and the magnitude of δ of the polymer chain of the gels governed aggregation and the growth of microgels in the process of gel formation.

Conclusion

(1) We found that the logarithm of the exclusion limits of the polyacrylamide terpolymer gels bears a linear relationship to the difference between the value of the solubility parameter of the polymerization solvent and the gels and that the magnitude of δ of the polymer chains of PAAm terpolymer gels governs the aggregation and growth of microgels in the process of gel formation. (2) The surface morphology of terpolymer gels containing a third monomer that had a lower δ value than AAm revealed acceleration of phase separation as the molar ratio of the third monomer to AAm increased.

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(4) The δ values of the monomers used were estimated from the δ values of their homopolymers.

(5) The reason we chosed the solvents was that they did not react with the gels and homopolymers in period of measurement (about 2 months), no self-decomposition occurred, and with respect to hydrogen bonding tendencies of the solvents the contribution fraction $[f_h = [\delta_h/(\delta_d + \delta_p + \delta_h)] \times 100]$ of hydrogen bonding components to δ values of the solvents was between 30 and 50%, in which f_h is the fraction represented by δ_h divided by $(\delta_d + \delta_p + \delta_h)$, δ_d is the dispersion component of δ, δ_p is the polar component of δ, and δ_h is the hydrogen-bonding component of δ.

(6) With regard to the measurement of the δ values of homopolymers and gels containing DMAPMA·HCl or DMAPAA·HCl as a component, mixed solutions of glycerin and water were used as solvents having δ values between 21.1 and 23.4. While there seems to be preferential solvation in aqueous solvents, the extent of this solvation is unknown.

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Registry No. (AAm)(MBAA) (copolymer), 25034-58-6; (AAm)(MBAA)(DMAAm) (copolymer), 125109-64-0; (AAm)(MBAA)(DMAPMA·HCl) (copolymer), 125109-65-1; (AAm)(MBAA)(DMAPAA·HCl) (copolymer), 125109-66-2; (AN)(AAm)(MBAA) (copolymer), 29825-75-0; (AAm)(MAAm)(MBAA) (copolymer), 34364-91-5.

Direct Evidence for Transesterification and Randomization in a Mixture of Homopolyesters of Poly(HBA) and Poly(HNA) above 450 °C

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ABSTRACT: Preparation of blends of the homopolymers of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) has been investigated via compression molding at temperatures up to 460 °C and pressures up to 8 kpsi. It has been found that 1:1 mixtures of finely divided powders of the homopolymers when compression molded under these conditions can transesterify rapidly to form a 1:1 random copolyester. When mixtures of low $\bar{M}_n$ homopolymers (3-5 K) were molded, the conversion to the 1:1 random copolyester was nearly complete. However, for mixtures of high $\bar{M}_n$ homopolymer (>30K) only partial conversion to the random copolyester was observed in the brief time available for processing before degradation reactions ensue. Presumably, the limited conversion is due to the higher viscosity of the melt or the much lower concentration of end groups which act to limit transesterification.

Introduction

Recently, as part of a general study of the properties of liquid-crystalline aromatic polyesters, we decided to examine the formation of blends of homopolymers of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA). In earlier work in this laboratory, attempts to form blends of the various commercial copolyesters were complicated by the large differences in their melting temperatures, melt viscosities, and thermal stabilities. However, the recent observations[1,2] that the homopolymers of HBA and HNA display almost identical thermal transitions, including crystal to liquid-crystal transitions in the temperature range 400–450 °C, prompted us to examine the possibility of forming compatible blends of the two homopolymers at high temperature. Earlier work[3] on melt processing of the HBA homopolymer at 450 °C indicated a stability of several minutes before the onset of degradation and suggested potential for successfully processing mixtures of the two polyesters. We were particuarly interested to see if traditional plastic forming techniques could be used to pro-

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Table I
Sample Preparation

exp no.	compositn of powder	molding conditns
	Low $\bar{M}_n$	
IA	1:1 p(HBA)/p(HNA)	390 °C, 2 kpsi
IB	as above	390 °C, 8 kpsi
IIA	as above	450 °C, 2 kpsi
IIB	as above	450 °C, 6 kpsi
IIC	as above	450 °C, 0.2 kpsi
IID	as above	450 °C, 0 kpsi
	High $\bar{M}_n$	
III	1:1 p(HBA)/p(HNA)	460 °C, 8 kpsi

Table II
Properties of Molded Materials

exp no.	DSC[a] transitn	MW[b]	compositn[b] (HBA/HNA)	transesterificatn obsd
IA	326 °C	~8K	50/50	no
IB	328 °C	~10K	50/50	no
IIA	253 °C	~30K	49/51	near complete
IIB	259 °C	~30K	49/51	near complete
IIC	277 °C	~30K	52/48	near complete
IID	325 °C	~10K	50/50	no
III	350 °C 253 °C	~35K	50/50	partial (35%)
III-f_1[c]	241 °C	~18K	52/48	yes
III-f_2[d]	354 °C	~37K	50/50	no

[a] After annealing 24 h at 205 °C. [b] By ^{1}H NMR. [c] Fraction soluble in PFP (after annealing). [d] Fraction insoluble in PFP (after annealing).

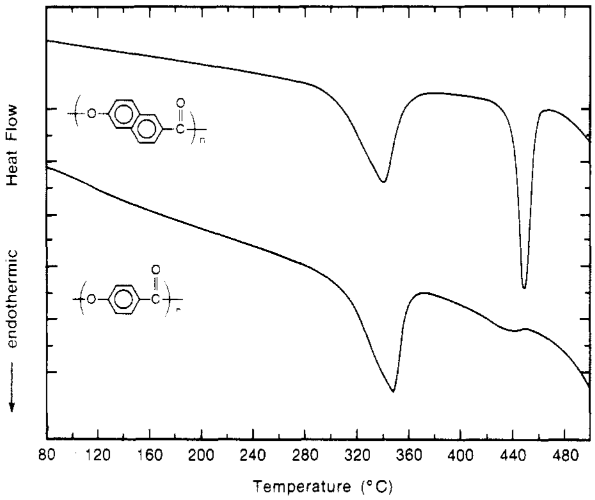

Figure 1. DSC thermograms of the homopolymers of HBA and HNA (heating rate: 40°C/min from ref 2).

duce a fused material before thermal degradation ensued and, if so, what would be the nature of the material produced. For isotropic melts of two polyesters, ester interchange reactions occur that eventually lead to random copolyesters. However, the time constraint on the processing period imposed by the degradation reactions of the homopolyesters at high temperature coupled with the fact that processing takes place in a liquid-crystalline rather than an isotropic state gives rise to a diverse range of possible products from the molding of these polyesters—e.g., a phase-separated system, a compatible blend of the homopolymers, a block copolymer, or a random copolymer. In this paper, we report the finding that transesterification plays a dominant role in determining the nature of the products formed from compression molding of 1:1 molar mixtures of low molecular weight and high molecular weight homopolymers of HBA and HNA at temperatures above the respective crystal–mesophase transitions.

Experimental Section

To explore the formation of blends from homopolymers of HBA and HNA, we prepared experimental samples by using compression-molding techniques as described previously for poly(HBA).[3] The samples selected for the molding experiments were a 1:1 molar mixture of low molecular weight homopolyesters (poly(HBA), DP = 49, and poly(HNA), DP = 18) and a 1:1 molar mixture of high molecular weight homopolyesters (poly(HBA), DP > 156, and poly(HNA), DP > 180). Since these polymers are insoluble in known solvents, samples for molding were prepared by mixing (gentle shaking) finely ground powders of the respective homopolyesters in ca. 1:1 molar ratios.

To carry out the high temperature molding, the mold is preheated (with band heaters located in the sidewalls) to the desired temperature as monitored by thermocouples located in the mold cavity and in an inset in the sidewall. A thermal gradient exists between the cavity and sidewall; thus relative calibration of the two thermocouples is necessary to provide monitoring the cavity temperature during the molding since the thermocouple in the cavity must be removed during the molding. Once the mold is at the desired temperature, ca. 0.8 g of the dried powder (vacuum oven, 60 °C) of the respective homopolymers is introduced into the cylindrical mold. The heaters are then turned off, and the mold is rapidly transferred (ca. 1–3 s) to the press along with the preheated piston for compressing the powders. As an example of a typical molding cycle, the temperature profile in the press of the mold when preheated to ca. 450 °C shows a residence time at maximum temperature of ca. 90–100 s, too brief for any significant decomposition.[3] The mold cools, under continued pressure, to below 100 °C in ca. 1 h, and then the sample is removed. The description of the mixtures prepared for molding, the molding conditions (pressure and temperature), and assignment of an experiment number (to provide a short-hand notation for the discussion of results) are summarized in Table I.

Each molded specimen was characterized by thermal analysis (DSC) using a Du Pont 910 equipped with a 1090 data station and by X-ray analysis. The composition and molecular weight of the molded materials were determined by the method of Kricheldorf and Schwarz[4] that employs hydrolysis of the polyester(s) and analysis by ^{1}H NMR (IBM Instruments NR 250/AF spectrometer operating at 250 MHz for proton observation). Compositional analysis is ±1.0% by this method. Molecular weight determination is based on analysis of the acetoxy end group concentration[2] and is considered accurate for as prepared samples heated to 350 °C. $\bar{M}_n$ values reported for samples heated at 390 °C and higher should be viewed as upper limits of $\bar{M}_n$ values, since the potential now exists for loss of the acetoxy end group by mechanisms other than further polymerization. Molded samples were further characterized by their solubility in pentafluorophenol (PFP) and, if soluble, were examined by ^{13}C NMR spectroscopy (Brüker AM 500 FT-NMR spectrometer operating at 500 MHz for proton observation and 125.8 MHz for carbon-13 observation). The results for the various molding experiments are summarized in Table II.

Results

Each of the homopolymers displays two prominent DSC transitions (see Figure 1): the first at 340–350 °C and the second at 440–450 °C.[1,2] The first transition has been described variously as a crystal–crystal,[1] crystal–condis-crystal,[5] crystal–plastic crystal[1] or crystal–smectic transition.[1] We now lean toward the third interpretation,[2] and thus the second transition can be described as a (one-dimensional)[1] plastic crystal to nematic transition. We presumed the potential for forming a compatible blend would only occur above the second transition. However, to check this hypothesis, we have explored molding above each of these transitions for 1:1 molar mixtures of the low molecular weight homopolymers.

The first moldings were carried out at 390 °C—a temperature well above the first DSC transition but signifi-

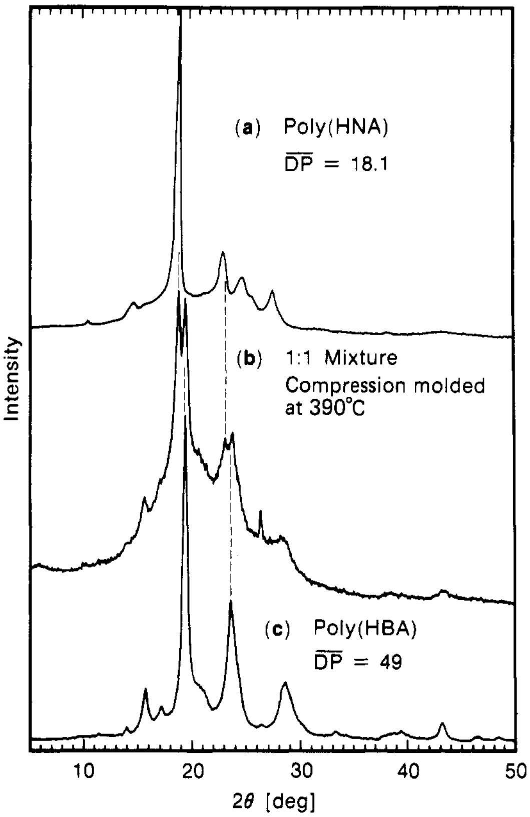

Figure 2. WAXD patterns of (a) low molecular weight poly(HNA), (b) sample IA of 1:1 molar ratio of homopolymer mixture molded at 390 °C and 2 kpsi, and (c) low molecular weight poly(HBA).

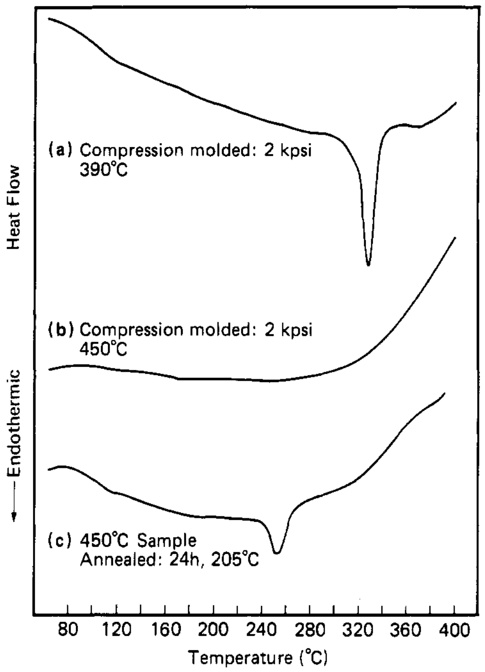

Figure 3. DSC thermograms, heating rate 40 °C/min, of (a) sample IA of 1:1 molar ratio of homopolymer mixture molded at 390 °C and 2 kpsi, (b) sample IIA of 1:1 molar ratio of homopolymer mixture molded at 450 °C and 2 kpsi, and (c) sample in (b) annealed for 24 h at 205 °C.

cantly below the second transition. (The actual temperatures of the first transition for the low molecular weight homopolymers used to produce the mixed powder occur at ca. 310 °C for the HBA homopolymer and at ca. 320 °C for the HNA homopolymer (DSC heating rate 20 °C/min).) The moldings were carried out at 2 or 8 kpsi and, in each case, yielded a brittle, partially sintered material (IA and IB; see Tables I and II) which was insoluble in PFP, a characteristic of each of the homopolymers. The powder X-ray diffraction pattern for the material molded at 2 kpsi (IA) is shown in Figure 2b which demonstrates that the molded material retains the principal features of the X-ray pattern of the two homopolymers (parts a and c of Figure 2). The DSC (Figure 3a) of the material displays an endotherm at ca. 326 °C (heating rate 40 °C/min) consistent with that of the lower temperature DSC transition in the two homopolymers but of somewhat higher molecular weight.[1,2] Proton NMR analysis of hydrolyzed material indicated that the overall composition was 50% HBA units and 50% HNA units—a result consistent with the composition of the initial mixture of the homopolymers. Additionally, the proton data indicated that $\bar{M}_n$ of the material did indeed advance during the molding to about 7900 g/mol, i.e., to about 2 times the mean molecular weight of the unheated, mixed powders. The approximate 2× advancement in molecular weight during the heating of 390 °C is consistent with the higher value observed for the DSC transition of the molded material compared to the initial mixture. In their totality, the results indicate that molding at a temperature well above the first DSC transition but below the second transition of the two homopolymers produces a product essentially the same as a mixture of chain-extended homopolymers. (It should be noted that the increased "background" in the X-ray pattern in Figure 2b over the sum of parts a and c of Figure 2 arises, in part, from the chain extension of the two low molecular weight homopolymers. The mixture of higher molecular weight homopolymers may not have the same degree of crystallinity or crystal perfection as the low molecular weight starting materials whose X-ray data appear in parts a and c, respectively, of Figure 2. A better comparison of background would be that of Figure 2b with that of Figure 7a which is the X-ray pattern from a mixture of very high molecular weight homopolymers. However, there is also a very small amount of transesterification in the 390 °C molding to produce copolyester—see the comment in ref 9. Nonetheless, the increased background of ca. 12% in Figure 2b over the sum of parts a and c of Figure 2 arises primarily from chain extension of the homopolymers.) Similar results were obtained on the material molded at 8 kpsi (see IB in Tables I and II).

A second set of molding experiments were carried out on the mixture of the low molecular weight homopolymers at 450 °C—a temperature above the second DSC transition for each of these low molecular weight homopolymers. The powder was molded at 2 kpsi (IIA) in one experiment and at 6 kpsi (IIB) in a second experiment. In both experiments, the sample almost immediately reached a sufficiently low viscosity that nearly all of it "flashed" into the annulus between the mold wall and the piston. The as-molded material IIA was characterized in a manner similar to IA, and the DSC of IIA shows (Figure 3b) the loss of the prominent DSC transition at 326 °C displayed by the mixture processed at 390 °C (Figure 3a). When sample IIA is annealed at 205 °C for 24 h,[6] an endotherm was observed (Figure 3c) at ca. 254 °C. This is the same temperature range in which an endotherm assigned to a crystal–nematic transition in similarly annealed 1:1 HBA/HNA random copolyesters is observed[6-8] and suggests that transesterification reactions have occurred between the homopolyesters during the molding to produce a copolyester. (We use the term transesterification in a general sense to include intermolecu-

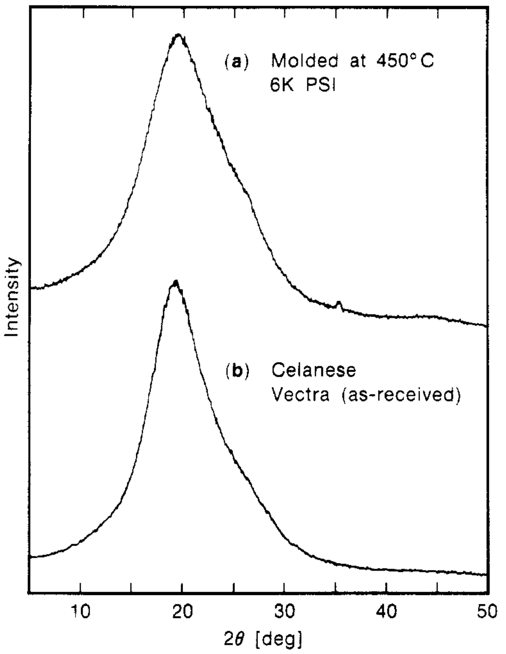

Figure 4. WAXD patterns for (a) sample IIA of 1:1 molar ratio of homopolymer mixture molded at 450 °C and 2 kpsi and (b) Celanese Vectra copolyester powder from as-received material—composition 73/27 HBA/HNA by ^{1}H NMR. (Note that the commercial material is a 3:1 HBA/HNA copolyester while the molded material is an ca. 1:1 copolyester; thus the somewhat greater intensity at higher angle in the X-ray pattern of the molded sample arises from increased HNA content.)

lar acidolysis and intermolecular ester interchange reactions.) Further evidence for reaction is obtained from the WAXD of the molded material (Figure 4a). The diffraction pattern compares directly with that of typical copolyesters of the HBA/HNA family quenched from the nematic melt (Figure 4b) and contrasts to that of the mixture of the low molecular weight homopolymers (Figure 2), where major features of the highly crystalline materials are distinguishable. Furthermore, the fact that IIA was almost completely soluble in PFP is additional evidence for ester interchange between the homopolymers since, as mentioned previously, neither homopolymer is soluble in PFP while copolyesters are soluble. (Insolubility in PFP was also a characteristic of the material molded at 390 °C (IA) and is evidence that, for other than chain extension, little or no transesterification takes place below the second DSC transition of the homopolymers.[9]) Proton NMR data on the hydrolyzed product from IIA yielded a composition of 49/51 HBA/HNA and a $\bar{M}_n$ of >30K, evidence for chain extension during the molding process. Thus, the solubility result, DSC, X-ray, and ^{1}H NMR data suggest that during the molding above 450 °C extensive transesterification occurred to produce a copolyester that has a higher $\bar{M}_n$ than the homopolymers.

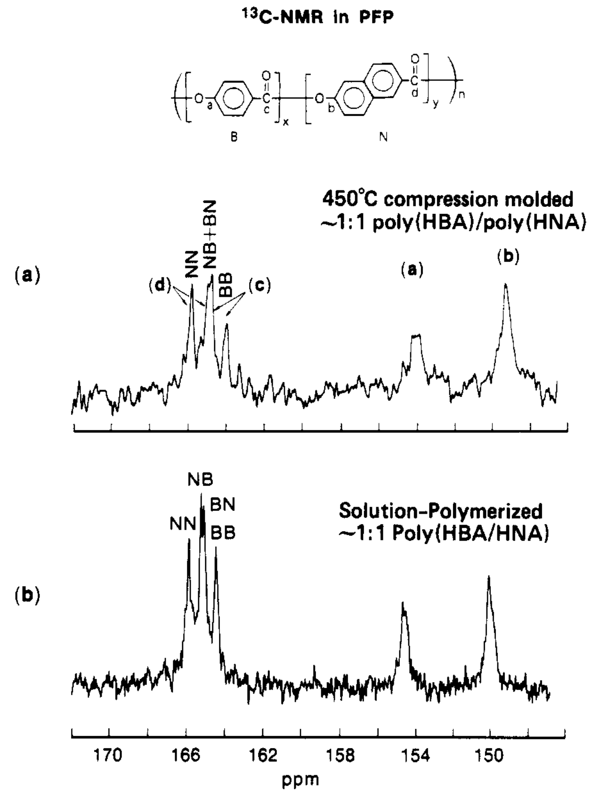

Figure 5. Carbon-13 NMR spectra in PFP at 80°C of (a) sample IIA of 1:1 molar ratio of homopolymer mixture molded at 450 °C and 2 kpsi and (b) a solution-polymerized HBA/HNA copolyester of 48/52 composition. Dyad sequences are indicated on the spectra. Chemical shifts are relative to TMS corrected for temperature effects.

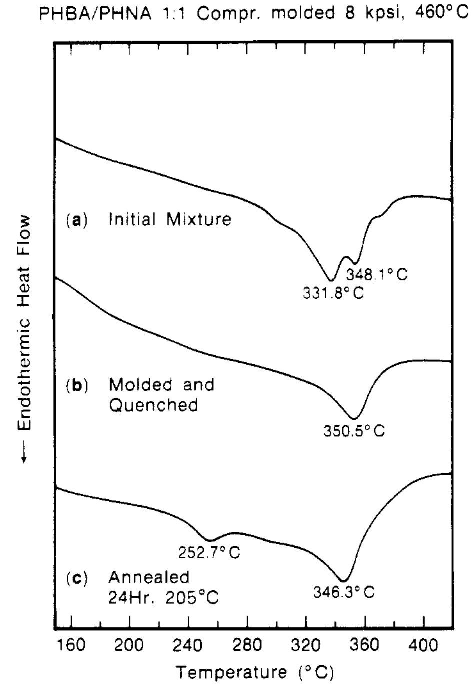

Figure 6. DSC thermograms, heating rate of 40 °C/min, for (a) sample III prior to molding, (b) sample III of 1:1 molar ratio of mixture of high molecular weight homopolymers molded at 460 °C and 8 kpsi, and (c) sample in (b) annealed at 205 °C for 24 h.

Definitive evidence that transesterification occurred during the molding at 450 °C and 2 kpsi is provided by the ^{13}C NMR results (Figure 5a) on IIA. In a related study, we have shown[7] that carbon-13 spectra can be obtained for solutions of HBA/HNA copolyesters in PFP and that the carboxyl carbon region of the ^{13}C spectrum of these copolyesters is sensitive to dyad sequences of the polymer chain. In that study, the four observed carboxyl resonances were unequivocally assigned to the four possible dyad arrangements using a combination of selectively ^{13}C-enriched copolyesters and different compositions of copolyesters. The spectrum of an ca. 1:1 HBA/HNA solution-polymerized (in Therminol)[7] copolyester is given in Figure 5b for comparison to that of the molded material IIA. The fact that the spectrum of IIA displays the presence of four carboxyl resonances and, in particular,

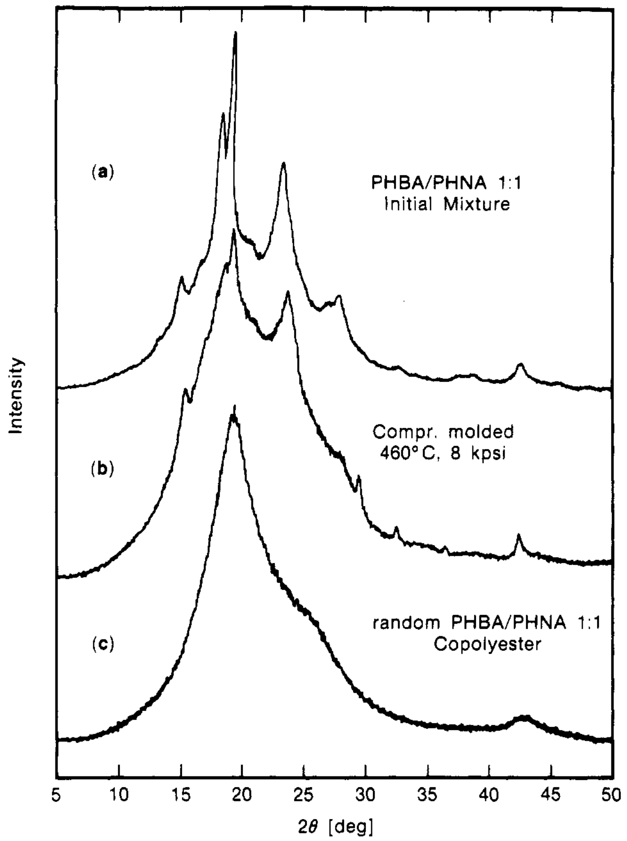

Figure 7. WAXD patterns of (a) mixture of high molecular weight poly(HBA) and poly(HNA) in 1:1 molar ratio, i.e., III prior to molding, (b) III of 1:1 molar ratio of mixture of high molecular weight homopolymers molded at 460 °C and 8 kpsi, and (c) high molecular weight 1:1 HBA/HNA copolyester.

resonances that are assigned to NB and BN dyads is unequivocal evidence for the transesterification during the higher temperature molding. Furthermore, the relative intensities of the resonances (Figure 5a) from the four dyads in the ^{13}C NMR spectrum are consistent with a sequence distribution from a random copolyester of 45/55 composition as is obtained from the proton data on the PFP-soluble material.

Results similar to the 2-kpsi molding were found for molding of the two low molecular weight homopolymers at 450 °C and 6 kpsi (IIB). Indeed, even a reduction of 10× in molding pressure (200 psi) produces a transesterified product at 450 °C (IIC). Although the actual molding pressure does not appear critical to the transesterification, application of some pressure to the mixture is necessary to produce a copolyester as witnessed by the result that heating the low molecular weight homopolymer mixture at 450 °C without the application of pressure results in little or no transesterification (IID) as assessed by DSC, X-ray, and insolubility in PFP. Thus, these results give rise to a picture in which the role of pressure is not to drive the reaction but only to produce the physical conditions under which reaction can proceed—i.e. to bring about intimate contact of the homopolymer powders and/or force the materials into liquid-crystalline melts from which reaction ensues.

Compression molding the mixture of the higher $\bar{M}_n$ homopolymers above their respective second DSC transition produced molded materials that had a dual nature. When the 1:1 mixture of HBA (DP > 156) and HNA (DP > 180) homopolymers was compression molded at 460 °C and 8 kpsi, a fused solid and some flash was produced (III). The solid and flash were ground to a powder, and a portion of the sample was annealed at 205 °C for 24 h. DSC of the as-molded and annealed powders (parts b and c of Figure 6) both showed an endotherm in the range ca. 345–350 °C characteristic of high molecular weight homopolyesters (Figure 6a) while the annealed sample also showed a smaller endotherm at ca. 253 °C, characteristic of a copolyester. The X-ray data (Figure 7b) appears to correspond to a superposition of the pattern from a mixture of the crystalline homopolymers (Figure 7a) and that of a copolyester (Figure 7c). These data are consistent with some, but far from complete, transesterification having occurred.

The transition enthalpies for the annealed compression molded product III provide a consistent picture of the dual nature of this sample. In previous work, we have annealed several 1:1 HBA/HNA random copolyesters at 205 °C for 24 h and have consistently found an enthalpy of ca. 4.2 J/g associated with the 250–260 °C transition in these copolyesters; e.g., a value of 4.2 J/g is found for the molded product IIA after annealing. Thus, comparison of the enthalpy (1.47 J/g) of the 253 °C transition in III to that of a fully 1:1 random copolyester (4.2 J/g) annealed under the same conditions gives an estimate of 35% random copolyester in sample III. This result is in excellent agreement with a value of about 35% random copolyester estimated from analysis of the WAXD spectrum (Figure 7b).

Further evidence of the dual nature of sample III was the finding of partial solubility in PFP (ca. 10% after 1 week at 100 °C). The soluble material (recovered from PFP) had a 52/48 HBA/HNA composition and $\bar{M}_n$ = 18K; the insoluble part had a 50/50 HBA/HNA composition and $\bar{M}_n$ = ca. 37 K. These data compare to the composition and molecular weight of III as-molded of 50/50 HBA/HNA content and an $\bar{M}_n$ > ~35K. After annealing, the DSC of the soluble part showed a 241 °C transition (Figure 8b) characteristic of a copolyester while the DSC of the insoluble part (Figure 8a) showed the ca. 350 °C transition of the pure homopolymers. Thus, there is direct evidence that part of the material has undergone transesterification to a random copolyester during the molding.

Discussion

The picture that emerges from this study is that the homopolymers of HBA and HNA at a relatively low molecular weight undergo extremely rapid transesterification in the nematic melt to yield random copolyesters of an increased molecular weight. Driven by an entropic process, the transesterification results in a copolyester of random sequence distribution. If the homopolyesters do not enter the nematic melt (where compatibilization or good interfacial contact can occur), no significant intermolecular transesterification takes place as evidenced by the results observed for molding at 390 °C.[9] The molecular weight advancement observed during the 390 °C processing occurs by polymerization of each homopolymer in the solid state as has been reported previously.[4,10]

For the molding above the crystal–nematic transition, it is not clear whether the two melts interdiffuse so that complete mixing takes place followed by chain extension and chain reorganization or that there is only interfacial contact but sufficient that transesterification rapidly produces copolyester, whose low viscosity enhances mixing with the remaining homopolymer chains, bringing about complete interchain reaction and chain reorganization. The results of molding the high molecular weight homopolymers, where only partial transesterification is observed, do not provide definitive data to dis-

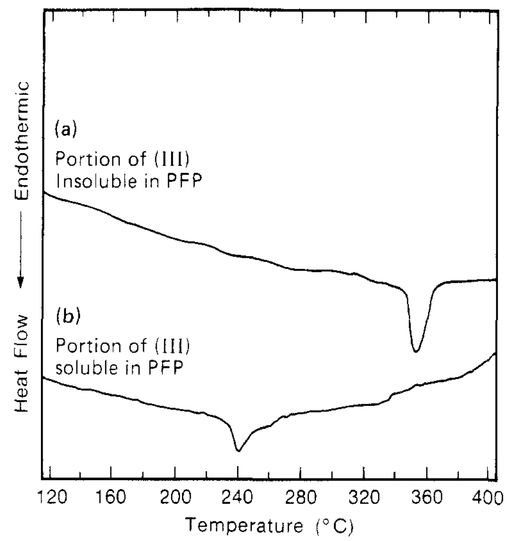

Figure 8. DSC thermograms, heating rate 20 °C/min, for (a) portion of III after annealing at 205 °C for 14 h that was insoluble in PFP and (b) soluble portion from III after annealing.

criminate among these mechanisms. If transesterification is initiated by end groups, then the reduced copolyester formation for molding of high molecular weight homopolymers may result from the many fewer chain ends compared to the low molecular weight mixture. However, incomplete mixing may well be the major contributor to the reduced copolyester formation as a much "stiffer" nematic melt is attributed to high molecular weight poly(HBA).[1] In this case, transesterification could take place at the interfaces between the polymers that results in miscible copolyester; however, the translational mobility of the remaining chains or chain segments is insufficient for complete reaction during the brief time at high temperature. A longer time at the high temperature could possibly promote further reaction; however, significant degradation ensues after ca. 5 min.[3]

Since the pressures applied in this study do not play a significant role in the transesterification process, it is reasonable to inquire as to whether the very rapid conversion (complete in <90 s) to copolyester we have observed[11] can be accounted for by standard transesterification kinetics or if it is peculiar to the anisotropic melt. The tendency for polyesters to undergo transesterification in the isotropic melt is well-documented in the literature.[12] Indeed, ester interchange in the melt forms the basis for production of poly(HBA/PET) and other liquid crystalline copolyesters. For these systems, ester interchange continues to take place in the anisotropic melt. Several studies[13-16] in the literature have found the kinetics of transesterification to be governed by an Arrhenius process with an activation energy in the range 130–150 kJ/mol. In a very recent study, Kugler et al.[13] have used neutron scattering to show that deuterated polyethylene terephthalate (PET) undergoes an ester interchange reaction with the undeuterated PET during melt pressing of their blends. Temperature studies over the range 250–280 °C yielded an activation energy of 152 kJ/mol for transesterification in PET. These workers presented an expression to calculate the number of transesterifications per molecule at a given temperature. If we assume the Arrhenius process holds for higher temperatures and use the lower temperature transesterification rate data of Kugler et al.,[13] we calculate a number of transesterifications/molecule of ca. 7–10K for a period of 90 s at 460 °C. Thus, it is clear the number of interchanges at 450 °C (in a melt state) are sufficient to produce a random copolyester during the short processing period. Times in the range of 100 s to produce random copolyester at 460 °C are consistent with the times of 2–3 h required to produce completely random copolyesters from melts of two homopolyesters, as observed for a number of systems, in the temperature range 250–275 °C.[16] Thus, mixtures of low molecular weight homopolymers of HBA and HNA molded under moderate pressure at a temperature above their transition to a nematic melt rapidly undergo transesterification reactions to produce a random copolyester (of extended molecular weight) in a manner similar to that reported for PET in the isotropic melt.[13]

The random copolyesters IIA–IIC produced in the nematic melt appear contradictory to several other reports in the literature. For example, Lenz et al.[17] reported a tendency for ordering of the aromatic copolyesters in the nematic melt (crystallization induced reaction). They also reported that this tendency decreases sharply as one approaches the nematic–isotropic transition. On the basis of Lenz's work, one might conclude that the nematic state has sufficient structure to confer ordering rather than randomization. It would therefore be surprising to observe rapid randomization occurring in poly(HBA) and poly(HNA) systems even under our molding conditions. However, the work of Lenz et al.[17] can be interpreted on the basis that the liquid crystalline copolyesters with which they worked have a distribution of ordered units even though the sequence distribution appears to be random. The longer strings of ordered units have the potential to exist as higher melting nuclei above the observed crystal to nematic transition. Hence they can act to nucleate further ordering by ester interchange in the nematic melt.[18] This process competes effectively with the tendency for randomization at temperatures just above the crystal to nematic transition. On the other hand, at higher temperatures, these incipient crystallites disorder and the potential for ordering is sharply reduced. Also, it should be noted that the ordering reported by Lenz et al. involves only 5–15% of the material, starts from a random copolyester, requires (usually) an ester interchange catalyst, and requires long time periods (>hours) to develop any significant amount of ordered material. In the case of the molding of the HBA and HNA homopolymers, none of these conditions hold and entropic considerations dominate to produce the random copolyester.

De Meuse and Jaffe[19] have reported that a stirred nematic melt of two liquid-crystalline copolyesters of HBA/HNA differing only in composition yields a compatible blend of the polyesters. The basis for the conclusion was the appearance of a single DSC transition at lower temperature than either component of the blend, e.g., a 50:50 blend of poly(HBA/HNA) of 30/70 composition (endotherm at 305 °C) and 75/25 composition (endotherm at 291 °C) produced a material having an endotherm at 236 °C. They ruled out transesterification in the melt to produce random copolyester based on the fact that the torque on the melt measured at constant mixing speed did not change during the mixing once the torque reached a steady value. Unfortunately, they did not present the actual temperature of the melt, the time scale for the mixing, nor any final compositional or sequence data. Thus, it is unclear whether or not transesterification could have taken place in their studies and account for their observations. In any event, it is clear in our study that rapid transesterification does take place between the homopolyesters under our experimental conditions.

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Conformation of Comblike Liquid-Crystalline Macromolecules

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ABSTRACT: We have determined the conformation of side-chain liquid-crystalline polymers in nematic solutions by small-angle X-ray scattering. We have shown that the macromolecules are conformationally anisotropic. Moreover, the direction of anisotropy has been determined: the macromolecules are prolate ellipsoids ($R_\parallel \vec{n}_0 > R_\perp \vec{n}_0$), where $\vec{n}_0$ is the mean field nematic director. The form of the anisotropy and its magnitude appear to be independent of the coupling strength of the side groups to the backbone for relatively long spacers ($3 \leqslant n \leqslant 6$). The isotropic sizes R_i are large compared to an ordinary polymer with the same degree of polymerization. We have also measured the radius of gyration in an ordinary solvent (toluene) and found that the results are consistent with the nematic case. These results allowed us to point out an effect of the polymer concentration of the absolute sizes of polymer chains in ordered solutions but not on the form of the anisotropy or its magnitude. The results are consistent with an independent viscoelastic study reported on these materials and with the Brochard assumption that explains the typical nematic rotational viscosity behavior in these systems. We have compared these results with a recent theoretical approach by Warner et al.; there is a qualitative agreement between our results and the major points outlined in this model. Thus the correlation between mesomorphic order and anisotropy of chains is meaningful.

I. Introduction

The study of side-chain liquid-crystalline polymers has advanced considerably in recent years. The intense interest motivated by industrial applications has been stimulated by two factors: a wide variety of such materials has been designed by using advanced chemical reactions and new experimental and theoretical physical approaches have been made.[1-7] In fact these molecules have two conflicting properties: flexibility of the backbone, an aspect of conventional polymers, and nematic constraints due to the pendant groups that tend to orient the system because of the orientational order of mesomorphic materials.

Many structural studies of these systems in the melt phase have been reported, in either the smectic or the nematic state, depending on whether the investigated system shows one or more mesophases.[8-13] For instance, the arrangement of the side groups and that of the spac-

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