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# THERMOTROPIC POLY(ESTER-AMIDES) BASED ON NAPHTHALENE MONOMERS.

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Abstract: The structure and properties of a range of thermotropic poly(ester-amides) derived from 2,6-naphthalene derivatives is described. Many of these polymers may be melt-processed into fibers, monofils, and molded structures having very attractive physical and mechanical properties. A variety of monomers has been used and structure/composition/property relationships are described along with details of synthesis and processing conditions. Both fibers and molded articles may be heat-treated to enhance their tensile properties. Molded articles and extruded rods have exceptional tensile moduli in the unfilled state.

## INTRODUCTION

Thermotropic polyesters are by now well-known materials and a large volume of literature exists on their synthesis and structure/property relationships. This has been reviewed by several authors[1-4]. Two of these aromatic polyesters have been commercialized as molding resins. Dartco division of Premark manufactures XYDAR®, a copolyester of terephthalic acid(TA), 4,4'-biphenol(BP) and 4-hydroxybenzoic acid(HBA)[5] while Hoechst Celanese Corporation produces VECTRA® which is a copolymer based upon 6-hydroxy-2-naphthoic acid (HNA)[6]. Other manufacturers in Europe and Japan are introducing new thermotropic polyesters.

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During the development of the VECTRA series of resins, extensive research was made into comonomers with other than ester forming units. Of these the most promising were a series of thermotropic copoly(ester-amides) based upon 6-hydroxy-2-naphthoic acid in combination with aromatic diamines or aminophenols and dicarboxylic acids. This paper describes the synthesis and properties of these novel copolymers.

## Background

As soon as the first HNA copolyesters were made at Celanese, thoughts were already being given to copolymers with alternative linking groups to the ester unit, one of which was the amide unit. This was as early as March 1977. At that time the goal of the liquid crystal polymer work was a high modulus organic fiber for in-rubber reinforcement applications. Polymers were sought that are comparable in mechanical properties to DuPont's aromatic polyamide KEVLAR®, but that were melt processable.

An objective of our work was to produce polymers that could be adhered to rubber. Even as the first melt-spinnable, aminolytically and hydrolytically stable, high performance polyesters were being produced on a small scale, there was concern that fiber-to-rubber adhesion might be inadequate. The remarkable chemical inertness of the polyesters, highly advantageous in resisting in-rubber degradation during vulcanization, might be expected to complicate the adhesion process. One obvious way around this would be to incorporate some adhesive-reactive units into the polymer chain. The amide unit was a natural choice, since the well-tried resorcinol/formaldehyde/latex adhesives work very well with polyamide fibers, possibly via

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N-methylol units[7]. It was also felt that the presence of some amide units might improve the structure/property profile of the fiber by adding a measure of inter-chain hydrogen bonding.

## Previous Work

Several patents have disclosed the preparation of aliphatic/aromatic poly(ester-amides)[8-12]. In addition Jackson and Kuhfuss[13] have described their work on liquid crystal poly(ester-amides) as an extension of their work on the thermotropic block copolymers of polyethylene terephthalate (PET) and poly(oxybenzoyl), usually referred to by the code name "X-7G". They acidolyzed PET polymer with 4-acetamidobenzoic acid (PABA) in the melt in exactly the same way as they had used 4-acetoxybenzoic acid (ABA), and subsequently re-polymerized the reaction product to give a PET/PABA block copolymer. The molded resin containing 25 moles percent of, PABA units had quite attractive properties. Noteworthy was a flex modulus of 0.76 Mpsi. However, despite a melting point of 254 C, the actual deflection temperature was low: 88 C at 264 psi.

While our studies were under way, McIntyre and coworkers at Leeds University, England, published their work on thermotropic copoly(ester-amides) derived from p-aminophenol and various alkoxyterephthalic acids. One interesting composition was the homopolymer from 1,2- bis(4-carboxyphenoxy)ethane and 4-(N-methylamino)phenol, which melted at 280 C[14-15].

## SYNTHETIC STUDIES

The thermotropic copolyesters developed at Hoechst Celanese were synthesized via an acidolysis route by reaction of the

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diacetate of a diphenol with a dicarboxylic acid, or by self-condensation of the acetate esters of aromatic hydroxy-acids [1,2,16]. Normally the acidolysis of amide units is a somewhat sluggish process [11,12] but in the case of N-acetylated aromatic amines, the reaction in our hands proceeded smoothly enough under normal melt polymerization conditions at up to 330 C.

The polymerization reactions were run in the melt under an argon atmosphere in a simple stirred three-neck flask, heated in an oil bath and controlled by a thermostat. For example, polymers prepared from 6-acetoxy-2-naphthoic acid (ANA), terephthalic acid (TA), and p-acetoxyacetanilide (AAA) were typically polymerized at a reaction scale of 0.5 to 3 molar. For still larger runs, a fluidized bed sand bath with microprocessor temperature control was used with special glass vessels up to 5 liters capacity. A gradual temperature ramp over several hours from about 230 degrees C to a final temperature of 300-330 degrees C was used, the latter stages being done under high vacuum to remove final traces of volatile by-products. During the early stages, acetic acid distilled over rapidly and the yields of acetic acid recovered were usually 90-95 percent theoretical. As the reaction proceeded, the melt became opaque and showed the shear-opalescence phenomena typical of other thermotropic polymer melts.

At the end of the polymerization reaction, the stirrer was withdrawn and the melt allowed to cool and solidify. It was removed by breaking the flask and the solid lump of polymer scraped and filed free of glass slivers, sawn up into chunks and finally ground to a powder for further processing. The polymers were very typical of thermotropic polymers in texture. They were tough and "woody" with a

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definite fibrous fracture. They were very similar in appearance to the polyester analogs, but were rather more yellowish, probably as a result of slight oxidative degradation at the high temperatures involved. It was noticeable that these polymers darkened more readily in air at high temperatures.

Few difficulties were encountered in scaling up the process to the 5-gallon autoclave scale and thence to a 50-gallon unit. The polymer was extruded as a ribbon into a water quench bath and chipped (e.g., Cumberland strand chopper). Possibly due to more efficient handling in the autoclave, the polymer color was often somewhat better than on the laboratory scale.

## CHARACTERIZATION

### Thermal Analysis

Samples melted on the polarizing hot-stage microscope between crossed polarizers showed typical nematic structures in the molten phase. It was usually impossible to observe a clearing-point or isotropic transition, as this transition was so high that the polymers thermally decomposed before reaching this point.

Characterization by DSC (Perkin Elmer DSC 2) utilized a sample of approximately 10 mg, heated at a rate of 20 C per minute (calibrated with an indium standard) from room temperature to above the melting point endotherm (eg. 350C); nitrogen was employed as the purge gas. The peak of the endothermic transition was recorded as the melting point of the polymer.

The thermal stability of the polymers was investigated

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on a DuPont 990 Thermal Analyzer by temperature programmed thermogravimetric analysis (TGA), using a temperature rate increase of 15 degrees C per minute. The polymer from 60/20/20 ANA/TA/AAA had essentially the same stability in a nitrogen atmosphere as in air; 3% weight loss occurred at 479 C in air and 482 C in nitrogen.

Solution and Melt Viscosity

Solution viscosities were measured in pentafluorophenol at 60 C at a concentration of 0.1% wt/vol. Those poly(ester-amides) with free amide (-CONH-) units had the characteristic high inherent viscosities (e.g.2-10) of liquid crystal aromatic polyesters. However, those copolymers with alkylated amide units had much lower solution viscosities. Since the mechanical properties of polymers with alkylated amide units were comparable to polymers synthesized with free amide units, it was assumed their molecular weights were of the same order.

Melt viscosity was determined on an Instron capillary rheometer at 300 C using a 4 in. x 0.03 in. die. For example, the melt viscosity of polymers from ANA/AAA/TA were typically within a range of 1800-2200 poise (for inherent viscosities of 5-6) when measured at a shear rate of 1000 cm-1.

## POLYMER PROCESSING

The polymers were dried for 24 hours at 130 C and a vacuum of 1 Torr prior to spinning. Fibers were spun through a single hole spinneret of 0.178 mm diameter and 0.254 mm in length. The fiber wind-up speed ranged from 100 to 1000 meters per minute. Typically filaments of 5 denier per fil

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were selected for testing. Fiber properties were determined at 21 C on an Instron Testing machine, using a gauge length of 2.54 cm and a strain rate of 20% per minute. Reported values are the average of 5 breaks.

Multifilament spinning utilized a 10 hole spinneret. Twenty strands of 10 fil yarn (5 denier per fil) were plied to form 1000 denier yarn.

Tensile and flexural test specimens were molded in an Arburg Model 221/150 injection molding machine, equipped with an 18 mm diameter screw. Barrel temperatures of 300 - 330 C were used; the mold was at ambient temperature. Flexural testing was conducted at room temperature on an Instron Testing Machine according to ASTM D790. Tensile testing of Type V tensile bars followed the procedures of ASTM D638.

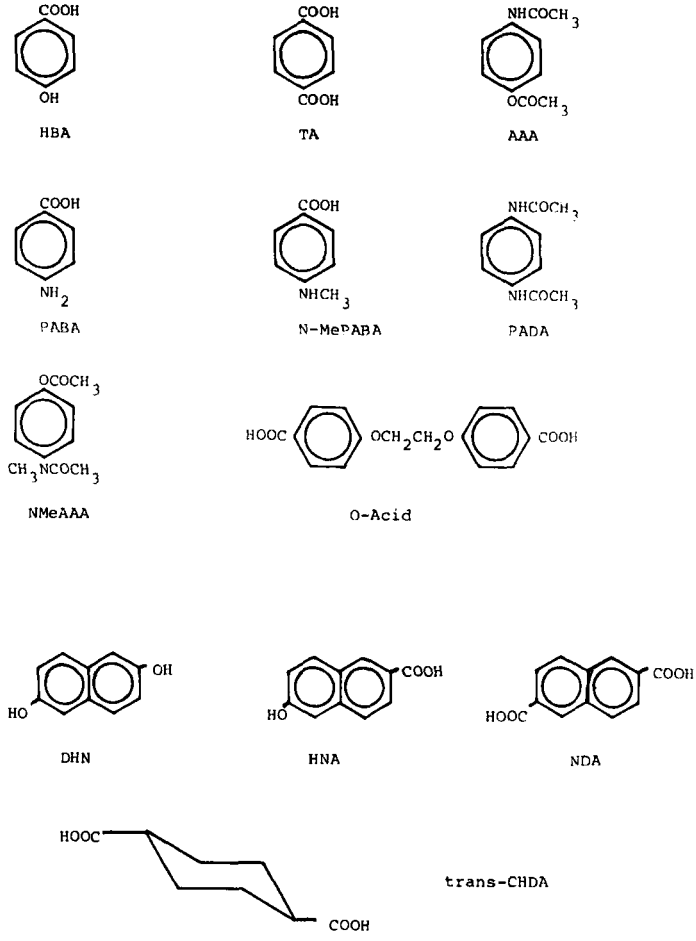
## STRUCTURE-PROPERTY RELATIONSHIPS

The copoly(ester-amides) described in this study were prepared from the N-acetyl derivative of an amino aryl acid, aminophenol or aromatic diamine. Some typical monomer structures shown in Figure 1. The molar proportion of amide units was deliberately kept low. It was reasoned that too high a molar percentage of amide links might result in the formation of intractable compositions of very high melting-point. However it was found possible to incorporate up to 30 moles percent of amide links using the appropriate comonomers.

### Polymers from 4-Aminophenol

One particularly useful monomer was the O,N-diacetyl derivative of 4-aminophenol, p-acetoxyacetanilide or "AAA". This

FIGURE 1. Monomers for Polyester Amides

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molecule has the advantage that it is dissymmetric; it introduces head-head/head-tail randomization which in turn gives an added "copolymer effect". Several copoly(ester-amides) from 6-acetoxy-2-naphthoic acid (ANA), acetoxyacetanilide (AAA) and terephthalic acid (TA) were prepared (Table I). A graphical representation of melting-point/composition for the polymers from 6,2-ANA, AAA and TA is shown in Figure 2; the lowest melting composition was a 60/20/20 copolymer with a melting point of 280 C.

Other dicarboxylic acids were used in place of terephthalic acid. The two most interesting alternative acids were 1,2-bis(4-carboxyphenoxy)ethane (O-Acid), and trans-1,4-cyclohexanedicarboxylic acid (CHDA) - see Figure 1. The copoly(ester-amides) made from these acids and their as-spun properties are set out in Table I.

The O-Acid copoly(ester-amide) was the only case found in our studies where the nematic-isotropic point could be observed directly. The solid polymer melted to a nematic liquid crystal phase at 256 C and the nematic-isotropic clearing point was at 451 C. This was confirmed by DSC thermograms. The CHDA copolymers had low softening points but no clearing points were observed. The properties of the two examples made are comparable with our own results on thermotropic polyesters derived from this alicyclic diacid: it gives polymers with a high degree of liquid crystalline character (note the high values for the inherent viscosity) combined with rather low solid-mesophase transition temperatures. This agrees with the properties of small-molecule liquid crystals based upon 1,4-cyclohexylene units described by Gray and McDonnell[17]. Bhaskar et al.[18] have also confirmed this trend in their studies on thermotropic polyesters containing cyclohexane-1,4-dimethanol units.

TABLE I COPOLY(ESTER-AMIDES) BASED ON p-ACETOXYACETANILIDE

| Composition, monomers | Ratio, molar | IV, dL/g | Tm, C | Ts, C | T/E/M[a] |
|---|---|---|---|---|---|
| HNA/TA/AAA[b] | 60/20/20 | 4.2 | 280 | 315 | 9/2.0/620 |
| HNA/TA/AAA[c] | 60/20/20 | 4.1 | 280 | 330 | 10/2.5/600 |
| HNA/TA/AAA | 50/25/25 | 5.1 | 325 | 360 | 10/2.2/625 |
| HNA/TA/AAA | 70/15/15 | 5.9 | 293 | 360 | 8/2.1/570 |
| HNA/TA/AAA | 80/10/10 | 4.3 | 360 | 375 | 8/1.9/510 |
| HNA/TA/AAA | 85/7.5/7.5 | d | 385 | 400 | 6/1.2/765 |
| HNA/O/AAA | 60/20/20 | 3.4 | 256 | 330 | 7/2.3/443 |
| HNA/CHDA/AAA | 60/20/20 | 6.5 | 185 | 370 | 3/1.3/240 |
| HNA/CHDA/AAA | 40/30/30 | 4.8 | 270 | 331 | 7/2.5/350 |

Tm = Polymer melting point.

Ts = Polymer spinning temperature.

a) T/E/M = Tenacity/Elongation/Modulus in grams/denier, elongation %, and grams/denier.

b) Small laboratory polymerization in glassware.

c) Five gallon stainless steel autoclave polymerization; single filament testing of 10 denier yarn.

d) Insoluble

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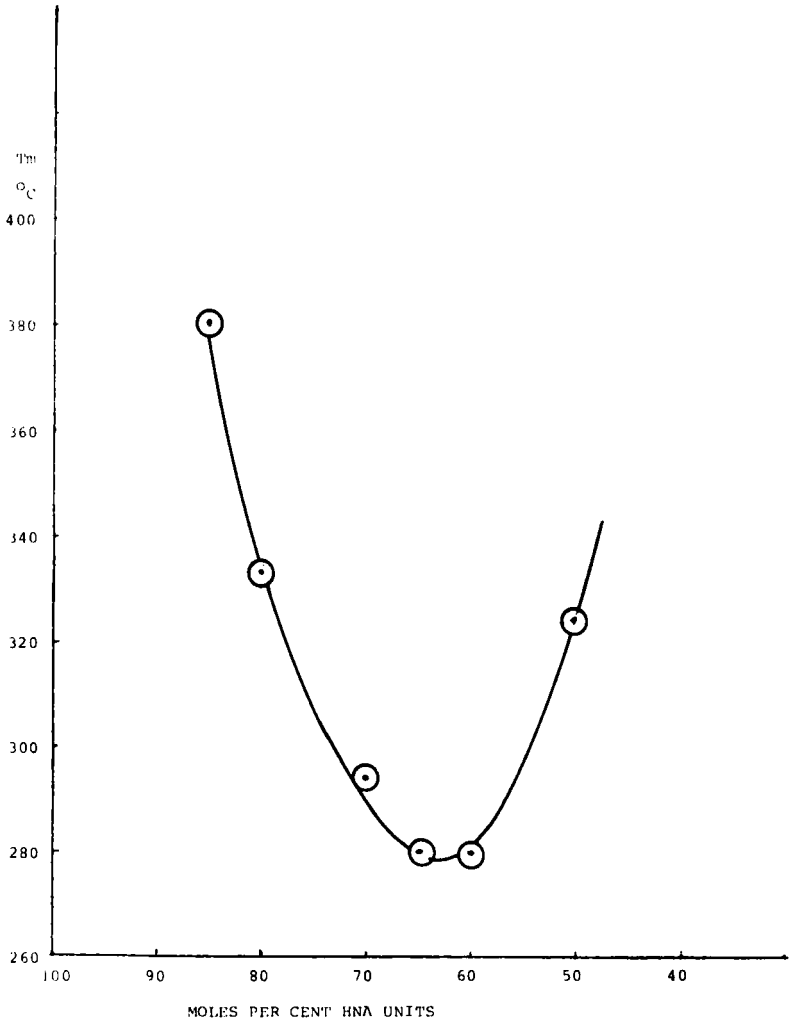
FIGURE 2. Melting Point vs HNA Content for Copolymer of HNA/AAA/TA.

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Polymers from 4-aminobenzoic acid

Copoly(ester-amides) derived from hydroxy-acids and 4-aminobenzoic acid (PABA) were obvious early candidates for evaluation, as all the monomers were of the AB type. Although the incorporation of p-aminobenzoic acid was examined at the start of the program, early results were not very encouraging. In fact, better fiber properties were obtained from 4-(N-methylamino)benzoic acid copolymers (see Tables II and III). At a later date, however, much better tensile results were obtained. One reason may be that the earlier work used 4-acetamidobenzoic acid recrystallized from boiling water[19] whereas the later work used material recrystallized from hot glacial acetic acid. It is conceivable that slight hydrolysis of the acetamido unit might lead to traces of PABA being present. Subsequent decomposition of the free amino-acid at elevated polymerization temperatures would lead to "dead" polymer chains and this might account for differences in the ability of the fibers to undergo heat-treatment.

The Effect of N-Alkylation

N-Alkylated poly(ester-amides) were examined to see whether the removal of hydrogen bonding between amide units on adjacent chains would affect polymer properties. In fact there was little effect on physical properties where direct comparisons could be drawn (see Tables II and III). The most notable effect was that the N-methylated poly(ester-amides) had much lower solution viscosities. However their mechanical properties suggested strongly that their molecular weights were similar to those of the non-methylated polymers, and that differences in molecular conformation in solution were the cause. We have not yet investigated this with light-scattering measurements, but one may hypothesize

TABLE II COPOLY(ESTER-AMIDES) BASED ON p-AMINOBENZOIC ACID

| Composition, monomers | Ratio, molar | IV, dL/g | Tm, C | Ts, C | T/E/M |
|---|---|---|---|---|---|
| HNA/HBA/PABA | 60/20/20 | 4.8 | 272 | 376 | 6/1.6/490 |
| HNA/HBA/PABA | 60/30/10 | 7.9 | 272 | 328 | b |
| HNA/HBA/PABA | 37.5/37.5/25 | 4.2 | a | 345 | 9/1.9/640 |
| HNA/HBA/PABA | 50/25/25 | 5.9 | a | 360 | 9/2.0/623 |
| HNA/HBA/PABA | 35/35/30 | 1.0 | 320 | - | b |
| HNA/PABA | 70/30 | c | 343 | - | b |

a) No endothermic melting point.

b) Polymer was unspinnable.

c) Polymer was insoluble.

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TABLE III COPOLY(ESTER-AMIDES) BASED ON N-METHYLATED MONOMERS

| Composition, monomers | Ratio, molar | IV, dL/g | Tm, C | Ts, C | T/E/M |
|---|---|---|---|---|---|
| HNA/HBA/NMePABA | 60/20/20 | 1.6 | 295 | 330 | 8/2.3/500 |
| HNA/HBA/NMePABA | 60/10/30 | 1.0 | 310 | 360 | 7/2.1/431 |
| HNA/HBA/NMePABA | 50/25/25 | 1.8 | 285 | 345 | 9/2.0/635 |
| HNA/NMePABA | 60/40 | 0.8 | 360 | - | a |
| HNA/TA/NMeAAA | 60/20/20 | 1.8 | 265 | 392 | 5/1.5/370 |
| HNA/TA/HQ/NMeAAA | 60/20/10/10 | 1.4 | 280 | 331 | 8/2.2/510 |

a) Polymer was unspinnable.

TABLE IV COPOLY(ESTER-AMIDES) BASED ON P-PHENYLENE DIAMINE

| Composition, monomers | Ratio, molar | IV, dL/g | Tm, C | Ts, C | T/E/M |
|---|---|---|---|---|---|
| HNA/TA/HQ/PDA | 60/20/15/5 | 4.1 | 273 | 330 | 6/1.5/543 |
| HNA/HBA/TA/PDA | 24/56/10/10 | 5.6 | 300 | 345 | 5/1.3/450 |
| HBA/NDA/IA/HQ/PDA | 60/10/10/10/10 | 1.6 | 297 | 331 | 1.5/1/180 |
| HBA/HNA/TA/DHN/PDA | 20/20/30/25/5 | 2.8 | 283 | 344 | 4/1.3/375 |

HQ = Hydroquinone.
DHN = 2,6-Naphthalene diol.
NDA = 2,6-Naphthalene dicarboxylic acid

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that these polymers may fall into the category of "worm-like" polymers[20].

Greenwood et al. have investigated thoroughly the properties of N-methylated all-aromatic polyamides and have shown that N-alkylation reduces crystallinity, lowers the glass transition temperature (Tg), raises solubility and improves thermal stability[21]. In the case of the poly(ester-amides), much less drastic changes result upon alkylation of the amide nitrogen than are shown by simple aliphatic nylons[22]. We suggest that there is not a high degree of interchain H-bonding in our thermotropic copoly(ester-amides), due to a combination of chain stiffness and the relative infrequency of amide units on adjacent chains making such interaction difficult due to lack of access.

### *Polymers from p-Phenylene Diamine*

Several copoly(ester-amides) were made from p-phenylenediacetamide. Here a new factor became apparent. Because two amide-units are present on one rigid unit the level of monomer was perforce limited to about 10 percent molar. Even so, the copolymers were less tractable and had less attractive fiber properties (see Table IV). The comonomer is symmetrical, and does not provide the randomizing effect that AAA does. Further the amide units appear to be concentrated in short blocks rather than being scattered along the chain.

## UTILITY

### Fiber Properties

Since the early thrust of this work was concerned with

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high-performance fibers, all the early work was devoted to melt-spinning the polymers into fibers (Tables I-IV), heat-treating them and evaluating the product for tenacity, extension to break and modulus (Table V). Those polymer compositions which did melt-spin usually spun very well, either on a small single-hole micromelt unit or on a larger multi-hole laboratory machine fitted with a small screw extruder (e.g., compare entry #1 and #2 in Table I). Indeed the 60/20/20 HNA/TA/AAA polymer was spun as ten filament yarn for many hours continuously without a break and the spun-yarn bobbins plied up to give a 1000 denier yarn which heat-treated to yarn tenacities of 27 grams/denier (entry #2 of Table V).

Tenacities of heat treated filaments often exceeded 20 grams/denier and the initial modulus was over 600 grams/denier. Individual single breaks over 30 grams/denier were noted and 1000 denier multifilament yarn was heat-treated to give yarn tenacities of 27 grams/denier, with a modulus of 650 grams/denier and a break extension of 5%.

Of note were those polymers with high levels of ANA units. The polymer with 85 moles percent ANA melted at 380 C and was melt-spun successfully at 400 C. The high melting point of this composition enabled it to be heat-treated at higher temperatures in shorter times. As little as ten minutes at 350 C gave tenacities of 30 grams/denier; similar properties were given by conventional heat-treatment temperatures over much longer times (Table VI). Thus the possibility of a continuous on-line fiber heat-treatment process was realized.

## Molding Resin

At about this time in the development of the project,

TABLE V HEAT TREATED FILAMENT PROPERTIES

| Composition, monomers | Ratio, | T/E/M(AS)[a] | HT,[b] | T/E/M(HT)[c] molar |
|---|---|---|---|---|
| HNA/TA/AAA[d] | 60/20/20 | 9/2.0/620 | 300/4 | 30/6.6/580 |
| HNA/TA/AAA[e] | 60/20/20 | 10/2.5/600 | 280/48 | 27/5.2/650 |
| HNA/TA/AAA | 50/25/25 | 10/2.2/625 | 300/8 | 24/4.3/650 |
| HNA/TA/HBA/AAA | 30/20/20/20 | 7/1.9/520 | 300/8 | 20/4.0/525 |
| HNA/HBA/PABA | 60/20/20 | 6/1.6/490 | 290/15 | 11/3.0/450 |
| HNA/HBA/NMePABA | 60/20/20 | 8/2.3/500 | 285/15 | 17/4.3/530 |
| HNA/HBA/NMePABA | 60/10/30 | 7/2.1/430 | 300/8 | 14/3.4/480 |

a) Tenacity/Elongation/Modulus, as-spun filament properties in grams per denier, elongation %, grams per denier.

b) Heat Treatment conditions in degrees C and hours.

c) Tenacity/Elongation/Modulus, heat-treated filament properties in grams per denier, elongation %, grams per denier.

d) Entry #1 from Table I.

e) Entry #2 from Table I; single filament testing of 1000 denier yarn.

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TABLE VI RAPID HEAT TREATMENT OF FILAMENT FROM 85/7.5/7.5 : HNA/TA/AAA

| As-Spun Fiber Properties: | | | |
|---|---|---|---|
| Sample # | Tm, C | Ts, C | T/E/M/D |
| 1 | 373(400)[a] | 399 | 9.6/2.3/580/5.8 |
| 2 | 373(390)[a] | 389 | 7.7/1.6/595/2.4 |

| Heat-Treated Fiber Properties: | | | |
|---|---|---|---|
| Sample | HT Temperature, C | HT Time, hours | T/E/M |
| 1 | 350 | 0.16 | 30/5.2/666 |
| 2 | 350 | 0.16 | 29/4.6/662 |
| 1 | 323 | 8.0 | 30/5.3/671 |

T/E/M/D = Tenacity/Elongation/Modulus/Denier per fil

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interest began to be shown in thermotropic polymers as high performance molding resins and one of the earliest to be evaluated was the 60/20/20 HNA/TA/AAA polymer. A large glassware batch (3 molar scale) was molded into "mini" test-bars on a small injection molding machine. The resulting tensile tests on the unfilled polymer were outstanding. Most notable was a tensile modulus of well over 4 million psi, a breaking load of 36000 psi, a flex modulus of 2.1 million psi and a notched Izod value of 5.8 ft-lb/in.(see Table VII). Other compositions were examined and a copolymer incorporating p-aminobenzoic acid, namely HNA/HBA/PABA:60/20/20, (made according to the improved method) gave very good properties also. A copolymer of HNA/TA/AAA in the ratios 80/10/10 gave excellent tensile strength with a high deflection temperature of 260 C at 264 psi.

Monofil Extrudates

It was discovered that the HNA/TA/AAA: 60/20/20 copolymer had moduli superior to any of the all-polyester thermotropic polymers in the form of thick extruded monofils. Typically a 0.030" rod had no more than 1% elongation under a 60 lb load. Hence the load bearing properties equaled those of a pultruded glass/epoxy rod.

The reason for the outstanding modulus of this composition emerged during some extrusion studies performed by S. Kenig[23]. In brief, the poly(ester-amide) is oriented more effectively by extensional flow fields than is an all-polyester liquid crystal composition. When extruding thick monofils, where the flow conditions are not so highly conducive to good molecular orientation, the poly(ester-amides) nevertheless still emerge with sufficient

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TABLE VII COPOLY(ESTER-AMIDE) PROPERTIES AS MOLDED MINI TENSILE BARS

| Composition, monomers | Ratio, molar | IV, dL/g | Tm, C | DT, C | T Str, Kpsi | T Mod, Mpsi | E, % | F Str, Kpsi | F Mod, Mpsi | Izod a |
|---|---|---|---|---|---|---|---|---|---|---|
| HNA/TA/AAA | 80/10/10 | 6.0 | 333 | 260 | 38 | 3.2 | 1.6 | 33 | 1.9 | 6.6 |
| HNA/TA/AAA | 60/20/20 | 6.3 | 280 | 195 | 36 | 4.4 | 1.2 | 32 | 2.1 | 5.8 |
| HNA/TA/AAA | 50/25/25 | 3.3 | 319 | 206 | 34 | 3.2 | 1.3 | 33 | 1.9 | 3.9 |
| HNA/TA/NMeAAA | 60/20/20 | 0.8 | 264 | NA | 19 | 2.3 | 1.0 | 23 | 2.0 | 1.2 |
| HNA/HBA/PABA | 60/20/20 | 3.7 | 293 | 170 | 36 | 3.5 | 1.4 | 21 | 3.2 | 3.5 |

DT = Distortion Temperature at 264 psi.

a) Ft-Lb/in.

molecular order to exhibit the desirable high tensile moduli.

Jaarsma recently disclosed the use of liquid crystal polyesters as non-metallic rivets, notably for bonding graphite fiber reinforced composite panels. The rivets are strong, light-weight and do not suffer from galvanic corrosion, in contrast to aluminum rivets[24]. The heads of the rivets are formed by an ultrasonic forging process. Hence the high modulus of poly(ester-amides) extruded rods suggests that they may also find utility as mechanical fasteners.

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## Matrix Resins

The poly(ester-amide) compositions developed at Hoechst Celanese have been investigated as thermoplastic matrix resins in high-performance composite structures. The work is described in a recent paper by Chung and McMahon[25]. The results indicated that the low zero shear melt-viscosity of the thermotropic poly(ester-amide) leads to excellent wet-out of the carbon fiber reinforcement in a novel melt-impregnation process. The resulting prepregs were then laminated into high quality composites. The tensile and flexural properties of these were as good as epoxy/carbon-fiber composites up to 200 F. and had better impact properties. However there were deficiencies in compressive and shear strengths. Poor matrix-fiber interfacial adhesion may be the cause.

## CONCLUSION

The novel poly(ester-amides) described in this paper were developed originally for fiber use and indeed they have

excellent properties as high modulus and high strength melt-spun fibers. However, during the course of our investigations, the excellent injection molded and extruded monofil properties of these materials were also recognized.

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REFERENCES

1. G. W. Calundann and M. Jaffe, In Proceedings of the Robert A. Welch Conferences on Chemical Research, XXVI, Synthetic Polymers, (1982); Chapter VII.
2. T-S. Chung, Polym. Eng. and Science, 26(13), 901-919, (1986).
3. C. Ober, J-I. Jin, and R. W. Lenz, Adv. Polym. Sci., 59, 103 (1984).
4. M. G. Dobb and J. E. McIntyre, Adv. Polym. Sci., 60-61, 61-98, (1984).
5. A. S. Wood, Modern Plastics, 62(4), 78-80, (1985).
6. J. R. Dole, CHEMTECH, 17 242-45 (1987)
7. R. H. Moult, In Handbook of Adhesives; I. Skeist Ed.,Reinhold: New York, NY, 1962; Chapter 42; p496.
8. J. R. Caldwell, US Patent 3 272 776, 1966.
9. J. R. Caldwell, US Patent 3 440 218, 1969.
10. J. R. Caldwell and R. Gilkey, US Patent 3,522,328, 1970.
11. J. R. Caldwell and R. Gilkey, US Patent 3,546 178, 1970.
12. J. R. Caldwell and W. J. Jackson, Jr., US Patent 3 598 864, 1971.

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13. W. J. Jackson, Jr. and H. F. Kuhfuss, J. Appl. Polym. Sci., 25, 1685-1694, (1980).
14. J. E. McIntyre and A. H. Millburn, Br. Polym J., 13, 5-10 (1981).
15. J. E. McIntyre, US Patent 4 272 625, 1981.
16. R. W. Lenz, In Recent Advances In Liquid Crystalline Polymers; L. L. Chapoy, Ed.; Applied Science: London, (1985); Chapter 1, p 9.
17. G. W. Gray and D. G. McDonnell, Mol. Cryst. Liq. Cryst., 53, 147-166, (1979).
18. C. Bhaskar, J. Kops, B. Marcher, H. Spangaard, In Recent Advances in Liquid Crystalline Polymers, L. L. Chapoy, Ed.; Applied Science: London, (1985); Chapter 4, pp 79-87.
19. Dictionary of Organic Compounds; Sir I. Heilbron and H. M. Bunbury, Eds.; Eyre and Spottiswoode: London, Vol. 1, p 87.
20. R. S. Irwin, Presented at the 189th National Meeting of the American Chemical Society, Miami FL, April 1985.
21. T. D. Greenwood, R. A. Kahley, J. F. Wolfe, A. St Clair and N. J. Johnston, J. Polym. Sci., Polym. Chem. Ed., 18, 1047-1059 (1980).
22. R. S. Hill and E. Walker, J. Polym. Sci., 3, 609 (1948).
23. S. Kenig, Polym. Eng. Sci., 27(12), 887-892 (1987).
24. F. C. Jaarsma, In International SAMPE Symposium & Exhibition Series, ;SAMPE: Covina, CA, 1987; Vol 32, pp 185-194.
25. T-S. Chung and P. E. McMahon, J. Appl. Polym. Sci., 31, 965-977 1986).

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