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Synthesis and Properties of Star-Branched Nylon 6

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Star-branched nylon-6 with six arms has been prepared by initiating ϵ-caprolactam polymerization with amine end groups of second-generation starburst poly(ethylenimines). The cationic polymerization is done in bulk above the melting point of the polymer. This star-shaped polymer has significantly decreased viscosity in the melt and in solution, yet most of the solid-state properties are retained. The branched nylon has the same tensile strength, tensile modulus, and oxygen barrier properties as linear nylon-6, yet its melt viscosity is only 30% of the linear polymer. Such star-branched polymers should provide advantages in processing such as easier injection molding, blending, lower processing pressures, and processing of higher molecular weight materials.

Introduction

Star-branched polymers are characterized by a branch point from which emanate a number of polymer chains or "arms". It is known that long-chain branching or star-branching decreases the molecular dimensions of polymers and results in a decrease in viscosity. Branching could result in lower processing pressures or temperatures, easier injection molding, or the ability to process higher molecular weight polymers.[1,2]

Star-branched polymers have been actively studied since the first star-shaped polystyrene was prepared by linking living anionic polystyrene with silicon tetrachloride.[3] However the star-branched polymers which can be made with this procedure are limited to polystyrene, polydienes, other anionically made polymers, and block copolymers of these. High purity of reagents is essential, along with stoichiometric amounts of linking agent. Any protic impurities will terminate the living polymer before it is linked, resulting in a mixture of linear polymer and star polymers with different numbers of arms. Also, the number of arms possible with this method is limited by the number of reactive sites on the linking agents.

Early calculations on the dimensions of branched polymers were published by Zimm and Stockmayer.[4] They defined g as the ratio of the mean square radius of gyration of a branched polymer to the mean-square radius of gyration of a linear polymer, where both polymers have the same total molecular weight:

$$g = \langle S^2 \rangle_{\mathrm{br}} / \langle S^2 \rangle_{\mathrm{lin}} \tag{1}$$

For f monodisperse arms of equal length

$$g = (3f - 2)/f^2 \tag{2}$$

Later Zimm and Kilb extended the hydrodynamic theory of intrinsic viscosity to branched polymers and defined another ratio, g', as the ratio of intrinsic viscosities of a branched to a linear polymer of the same total molecular weight.[5]

$$g' = [\eta]_{\mathrm{br}} / [\eta]_{\mathrm{lin}} \simeq g^{1/2} \tag{3}$$

Bueche calculated the viscosity of branched polymers in concentrated solution and in the melt.[6] For highly entangled chains he found

$$\eta_{\mathrm{br}} / \eta_{\mathrm{lin}} = g^{7/2} \tag{4}$$

and for nonentangled chains

$$\eta_{\mathrm{br}} / \eta_{\mathrm{lin}} = g \tag{5}$$

Figure 1 shows the ratio of viscosities of branched to linear polymers versus the number of arms for the various exponents given in eqs 3–5.

Data are sparse on the mechanical properties of star-branched homopolymers, but these are expected to be the same as the corresponding linear polymers. More studies have been reported on the mechanical properties of star-branched block copolymers; the tensile strength of polystyrene–polydiene star block copolymers with at least nine arms is greater than that of linear block copolymers having the same segment molecular weight. It is believed that the property differences of the star blocks are due to a permanent cross-link at the center, a more orderly polystyrene phase, and a smaller polystyrene domain—all of which facilitate phase separation.[7] Electron microscopy studies of star-branched block copolymers show a new "double diamond" or "ordered bicontinuous" morphology for star blocks with at least eight arms and certain block molecular weights.[8]

The glass transition of noncrystalline star-branched polymers is expected to be slightly lowered for a given molecular weight due to a larger number of chain ends per molecule, but this effect would only be especially pronounced at low molecular weight.[9]

Star-branched polymers can be made by two general methods: (a) by terminating polymerization of linear polymers with a multisited reagent; (b) by initiating polymerization from a multisited center. Starburst macromolecules have a well-defined structure with a known number of uniform functional groups on the exterior.[10-12] For example, second-generation starburst poly(ethylenimine) having six primary amines is shown in Figure 2. Controlled branching from each of these yields the third generation starburst macromolecule having 12 primary amines. These amines can be replaced with other functional groups to be used as a variety of multisited polymerization initiators or linking agents.

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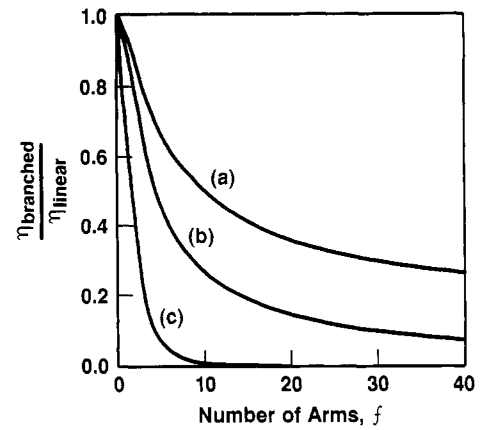


Figure 1. Ratio of viscosities of branched to linear polymers versus number of arms, curves calculated from eqs 2–5:[4–6] (a) intrinsic viscosity, (b) melt viscosity, nonentangled chains; (c) melt viscosity, entangled chains.

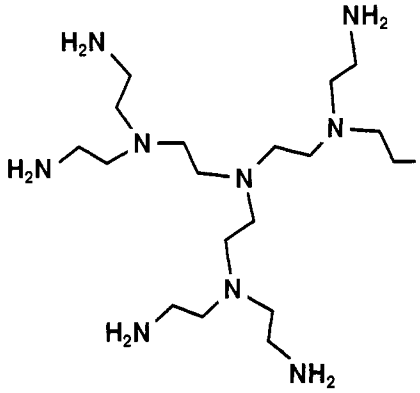
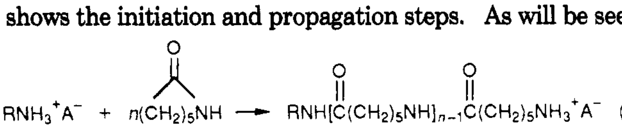


Figure 2. Structure of second-generation starburst poly(ethylenimine) macromolecule.

This paper summarizes the use of starburst poly(ethylenimine) macromolecules as polymerization initiators of ε-caprolactam to form nylon-6. Amines and amine hydrochlorides are known to initiate the cationic polymerization of caprolactam.[13,14] The first step is the formation of the initiator which is the amine salt; HA is a proton source which could be the monomer (eq 6). Equation 7 shows the initiation and propagation steps. As will be seen in the results, directly using an amine salt rather than an amine as the initiator eliminates eq 6 and results in faster polymerization.

$$\mathrm{RNH_2} + \mathrm{HA} \rightleftharpoons \mathrm{RNH_3^+A^-} \qquad (6)$$



$$\mathrm{RNH_3^+A^-} + n\overset{\mathrm{O}}{\overbrace{(\mathrm{CH_2})_5\mathrm{NH}}} \longrightarrow \mathrm{RNH}[\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}(\mathrm{CH_2})_5\mathrm{NH}]_{n-1}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}(\mathrm{CH_2})_5\mathrm{NH_3^+A^-} \qquad (7)$$

The mechanisms of initiation with $\mathrm{RNH_3^+}$ ions and propagation must involve the transfer of two protons from the active species. Two possible mechanisms for this step might be loose association or complete protonation.[13]

Branched nylon has been previously been reported on two occasions. It was first made by the water catalyzed polymerization of caprolactam with multisited carboxylic reagents as linking agents.[15,16] More recently, it has been made by anionic polymerization and a tris-caprolactam reagent.[17,18] This cationic route, therefore, is a third method.

Experimental Section

The ε-caprolactam (Aldrich) was recrystallized twice from cyclohexane and stored in a vacuum desiccator over phosphorus pentoxide. The monofunctional amines (Aldrich) were dried by adding a few pellets of potassium hydroxide. The monofunctional amine hydrochlorides (Aldrich) were dried by storing in a vacuum desiccator over P_2O_5.

The first-generation starburst poly(ethylenimine) is more commonly called tris(2-aminoethyl)amine or 2,2′,2″-triaminotriethylamine (registry number 4097-89-6) and was obtained from Aldrich. Higher generation starburst poly(ethylenimines) were made by published procedures[11,12] and dried by azeotropic reflux in toluene. The second-generation starburst poly(ethylenimine) has the name *N*,*N*-bis(2-aminoethyl)-*N′*,*N′*-bis[2-[bis(2-aminoethyl)amino]ethyl]-1,2-ethanediamine (registry number 104583-47-3). The third-generation starburst polyethyleneimine has the name 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9-[2-[bis[2-bis(2-aminoethyl)amino]ethyl]amino]ethyl]3,6,9,12,15-pentaazaheptadecane-1,17-diamine (registry number 109131-77-3).

The hydrochlorides of the starburst poly(ethylenimines) were made by bubbling anhydrous HCl through dry toluene solutions of the starburst poly(ethylenimines) or by adding concentrated HCl to ethanol solutions of the starburst poly(ethylenimines) with vigorous stirring.

All reagents in the polymerization were kept dry since water can initiate ε-caprolactam polymerization. Monomer and initiator were weighed into glass ampules of 5- or 50-g capacity in a nitrogen-filled glovebag. The ampules were capped, cooled with dry ice, evacuated at 0.1 mmHg, and then flame sealed. The ampules were placed in a 100 °C oil bath to melt the monomer and dissolve the initiator, and then the ampules were placed in a wire basket in a 230 °C, thermostated silicone fluid bath, located in a hood behind a polycarbonate shield and the glass hood door. For larger quantities, a glass-lined 1-L Parr reactor of 316 stainless steel construction was loaded and sealed in a glovebag under nitrogen and then moved to a shielded location for heating with stirring.

After cooling, the product was removed from the reactor and then cracked and ground in a Wiley mill. The ground polymer was boiled in 1% sodium bicarbonate solution for 1 h to neutralize the HCl, extracted in a Soxhlet extractor with deionized water for 24 h, and then dried in a vacuum oven at 100 °C.

The percent conversion was calculated by dividing the weight of polymer after washing and drying by the weight of polymer before washing. The conversion amount was checked by analyzing the wash solution for ε-caprolactam by liquid chromatography. A Partisil ODS-2 10-μm column was used with 1:1 water/methanol eluent and a UV detector set at 205 nm.

The degree of polymerization (DP) was estimated from the product of the fractional conversion and monomer-to-initiator molar ratio. Four polymers made under the same conditions using the difunctional 1,5-diaminopentane hydrochloride initiator had DPs of 270, 310, 290, and 290 (mean = 290, median = 290, standard deviation = 16 (6%)).

For end-group titration, a 1-g polymer sample was dissolved in 25 mL of freshly distilled *m*-cresol at 100 °C, cooled, diluted with 10 mL of methanol, and then titrated with 0.1 N HCl (standardized against Na_2CO_3) to the methyl orange endpoint (yellow to red). Calculations were corrected with a blank titration.

Inherent viscosities were measured at 0.1 g/100 g of solution in 40% H_2SO_4 in a 25 °C bath using a Canon-Fenske viscometer.

Dry samples were compression molded at 250 °C and 1 ton of pressure for 3 min and then under 25 tons of pressure for 6 min and finally cooled under 25 tons of pressure for 12 min. Injection molding was done on an Arburg 221-55-250 injection molding machine.

Melt viscosities were measured on dry compression molded disks on a Rheometrics dynamic mechanical spectrometer from

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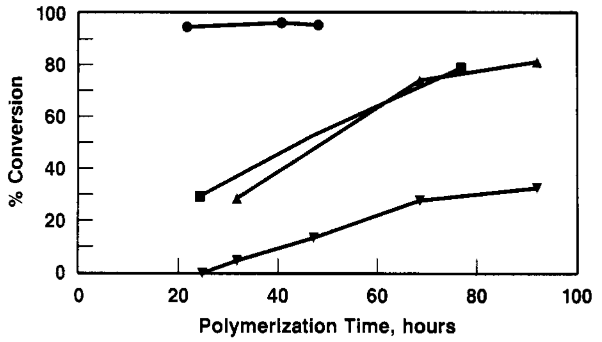

Figure 3. Percent conversion versus polymerization time, M/I = 125: circle, tris[(2-aminoethyl)amine] trishydrochloride initiator; square, tris[(2-aminoethyl)amine] initiator; triangle, ethylenediamine initiator; inverted triangle, amylamine initiator.

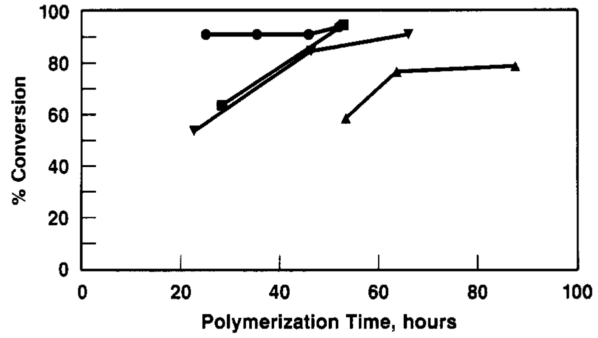

Figure 4. Percent conversion versus polymerization time: circle, second-generation SPEI hexahydrochloride initiator, M/I = 175; square, second-generation SPEI initiator, M/I = 400; triangle, second-generation SPEI initiator, M/I = 175; inverted triangle, 1,5-diaminopentane dihydrochloride initiator, M/I = 400.

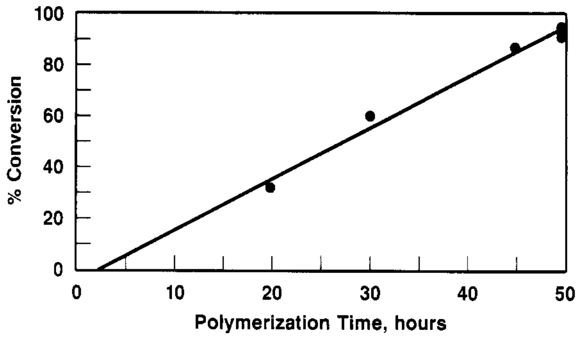

Figure 5. Percent conversion versus polymerization time for caprolactam polymerization with ethylenediamine hydrochloride initiator, M/I = 400.

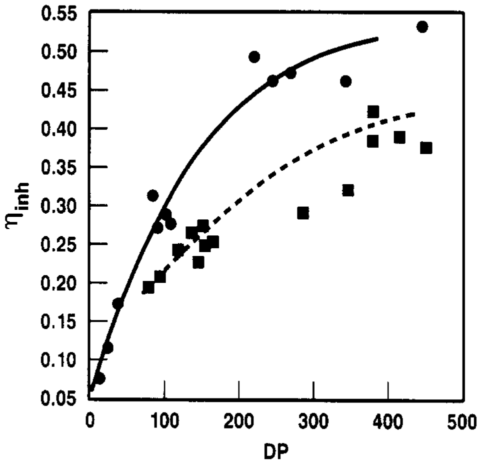

Figure 6. Inherent viscosity versus degree of polymerization for linear (circles) and six-armed (squares) nylon 6.

0.1 to 100 rad/s from 235 to 275 °C.

Tensile tests were done on small compression and injection molded tensile bars at a crosshead speed of 0.05 in./min.

Oxygen permeability was measured on an Oxtran apparatus at 42, 52, and 62 °C and then extrapolated back to room temperature.

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 from 25 to 280 °C at 20 °C/min under nitrogen.

Results and Discussion

Infrared spectra of the polymers prepared are consistent with that of nylon-6. Solubility is the same as for nylon-6: in trifluoroethanol, 40% formic acid, 40% sulfuric acid, and *m*-cresol.

Figures 3 and 4 show the conversion of ε-caprolactam to nylon-6 versus polymerization time. For a given monomer-to-initiator molar ratio, the polyamines polymerize the monomer faster than monoamines since there are more initiator groups available per mole of initiator. Previous work has shown that the polymerization rate is proportional to the initiator concentration while the length of the induction period is inversely proportional to the initiator concentration.[13,14] It has also been shown that for amine hydrochloride-initiated polymerization of ε-caprolactam, the degree of polymerization increases linearly with conversion.[13] Long polymerization times are therefore necessary in these polymerizations to achieve high molecular weight. The long induction period may cause initiation to occur over a period of time, giving polymers with a distribution of the number of arms. Slow initiation could result in less than the expected number of arms since some of the initiation sites on an initiator may become encapsulated by polymer before they initiate any polymerization. Such encapsulation would be unlikely to occur if the initiation rate is much greater than the propagation rate. For these reasons it was desirable to use amine salts such as hydrochlorides. Note in Figure 3 that polymerization with a diamine dihydrochloride reaches high conversion rapidly.

Figure 4 shows the progress of polymerizations aimed at obtaining higher molecular weight polymers with more arms. Note again that the amine hydrochloride causes faster polymerization than the amine, that the amine-initiated system will not easily reach high conversion (and therefore will not form readily high molecular weight polymer), and that fewer initiation sites per initiator molecule result in slower polymerization. Figure 5 shows linear conversion versus polymerization time for monomer/initiator ratio of 400 for the two-armed or difunctional initiator.

Figure 6 shows the inherent viscosity in 40% sulfuric acid at 25 °C versus estimated degree of polymerization (DP) of nylons with various numbers of arms. The DP was calculated from the product of fractional conversion and monomer/initiator ratio. The six-armed polymers show a significant lowering of viscosity compared to the linear polymers, although the three-armed nylons (data not shown) have viscosities which are similar to the linear polymers. If guide lines are drawn through the data, the ratio η_{br}/η_{lin} can be estimated by moving up the ordinate to determine the viscosities for linear and branched nylons having the same DP. Values of this viscosity ratio were calculated to range from 0.7 to 0.8, although the data scatter preclude an accurate evaluation. Using eqs 2 and 3, a viscosity ratio $[\eta]_{br}/[\eta]_{lin}$ of 0.67 is predicted.

Figures 7 and 8 show the melt viscosities of various nylons at low and high shear rates. In Figure 7, the 6-armed nylon with DP = 450 has lower melt viscosity than the linear nylon with a lower DP of 340. The exact mo-

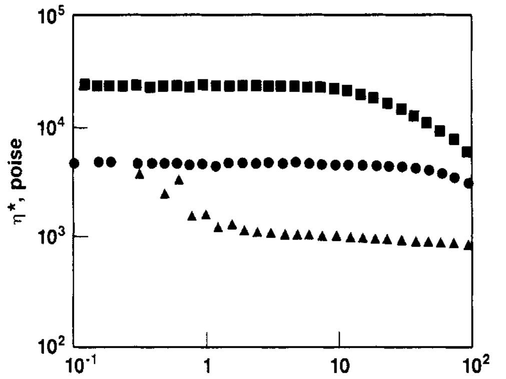

Figure 7. Complex viscosity of nylons at 250 °C versus frequency: square, allied capron 8207F; circle, linear, DP = 340; triangle, six-armed, DP = 450.

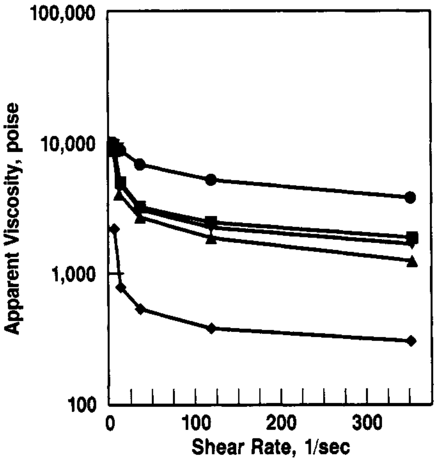

Figure 8. Apparent viscosity of nylons by capillary rheometry versus shear rate: circle, Allied Capron 8200; square, linear, DP = 300, 250 °C; inverted triangle, six arms, DP = 1160, 250 °C; triangle, three arms, DP = 300, 220 °C; diamond, six arms, DP = 300, 220 °C.

Table I. Tensile Properties of Compression Molded Linear and Branched Nylons

no. of arms	DP	modulus, N/m^2 × 10^{-9}	strength at rupture, N/m^2 × 10^{-7}	elongation at rupture, %
1[a]		1.03	4.83	89
1	260	1.20	4.67	87
6	230	1.10	4.74	28
6	350	1.28	5.17	37
6	380	1.21	5.15	59

no. of arms	DP	modulus, N/m^2 × 10^{-9}	Ty,[b] N/m^2 × 10^{-7}	Tr,[c] N/m^2 × 10^{-7}	Ey,[d] %	Er,[e] %
1[f]		0.90	3.91	7.10	22	260
1	310	1.10	4.80	8.00	18	300
6	220	0.76	3.99	4.01	23	120
6	300	0.76	3.96	4.55	23	180
6	1160	0.90	4.13	5.83	24	220

[a] Allied CAPRON 8207F. [b] Tensile strength at yield. [c] Tensile strength at rupture. [d] Elongation at yield. [e] Elongation at rupture. [f] Allied CAPRON 8200.

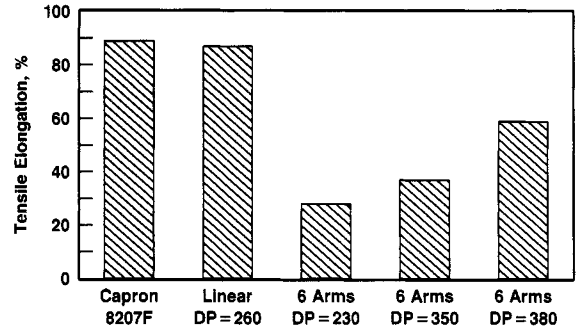

Figure 9. Tensile elongation at break for compression molded specimens.

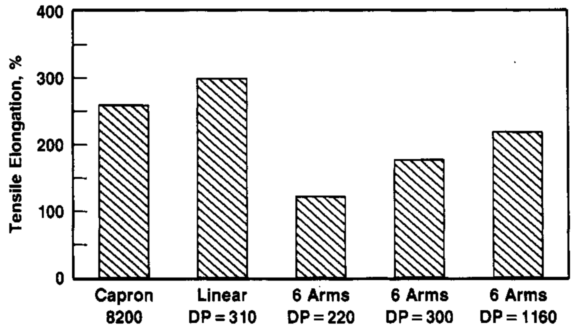

Figure 10. Tensile elongation at break for injection molded specimens.

lecular weight of the commercial Allied 8207F is not known but is probably 30 000–50 000, corresponding to a DP of 250–450; comparison is difficult because this material has also been compounded. That branching has a stronger effect on melt viscosity than dilute solution viscosity is expected from theory as summarized in Figure 1.

Figure 8 shows the melt viscosity of linear and branched by capillary rheometry. The temperature was 250 °C except for branched nylons which dripped through the barrel without the application of force; lower temperatures were required for the branched nylons. The capillary diameter (d) was 0.050 in., its length (l) was 1.00 in, and the l/d was therefore 20.0. At 250 °C and rate of 352.2 s^{-1}, the 6-armed nylon had a viscosity 30% lower than a linear nylon that has one-fourth its molecular weight. At 250 °C the viscosity of branched nylons could not be measured because they were so low. While linear nylon with DP = 290 at 250 °C and three-armed nylon with DP = 300 at 220 °C both have similar viscosities, a six-armed nylon of the same molecular weight has a viscosity at 220 °C that is only one-sixth that of the linear nylon at 250 °C.

Such a decrease in viscosity is predicted by theory but may not be useful unless the polymer retains its strength in the solid state. Table I summarizes tensile tests of injection and compression molded nylons. The ultimate tensile strength of compression molded nylons was not affected by branching, although branching did decrease the tensile strength of injection molded pieces. This can be explained by decreased orientation in the injection molded branched samples. A more important property for these materials in practical applications, however, is the yield stress, which is unaffected by branching. The modulus is unchanged by branching as shown for both injection and compression molded samples. Star-branching lowers the ultimate tensile elongation or elongation at break, as expected, due to the more compact size of the branched polymer and inability of the star molecules to undergo as much reorientation and molecular "slippage". However, if the elongation at yield is considered, branching has no effect. The important conclusion to draw is that star-branching can significantly lower the viscosity while maintaining the tensile strength and modulus.

As an illustration, Figures 9 and 10 show the tensile elongation at break for compression molded and injection molded samples, respectively. Several points should be noted: (1) the elongations of the injection molded specimens are 3 times those of the compression molded ones due to orientation; (2) branching with six arms decreases the elongation values by up to two-thirds; (3) as the degree

Table II. Differential Scanning Calorimetry Results for Linear and Branched Nylons

no. of arms	DP	Tm major, °C	Tm minor, °C	ΔH_{fus}, J/g
1[a]		220	214	61
1	290	220	210	52
6	220	215	204	56
6	300	217	203	57
6	1160	220	208	58

[a] CAPRON 8200.

Table III. Oxygen Permeability of Compression Molded Films of Linear and Branched Nylon 6

sample	$P(O_2)$[a]
linear, DP = 250–300	0.8–0.9
six-armed, DP = 350–400	0.8–0.95
CAPRON 8207F	0.85

[a] $P(O_2) = [(\text{cm}^3)(\text{mils})/[(100 \text{ in.}^2)(\text{day})(\text{atm})]$.

of polymerization of the branched nylons increases, so does the elongation at break.

Molded parts of some six-armed star nylons showed a skin-core morphology. This may be due to faster crystallization kinetics of the branched polymers compared to linear polymers as noted for star-branched polyethylene.[19] It has been shown that crystallization half-times were reduced by one-half in the branched systems for equivalent values of supercooling.[20]

Differential scanning calorimetry (DSC) showed no differences in melting points and glass transition temperatures of the nylons, whether star-branched (six arms) or linear. Star-branched and linear nylons of high molecular weight showed no differences in heats of melting (determined from area under the melting peak), indicating that crystallinity is maintained even with star-branching. Table II summarizes DSC results for linear and six-armed nylons. That the crystallinity is unaffected by branching is also supported by the unchanged rates of oxygen transport, as shown in Table III. It is well-known that solubilities, diffusivities, and permeabilities of gases in polymers depend in part on crystallinity.[21] The oxygen permeability data are given for star-branched nylon-6, linear nylon-6, and commercial Allied Capron 8207F nylon-6. At room temperature and 50–70% humidity all samples showed the same values; therefore, star-branching does not increase the permeability of nylon.

Summary

Polymerizations of ε-caprolactam initiated by various amines and amine hydrochlorides have been studied. More amine functionalities per molecule results in faster polymerizations and the formation of star-branched polymers. The use of amine hydrochlorides eliminates the induction period, resulting in even faster polymerizations. End-group titrations confirm the branched structures and allow DP estimates.

Star-branched nylons with six arms have been prepared by initiating ε-caprolactam polymerization with starburst poly(ethylenimines). These star-shaped polymers have significantly decreased viscosities in the melt and in solution, yet the solid-state properties are retained. The branched nylons have the same tensile strengths, tensile moduli, melting points, heats of fusion, and oxygen barrier properties as linear nylon-6, yet their melt viscosities are only 30% of the linear polymers. Such star-branched polymers should provide advantages in processing such an easier injection molding, lower processing pressures, and processing of higher molecular weight materials.

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Registry No. Nylon 6, 25038-54-4; tris(2-aminoethyl)amine, 4097-89-6; *N*,*N*-bis(2-aminoethyl)-*N'*,*N'*-bis[2-[bis(2-aminoethyl)amino]ethyl]-1,2-ethanediamine, 104583-47-3; 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9-[2-[bis[2-bis(2-aminoethyl)amino]ethyl]amino]ethyl]-3,6,9,12,15-pentaazaheptadecane-1,17-diamine, 109131-77-3.

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