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Synthesis and characterization of in situ anionically polymerized p-aminobenzoylcaprolactam using di-and tri-functional initiator systems

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SUMMARY

p-Aminobenzoylcaprolactam has been polymerized anionically in a two-step process to produce aramide-amide copolymers. Both drawn fibers and unoriented films may be produced using this method. The samples were characterized using FTIR, solution NMR, thermal analysis, viscosity, and mechanical testing. FTIR and NMR revealed the incorporation of both the aramid and amide linkages into the polymer backbone. TGA results gave a lower decomposition temperature than that of both aramide and nylon 6 materials. Intrinsic viscosities averaged 0.5 dL/g for the drawn copolymer samples polymerized by the di-functional initiator. Light microscopy displayed crystalline domains that did not appear to melt even up to 300°C. Mechanical testing showed that the initial moduli of drawn fiber samples to be in the range of 30-80 MPa, while homopolymers of nylon 6 and p-benzamide possessed values of 25 MPa and 2.70×10^5 MPa, respectively.

INTRODUCTION

p-Aminobenzoylocaprolactam (p-ABC) 1 may be polymerized in situ to form self-reinforcing composites via a one-pot process by the reactions given in Figure 1 (1). The upper path involves attack at the caprolactam ring carbonyl carbon and forms an alternating p-benzamide-caproamide polymer 2 in a ring-opening reaction. The lower path forms aromatic blocks in a nylon 6 matrix via reaction through the aromatic carbonyl in a two-step process. Both possibilities allow polymer composite formation without non-reactive by-product generation. However, polymerization takes up to 24 hours making this approach unsuitable for applications requiring rapid polymerization.

In order to circumvent the long reaction times, anionic polymerization with an imide-containing activator 3 (iso-phthaloyl-bis-caprolactam (2), PBC) was tried. As shown in Figure 2, the activator 3, p-aminobenzoylocaprolactam 1, and caprolactam 4 together form a reactive solution for p-aminobenzoylcaprolactam polymerization. In a second step, the activated solution reacts with sodium caprolactam 5 to form the nylon portion of a blocky aramid-amide composite 6.

A trifunctional activator (trimesoyl-tris-caprolactam (2), TTC) was used to create branch points in the aramid-amide backbone. This species was also used to generate a crosslinked material through a side-reaction shown to occur in nylon 6 polymerization (3-5).

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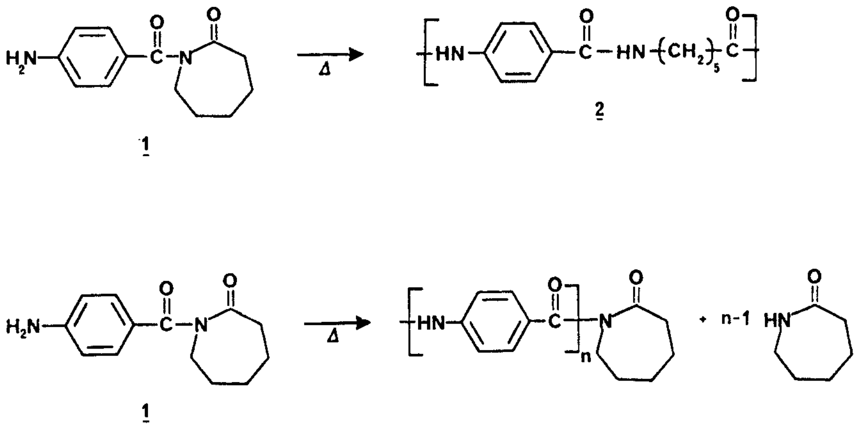

Figure 1. p-Aminobenzoylcaprolactam Polymerization Pathways

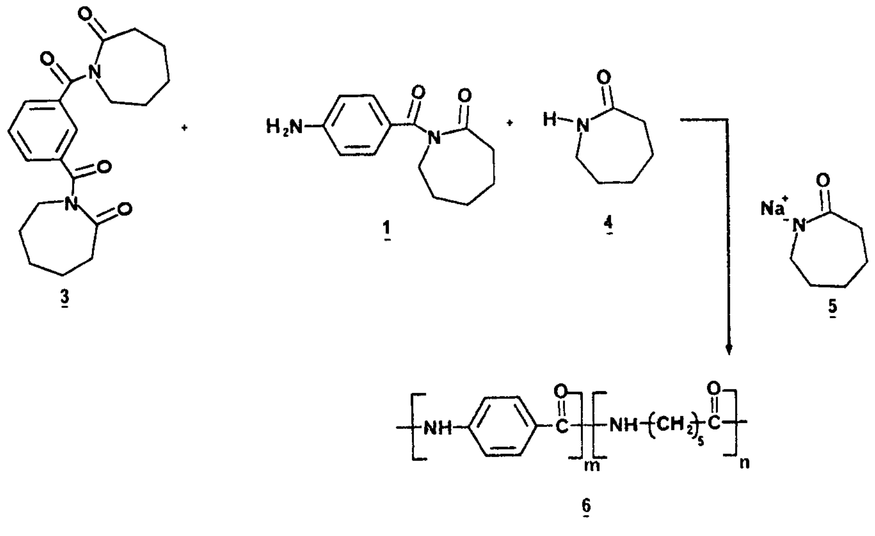

Figure 2. Anionic Polymerization of p-Aminobenzoylcaprolactam Using A Di-functional Initiator

EXPERIMENTAL

p-Aminobenzoylcaprolactam was synthesized as described (1) and characterized by C-13 NMR, FTIR, and elemental analysis. Both activators, PBC and TTC, were prepared using a modified method of Donaruma (6). The commercially available phthaloyl acid chloride and trimesoyl chloride were reacted with excess amounts of caprolactam in the presence of pyridine. Successive recrystallizations from acetone/petroleum ether solutions produced white, crystalline materials that were characterized by C-13 NMR, FTIR, thermal analysis, and elemental analysis.

Aramid-amide polymers were synthesized in a two-step process to simulate reaction injection molding. Varying ratios of p-ABC, PBC or TTC, and caprolactam were "pre-reacted" at 210°C under nitrogen until the solution became opaque indicating the precipitation of the aramid-amide prepolymer. Depending on the ratio of imide-initiator to p-ABC, this usually took 20 to 120 minutes. The second solution was formed by reacting NaH with molten caprolactam. The sodium caprolactam solution was added to the p-ABC solution and the reaction heated to 210-220°C. Polymeric material formed rapidly, usually in 2 to 15 minutes. This viscous mass could be drawn into golden-orange fibers. Depending upon the initial ratio of imide activator to p-ABC monomer, the polymer ranged from very flexible and weak to brittle and strong. The drawn fibers and the *in situ* composite material were analyzed by C-13 NMR (solution and solid state), FTIR, thermal analysis, solution viscosity, and tensile testing.

C-13 spectra were obtained in 93.6% sulfuric acid with a JEOL FX90Q NMR. Tensile testing was performed using an Instron 1200C mechanical testing device. Thermal analysis was performed with a DuPont 9900 system. Viscosities were obtained in 93.6% sulfuric acid at 25°C with Cannon-Ubelohde microviscometers.

RESULTS AND DISCUSSION

Figure 3 shows a typical C-13 spectra of a drawn fiber dissolved in H_2SO_4. The spectrum indicates that three types of carbonyls are present in the polymer. Aramid-aramid, aramid-amide, and amide-amide linkages are present (1), with the highest concentration of linkages being of the amide-amide type indicating that the polymer is mainly composed of blocks of nylon 6. Previous workers have found that poly(p-ABC) formed at temperatures above 200°C contain mainly aramid blocks with an occasional nylon 6 unit (1). In this case, using caprolactam as a solvent in the polymerization scheme produces blocks of aramid with blocks of nylon 6 that form at the end of the reaction. It was found that polymers produced with the tri-functional TTC initiator produced fibers that only swelled upon attempted dissolution in H_2SO_4 indicating that these systems were highly tangled or crosslinked to some extent.

DSC's of drawn fiber samples showed broad melting curves beginning at 70°C and continuing to 180°C. Observation of polymers over this temperature region under a microscope and a Mettler hot stage showed that the fibers shrank in this region from 30 to 60% of the original length. Hot stage microscopy also revealed crystalline regions that did not melt below 300°C. These crystalline domains appear to consist of aramid regions surounded by a nylon 6 matrix.

TGA curves given in Figure 4 show the thermal degradation behavior of a typical aramid, an anionically produced nylon 6, and the aramid-amide polymer. These curves indicate that the onset of degradation in the aramid-amide polymer is lower than that of nylon 6. The blocks of aromatic material in the aramid-amide polymer possibly are short allowing easier thermal degradation of the polymer by residual NaOH (7) (the by-product from the use of NaH as an initiator).

Tensile analysis of drawn aramid-amide fibers gave tensile strengths ranging from 30 to 80 MPa. The value for nylon 6 was measured to be 25-100 MPa, while a literature value for poly(p-benzamide) was reported to be 2.7 X 10^3 MPa (8). Polymers with a high initial ratio of caprolactam to p-ABC had lower tensile strengths than high initial ratio p-ABC polymers indicating that aromatic incorporation increased the tensile strength.

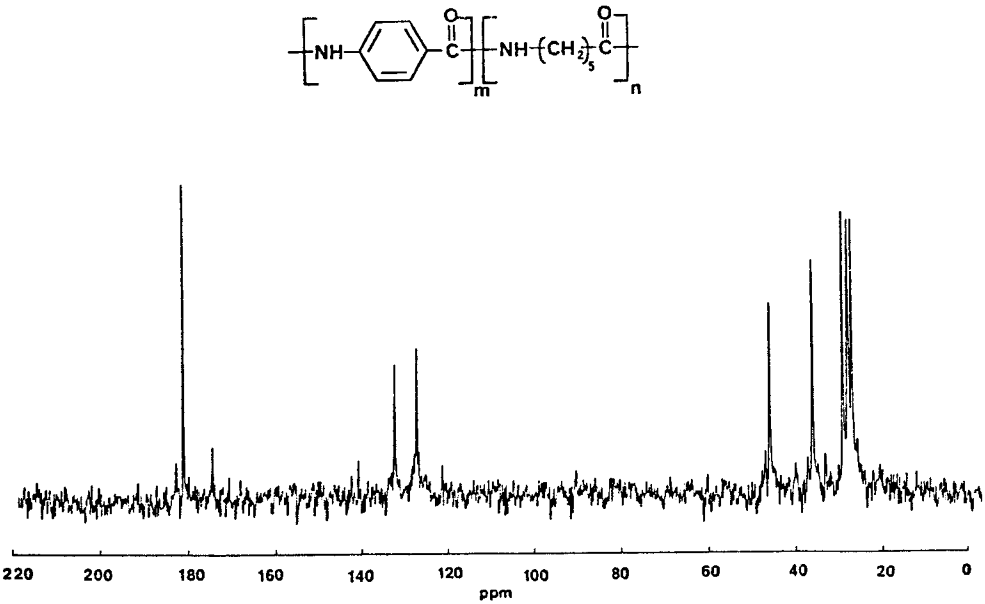

Figure 3. C-13 NMR of in situ Composite in 96.3% H_2SO_4

CONCLUSIONS

A blocky aramid-amide polymer produced anionically has been generated that contains crystalline domains that do not melt at temperatures up to 300°C. The polymer forms blocky aromatic regions that are short. Using the tri-armed initiator allows formation of entangled and/or crosslinked material. Tensile strengths increased somewhat with increasing aramid content.

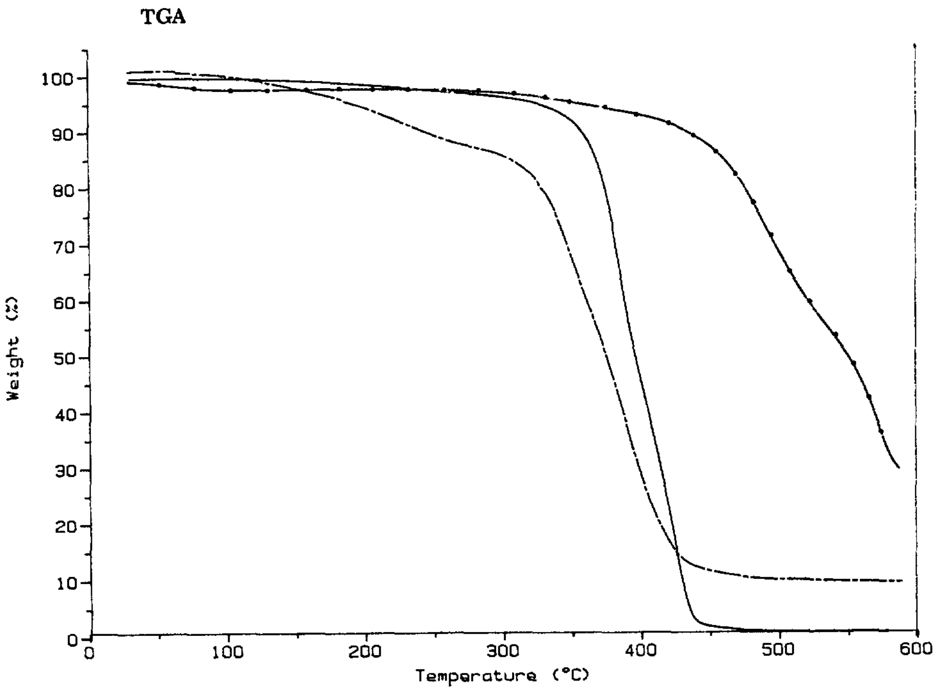

Figure 4. TGA Scans of Aramid (—•—), Nylon 6 (——), and Aramid-Amide (— — —) Polymers

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