interpretation, the step ordered sample (S_{260}) was further annealed at 330 °C, which is above the new transition temperature (316 °C) for 12 h. The complex viscosity was measured with a dynamic viscometer after annealing at 330 °C for 12 h. Figure 9 shows the complex viscosity of the untreated sample and the annealed sample at 330 °C after randomizing at 370 °C for 1 min. There is no detectable change in complex viscosity between untreated and annealed sample at 330 °C. This result indicates that the degradation must occur only within highly ordered crystalline structure.

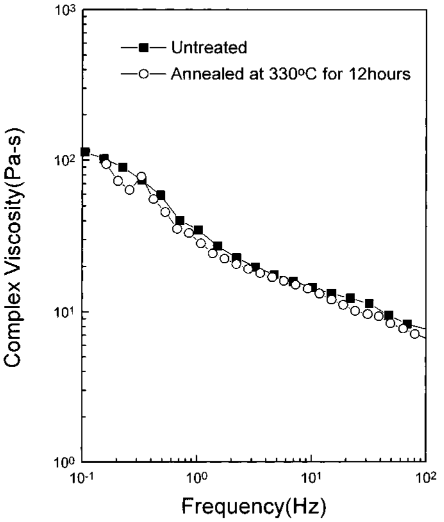

Figure 9. Complex viscosity of the untreated sample and the annealed sample of S_{260} at 330 °C for 12 h after heating at 370 °C for 1 min.

Thermal and Rheological Properties of the Synthesized 73/27 HBA/HNA Including 1 wt % 4-Functional Oligomer. With respect to cross-linking, Mather et al.[27] investigated the effect of cross-linking in the 75/25 HBA/HNA copolyester on the rheological properties by including a cross-linkable terephthalic acid monomer (XTA). They reported that the complex viscosity increased to 2 orders of magnitude by inclusion of a small amount XTA (1 wt %). To simulate the existence of branching and cross-linking within the degraded 73/27 HBA/HNA, the copolyester was prepared with 1 wt % 4-functional oligomer by melt polymerization and characterized by DSC and a dynamic rheometer. In contrast to the degraded 73/27 HBA/HNA copolyester, the copolyester including 1 wt % oligomer displayed 0.67% crystallinity as shown in Table 1. In the case of the degraded copolyester, the branching reactions occurred only within the orthorhombic crystalline structure while the branching structure of the synthesized copolyester would be randomly distributed by melt polymerization.

The rheological properties of the synthesized copolyester involving thermosetting oligomer were measured using a dynamic rheometer at 320 °C. The plots of storage against loss modulus were made for the synthesized copolyester with and without 1 wt % oligomer (see open symbol in Figure 10). The copolyester with 1 wt % oligomer displayed a slight shift toward the left as shown in the degraded 73/27 HBA/HNA copolyester. In general, shifting toward the left indicates an increase in elasticity for the polymeric materials, and an increase in elasticity indicates that branching (or cross-linking) is formed by addition of a thermosetting oligomer in the HBA/HNA copolyester. The complex viscosities of the copolyesters at 320 °C are given in Figure 10. In the low-frequency region, the complex viscosity increased to 0.7 orders of magnitude by inclusion of 1 wt % oligomer. One the other hand, the degraded material displayed a 0.3 orders increase in magnitude as shown in Figure 5. From complex viscosity of degraded material and synthesized HBA/HNA copolyester with 1 wt

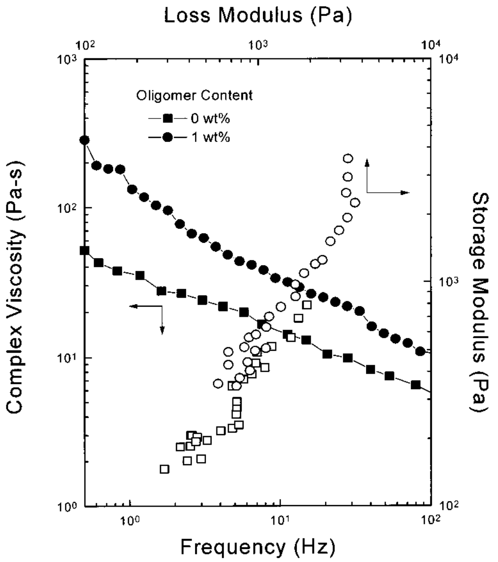

Figure 10. Complex viscosity (close symbol) and dynamic moduli (open symbol) of the synthesized 73/27 HBA/HNA copolyester at 320 °C after heating at 370 °C for 1 min.

% oligomer, it could be concluded that the amount of degradation is very small (below 0.5 wt %).

Conclusion

When a sequence ordered 73/27 HBA/HNA copolyester is further annealed at 305 °C, a thermal degradation reaction occurs (confirmed by DSC and WAXD). The new phase formed by thermal degradation exhibits an irreversible annealing phenomenon such as an increase in melt viscosity at low frequency, high shear thinning, and an increase in elasticity. These degradation reactions occur only within the orthorhombic crystalline structure, and the amount of degraded material is very small (below 0.5 wt %). Even though FT-IR and NMR results could not provide conclusive evidence for the degradation mechanism, these results are all consistent with a dehydrogenation coupling of naphthalene units in adjacent chains leading to chain branching and cross-linking. There is no evidence for a thermal Fries process. The reaction is only observed in the orthorhombic crystalline region where the proximity of the naphthalene rings is increased.

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