Preparation and Characterization of Polyamide-6 with Three-Branched Chains

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ABSTRACT: With trimesinic acid as a molecular weight regulator, the hydrolytic polymerization of ϵ-caprolactam was carried out, and nylon-6 or polyamide-6 with three-branched chains was obtained. Through a systematic study of the effects of conditions such as the reaction time and concentration of trimesinic acid on the polymerization, we found that the conversion of caprolactam was almost insensitive to the initial concentrations of the regulators, but the relative viscosity of the polymer decreased with increasing trimesinic acid. Characterization investigations showed that differential scanning calorimetry curves changed from a single peak for normal nylon-6 to one main peak and one shoulder or one small peak for the branched polymer; the melting point of the star-shaped nylon-6 decreased with an increasing amount of trimesinic acid, whereas its crystallization temperature was higher than that of linear-chain nylon-6. A wide-angle X-ray diffraction study indicated that the crystal structure of the star-shaped nylon-6 still belonged to the α form, and the crystallizability of the branched polymer with an elevated amount of trimesinic acid during polymerization did not seem to be weakened; the characteristic absorption of infrared spectra provided indirect evidence for the existence of branched chains in the polymer. Moreover, the mechanical properties of star-shaped nylon-6 and linear-chain nylon-6 were compared. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3184–3193, 2001

Key words: polyamide-6; star polymer; molecular weight regulator; polymerization; characterization

INTRODUCTION

Nylons are polymers with amide linkages, among which nylon-6, or polyamide-6 (PA-6), serves as the most commercially important synthetic polyamide; it is used for a variety of purposes, such as in fibers for tire cords, apparel, fishing nets, upholstery, and hosiery and in the manufacture of injection-molded and blow-molded objects. There are two common industrial routes to manufacture the polymer from the monomer ϵ-caprolactam. The first one is called *hydrolytic polymerization* and is usually performed on a large scale,[1,2] and the second route is through the *ionic chain-growth mechanism*. In the process of the hydrolytic polymerization of ϵ-caprolactam, different amounts of molecular weight (MW) regulators need to be present in the reaction system to provide a series of products fulfilling the requirements designated for various ultimate performances. As MW-controlling reagents of the hy-

Table I   Initial Concentrations

Run	ε-Caparolactam (mol/kg)	ε-Aminocaproic Acid (mol/kg)	Trimesinic Acid (mol/kg)	Water (mol/kg)
A	7.8878	0.2721	0.1337	2.4751
B	7.9636	0.2748	0.0899	2.4988
C	8.0018	0.2761	0.0679	2.5109
D	8.0406	0.2774	0.0454	2.5229
E	8.0798	0.2788	0.0228	2.5353
F	8.1034	0.2796	0.0092	2.5427
G	8.1183	0.2801	0.0000	2.5485

Polymerization conditions: temperature = 265°C, nitrogen atmosphere.

drolytic polymerization of caprolactam, monofunctional regulators such as acetic acid and bifunctional regulators such as adipic acid are generally used.[3] When these reagents are used, the chain-ended chains are still linear. However, if polyfunctional or multifunctional regulators are used in the polymerization system, star-branched or multichain polymers will be obtained. Schaefgen and Flory,[4] Scheulz,[5] Billmeyer,[6] and Yang et al.[7] have done much work on star-branched or star-shaped polymers. Fantoni[8] mentioned that the properties typical of polyamides change as the branching degree increases. The MWs being the same, the viscosity of star nylon-6 decreases as the branching degree increases because the macromolecules tend to become spherical and noncoilable like random coils, which are characterized by branches that are too short, making good binding particularly difficult. The star-branched polymers attracted much attention during the past decade. As indicated by Romiszowski and Sikorski[9] and Hutchings and Richards,[10] models of star-branched molecules can be created in many interesting ways, and they answer some of the fundamental theoretical problems; someone could find quite different properties if he compared the molecules with their linear counterparts. Star-shaped polymers exhibit special functions that might be employed in many applications. Functionalized star polymers are useful in making adhesives, sealants, coatings, films, and fibers. Moreover, multiarm star polymers are being investigated as rheology-control agents, viscosity modifiers, motor oil additives, and so forth.

There have been enough studies on the polymerization systems with monofunctional and bifunctional regulators successfully used in industry for years.[11] However, the polymerization of ϵ-caprolactam with a trifunctional regulator has not received the attention it deserves. This article presents the results for the polymerization of ϵ-caprolactam with trimesinic acid as a regulator to form three-branched-chain PA-6 and the characterization of the polymer.

EXPERIMENTAL

Polymerization

According to the initial concentrations shown in Table I, weighted caprolactam was put in a glass polymerization tube 2.5 cm in diameter and 25 cm long, and then water, ϵ-aminocaproic acid, and regulators were pipetted into the tube at 80°C. The polymerization conditions were selected on the basis of the monofunctional-regulator and bifunctional-regulator systems and the particular situation of the trifunctional-regulator system. Polymerization was performed under a nitrogen atmosphere with the reaction tubes kept at the required temperature for the required time. A set of tubes were inserted into a multitubular furnace thermostated to an accuracy of ±5°C. Then, the sample tubes were withdrawn from the furnace at specific time intervals and quenched in cold water. The rod-shaped polymers taken off the broken tubes were turned on a lathe, cut into spiral cords, and then cut into chips. The weighted samples were extracted with 20 times their weight of freshly distilled water at 90°C under a nitrogen atmosphere for 16 h, filtered, and dried to a constant weight via heating to 105°C under high vacuum. The conversion can be calculated as

Conversion (%)

$$= \left(1 - \frac{\text{weight of extractives}}{\text{Weight of sample}}\right) \times 100$$

For comparison, the linear-chain nylon-6 sample G-1 [relative viscosity (RV) = 2.5] from BASF Corp. (Germany) was also used in this study.

Viscosity Measurement

The extracted sample (5 g) was placed into a 50-mL volumetric flask and weighed quickly to the closest 0.0001 g on an analytical balance. Then, it was dissolved with 95.7% sulfuric acid at 55°C. After being kept in a constant-temperature bath (20 ± 0.1°C) for 15 min, the polymeric solution was inserted into a Ubbelohde viscometer through a wide tube, which was placed into the same constant-temperature bath for 15 min. Then, the flow time was measured. RV was calculated as

$$RV = t/t_0$$

where t is the average flow time of the solution and t_o is the average flow time of the solvent.

Differential Scanning Calorimetry (DSC)

Thermodynamic studies were conducted with a PerkinElmer DSC7 differential scanning calorimeter (PE Inc., United States). The scans were always performed under a nitrogen atmosphere at a heating rate of 20°C/min.

Wide-Angle X-Ray Diffraction (WAXD)

WAXD experiments were carried out with a Rigaku D/MAX-3. The monochromatized X-ray beam was Cu Kα radiation with a wavelength of 0.15438 nm.

Infrared (IR) Spectroscopy

IR spectra were measured with a Magna-550 Fourier transform infrared spectrometer from Nicolet Co. At least 32 scans at a resolution of 4 cm^{-1} were signal-averaged. The samples were measured in the form of films with a thickness of 5–6 μm.

Fiber Formation

Dried nylon-6 was forced through a spinning hole with a diameter of 1 mm at 230°C. Then, the as-spun fiber was drawn with a draw ratio of 3.8 at room temperature.

Dynamic Mechanical Analysis (DMA)

DMA measurements were made with a DDV-II-EA dynamic viscoelastometer from TMI (Japan) with a frequency of 110 Hz and a heating rate of 2°C/min. The fibers made from linear and star-shaped nylon were used as specimens.

Mechanical Properties

A single-thread tensile-strength tester made by China Taichuang Textile Instrument Factory was used under the following conditions: a specimen gauge length of 20 mm and a close head speed of 20 mm/min. Elasticity was measured after the fiber was relaxed with 3% elongation for 120 s. The moisture content of the samples was regulated under standard conditions.

RESULTS AND DISCUSSION

Reaction Mechanism

The formation mechanism of PA-6 in the hydrolytic polymerization of ϵ-caprolactam was reviewed by Reimschuessel.[12,13] Using the early experimental work of Hermans et al.,[14] Kruissink et al.,[15] and Wiloth[16] as well as the work of his own group,[17] Reimschuessel showed that polymerization consists of three main reactions: the ring opening of caprolactam by water, polycondensation, and polyaddition. Moreover, the formation of higher cyclic oligomers is an important side reaction.[15] Even though the total amount of these compounds formed is small (<2–3 wt %), it is known that they cause problems in the spinning and molding of the final polymer. Sometimes, monofunctional acids, bifunctional acids, and even trifunctional acids are added to the reaction mass to control the MW of the polymeric product or to increase the rate of polymerization.

When a trifunctional acid is involved, the final product will be star-shaped. One of the approaches for synthesizing star-branched polymers is the polycondensation of AB-type monomers with a small amount of a multifunctional compound RA$_f$ (where f is the number of A-type functional groups and R is the core of the compound). For instance, in the polymerization of ϵ-caprolactam with a trifunctional chain ending of type RA$_3$, all the growing chains end with an A. With trimesinic acid used as a regulator, all terminated chains should end with COOH. Based on an integrated recapitulation of the

Table II   Mechanism of Hydrolytic Polymerization of ε-Caprolactam with Trifunctional Regulator

1. Ring opening:	$C_1 + W \rightleftharpoons P_1$	
2. Polycondensation:	$P_n + P_m \rightleftharpoons P_{n+m} + W$	$n, m = 1, 2, 3\cdots$
3. Polyaddition:	$P_n + C_1 \rightleftharpoons P_{n+1}$	$n = 1, 2\cdots$
4. Ring opening of cyclic dimer:	$C_2 + W \rightleftharpoons P_2$	
5. Polyaddition of cyclic dimer:	$P_n + C_2 \rightleftharpoons P_{n+2}$	$n = 1, 2$
6. Reaction with trifunctional acid:	$P_n + P_{x(k,l,m)} \rightleftharpoons P_{x(k,l,m),+n} + W$	$n, m, k, l = 1, 2\cdots$

W = water; C_1 = caprolactam; P_m or P_n = polymer chain of chain length m or n; C_2 = cyclic dimer; $P_{x(k,l,m)}$ = polymer molecules containing a trifunctional acid with k, l, and m monomericunits on each side; $P_{x(k,l,m)+n}$ = polymer moles having n chains added on either the k, l, or m branch of $P_{x(k,l,m)}$.

main reactions given by Reimschussel and others, the formation reaction of cyclic dimer suggested by Arai et al.[16] with monofunctional acids as regulators, and the scheme of polymerization with bifunctional regulators given by Tang et al.,[3] reactions with trifunctional regulators, as shown in Table II, are proposed. In the sixth reaction, $P_{x(k,l,m)}$ represents the polymer molecule containing a trifunctional acid on behalf of a substituted benzene ring x with k, l, and m monomeric units on respective branches, and $P_{x(k,l,m)+n}$ represents that polymer molecule with n more chain units added to any of the three branches of $P_{x(k,l,m)}$. There seem to be three major approaches for the chain growth of PA-6 star polymer: step growth of the core (regulator), arm-first growth (individual linear chain first), and a mixture of both. In fact, there are both linear-chain polymers and star-branched polymers present in the reaction system.[8]

Effect of the Regulator Concentration on Polymerization

Conversion

Figure 1 shows the variation of conversion of runs B and E with the reaction time. Although there are great differences in the regulator concentrations of the two systems, these two curves are almost identical. During the 1st h of the reaction for both B and E, the reaction rate is fairly high, and the conversion reaches about 70%. However, the reaction slows down with the reaction time, levels off, and gradually approaches the equilibration conversion of about 90%. It is apparent from the diagram that the conversion of caprolactam is almost insensitive to the initial concentrations of regulators. Furthermore, it is interesting that the other runs with different concentrations of trimesinic acid in this study produce the same results.

RV

The function of a regulator in commercial production is to control the MW with various regulator concentrations. The relationship between the RV as a measure of the PA-6 MW and the concentration of trimesinic acid used in the polymerization is shown in Figure 2. The increase in the trimesinic acid concentration is observed to decrease RV; with an increasing regulator concentration, MW decreases almost linearly. Figure 3 shows the relationships between the RV and reaction time for runs A–F with different concentrations of trimesinic acid. All reactions take place rapidly at first and then reach equilibration values. For example, in run B, which has a higher concentration of trimesinic acid (0.0899 mol/kg), after the 1st h of reaction, the system reaches an equilibration RV as low as 1.5. However, in run E, which has a lower concentration of trimesinic acid (0.0092 mol/kg), after 2 h the reaction starts to slow down, reaching its equilibration RV of 2.5, which is much higher than that of run B. It is thought that the higher the regulator concentration is, the
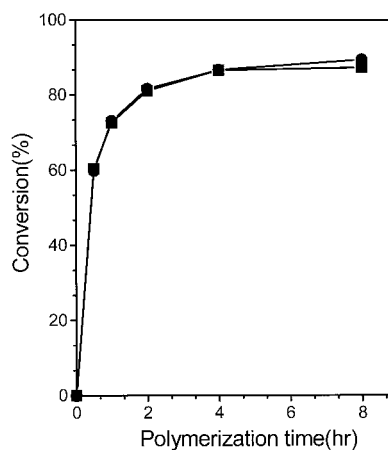

Figure 1   Effect of the polymerization time on the conversion of caprolactam: (■) run B and (●) run E.
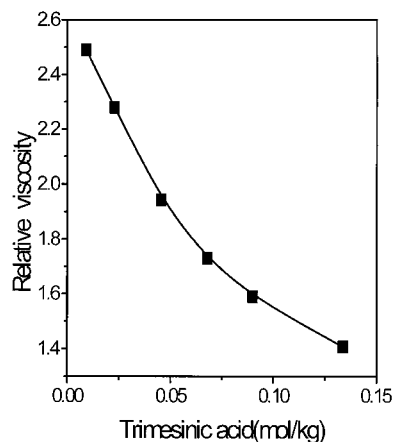
Figure 2   Variation of RV with the concentration of trimesinic acid (polymerization time = 4 h).

Figure 4   Variation of the melting point with the concentration of trimesinic acid (polymerization time = 4 h).

greater the number of branched chains is, leading to a limitation on the competitive growth of individual chains and the formation of shorter branched chains. Furthermore, trimesinic acid has the ability of promoting the ring opening of caprolactam, catalyzing the reaction system with a higher regulator concentration to reach the equilibration viscosity faster.

Characterization

Thermal Properties

Figure 4 shows the melting points of PA-6 from runs A–G estimated from the main peak temperatures of DSC curves. It is clear that with an increasing amount of trimesinic acid, the melting
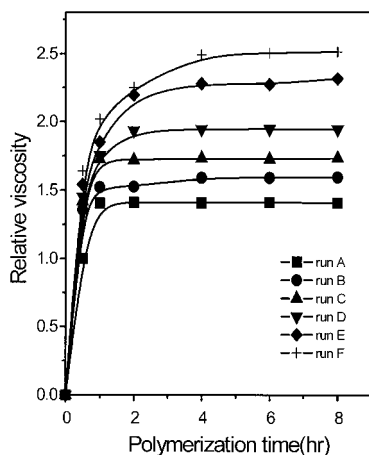
point drops. For example, as the concentration of the regulator rises from 0 to 0.1337 mol/kg, the melting temperature decreases from 227.15 to 216.31°C, reflecting the strong effect of the regulator concentration on the melting points. Generally, the drop in the melting point in Figure 4 and the drop in the RV in Figure 2 show the degree of branching rising and the MW decreasing. Figure 5 provides DSC diagrams of nylon-6 with different concentrations of trimesinic acid. With an increased concentration of trimesinic acid, the endothermic peaks shift toward a lower temperature. As the concentration of trimesinic acid in-

Figure 3   Effect of the polymerization time on RV: (■) run A, (●) run B, (▲) run C, (▼) run D, (◆) run E, and (+) run F.
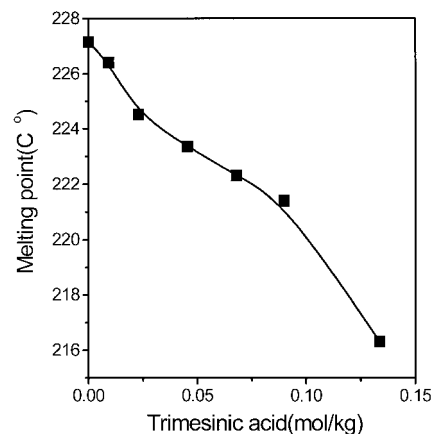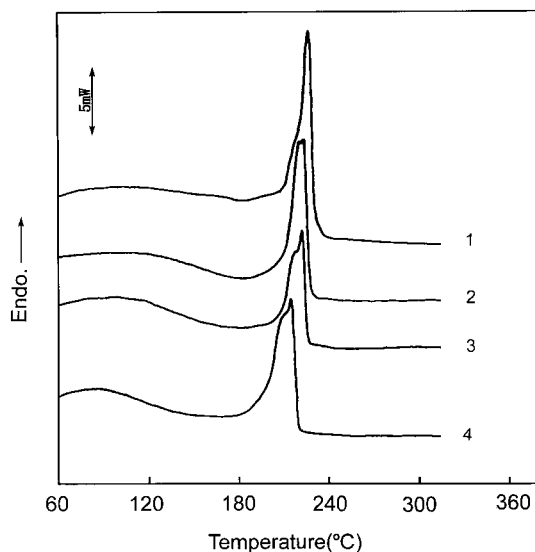

Figure 5   DSC curves of PA-6 star polymers with different trimesinic acid contents: (1) run G, (2) run E, (3) run D, and (4) run A (polymerization time = 4 h).
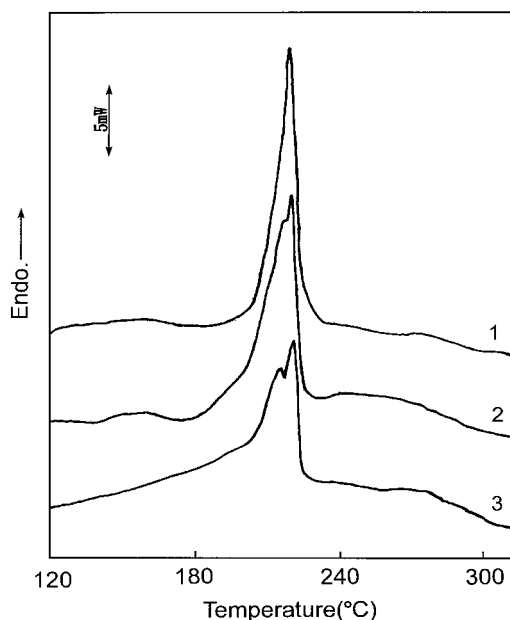
Figure 6 DSC curves of PA-6 star polymers (run B) with the same trimesinic acid content and polymerization times of (1) 0.5, (2) 2, and (3) 8 h.

creases, not only do branch points increase on the whole, but branch points that cannot insert into the crystal lattice also increase, thereby decreasing the crystal perfection. Conversely, at a low concentration of trimesinic acid, longer branched chains would be close to linear chains, enabling the polymer to retain higher melting points. In addition, increasing the branched chains may disturb the original arrangement of molecular chains and make polar groups between molecules hard to match with one another, resulting in a lower content of hydrogen bonding and a low melting point.

Moreover, in Figure 5, curve 1 without trimesinic acid demonstrates a sharp, single peak, whereas for curves with increasing trimesinic acid, a shoulder peak on the left of the original peak is observed. The higher the concentration of trimesinic acid is, the wider the shoulder appears. Compared with the shoulders of curves 3 and 4, the shoulder of curve 2 is somewhat weak. Figure 6 shows DSC curves of the same star polymer after polymerization for different times. When the reaction time is longer, the shoulder shrinks into a peak, which means the emergence of more and longer branched chains. The coexistence of the shoulder or peak and main peak demonstrates the coexistence of both linear and branched parts in the system. It is suggested that at first, imper-

fect crystals attributed to branched chains melt at a lower temperature, whereas more perfect crystals attributed to linear chains melt at a higher temperature. Unlike melting, the crystallization process behaves contradictorily. Table III shows the DSC results of star-shaped nylon-6 (run B) and linear-chain nylon-6 (G-1). They were first heated to 300°C and then cooled to room temperature at a heating or cooling rate of 20°C/min; afterward, the process was repeated. During the first heating–cooling process, the melting point of run B is 4.2°C lower than that of G-1, whereas the crystallization temperature of the former is about 3°C higher than the latter. The results indicate that the star-shaped molecules are easy to nucleate at a higher temperature because they are less mobile than the linear-chain molecules at the same temperature. Even though the crystallization temperature during the second heating–cooling process appears to be the same as the first one, the melting points are different for the respective processes, with the second lower than the first. Furthermore, the melting points in G-1, representative of linear polymers, are just slightly changed, whereas the difference in the melting points of run B, indicative of star-shaped polymers, is as high as 4°C. These features suggest that, compared with the crystal of linear-chain PA-6, although the crystallization temperature of star-shaped PA-6 is higher after the first heating, the crystal is less perfect because of branching, causing a lower melting point. As for the same star-shaped PA-6 (run B), first heating to 300°C, because of the factors relating to thermal stabilization, gives rise to less perfect crystallization, which leads to a lower melting point.

Microstructure

Figure 7 shows WAXD patterns of three samples prepared with different initial regulator concen-

Table III Crystallization and Melting Temperature of Linear and Star-Shaped PA-6

Run	First Heating and Cooling		Second Heating and Cooling	
	T_m (°C)	T_c (°C)	T_m (°C)	T_c (°C)
G-1	225.0	169.0	224.4	168.7
B[a]	220.8	172.9	216.8	172.5

T_m and T_c stands for melting and crystallization temperatures, respectively.
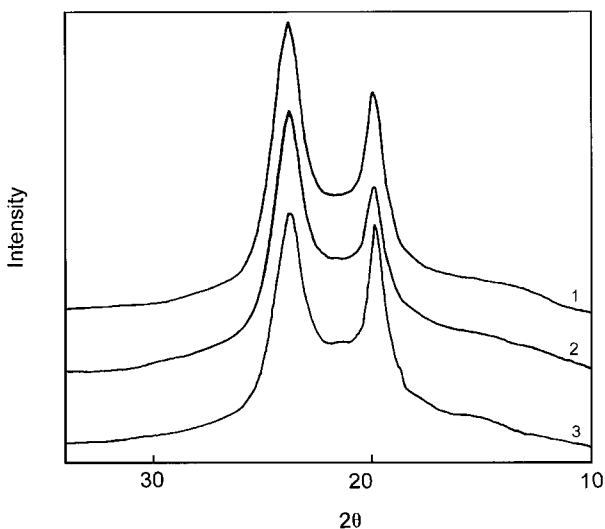
[a] Reaction time for run B = 8 h.

Figure 7   WAXD patterns of PA-6 star polymers: (1) run F, (2), run D, and (3) run A (polymerization time = 4 h).

trations. In contrast to normal PA-6, the star polymers do not change the positions of the two peaks at $2\theta = 20$ and $24°$, indicating the crystal structure still belongs to the α form and that the addition of trimesinic acid to the polymerization system does not change the crystal form. The molecules in the α form are in the fully extended

zigzag conformation and are grouped into essentially planar, hydrogen-bonded sheets. The peak at about $2\theta = 20°$ is related to the equivalent reflections of (200) planes, and the peak around $24°$ responds to the reflections of (002) and (202) planes. As shown in Figure 7, the diffraction intensities of the peaks at $24°$ for run A, D, and F do not show distinct differences. However, the intensity of the peaks at $20°$ of run F is higher than that of run D, and the peak intensity of run A is the highest among the three runs. Run A has a low MW and short branched chains, and the branched-chain length difference is relatively small. This means that run A is more symmetrical, that is, a benzene ring with three 1,3,5-substituted chains of almost equal length. Therefore, better crystallizability but poor crystal perfection, as described previously, induce a low melting point in this case. With the decrease of the trimesinic acid content in polymerization, the length difference of star-shaped-polymer (run D) arms increases, the symmetry decreases, and the crystallizability may be weakened. Run F with a much lower trimesinic acid content during polymerization may produce long branched chains and diminish the number of cores of star-shaped polymer, accounting for the high crystallizability.
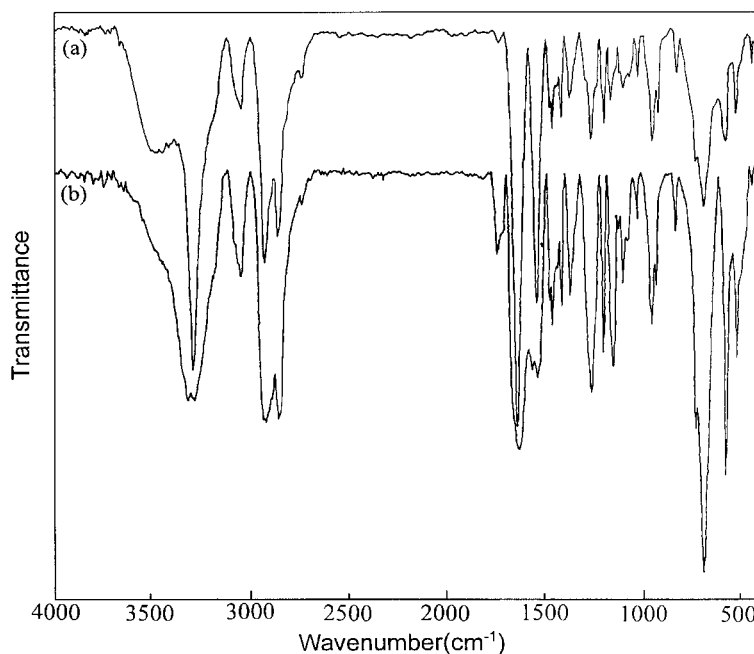

Figure 8   IR spectra of star-shaped and linear-chain PA-6: (a) G-1 and (b) run B (polymerization time = 8 h).

Table IV Mechanical Properties of Linear and Star-Shaped PA 6

Run[a]	Strength (cN/dtex)	Elongation at Break (%)	Initial Modulus (cN/dtex)	Elasticity (%)
A	—	—	—	—
B	—	—	—	—
C	2.47	9.22	15.20	93.2
D	3.21	12.83	24.92	93.4
E	4.70	12.36	25.81	94.1
F	4.65	22.51	34.88	91.2
G-1	4.86	26.49	39.52	91.0

[a] Reaction time from run A to F = 4 h.

The IR spectra of G-1 and run B are given in Figure 8. The IR spectra of the samples show the characteristic absorption bands[18] of PA-6, such as N—H stretching at 3300 cm^{-1}, C—H stretching between 3000 and 2800 cm^{-1}, C=O stretching of amide at 1640 cm^{-1}, and N—H bending and C—N bending at 1545 cm^{-1}. The position of the absorption bands of both samples does not change much, but the intensities of the bands are different. Compared with a spectrum of the linear-chain polymer G-1, the spectrum of run B shows that the sharp main characteristic bands at 3300, 3000–2800, 1640, and 1545 cm^{-1} have been greatly blunted. However, the absorptions in the 1500–500-cm^{-1} region are sharpened; this is related to the characteristic absorption of substituted benzene and COOH. In particular, the absorption at 690 cm^{-1}, whose peak heights are about three times as high as those of linear nylon-6, is a combination of characteristic absorptions of 1,3,5-substituted benzene and N—H vibration, indicating the existence of star-branched molecules. The absorption at about 1740 cm^{-1} (C=O) of G-1 is a very small peak, whereas the absorption of star-shaped nylon-6 becomes a sharp one that can be attributed to the stronger absorption of carboxyl end groups of the star polymers.

Mechanical Properties

Table IV shows some mechanical properties of star-shaped nylon-6 and linear-chain nylon-6 in the form of drawn fibers. However, no data from runs A and B appear in Table IV because both runs have MWs too low and branched chains too short for the formation of fibers under the experimental conditions without difficulty. The other runs in Table IV have longer branched chains, even long enough to be close to linear chains (e.g., run F), so fiber formation is possible under certain conditions. As shown in Table IV, with the trimesinic acid content decreasing in the reaction system or the number of star-shaped polymers decreasing, the strength of the fiber made from such polymers increases, but when the trimesinic acid content decreases to some extent, the strength remains at a certain level, approaching the strength of linear-chain nylon-6. The elongation and modulus increase as the number of star-shaped molecules decreases or the branched chains become longer. However, the elasticity of star-shaped nylon-6 is higher than that of linear-chain nylon-6. With the release of the stress applied on the ends of the fibers, the star-shaped-polymer chains seem to be more easily returned to their original positions as more chains of a star-shaped polymer play the role of being against the stress, which makes fibers elongated, instead of being single chains of a linear-chain polymer.

The results of dynamic properties on star-shaped nylon-6 (run D) and linear nylon-6 (G-1) fibers are shown in Figure 9. The tan δ–temperature curve [Fig. (b)] shows two peaks. The peak at the higher temperature is the α transition, which is believed to involve the motion of longer chain segments in the amorphous portions of the polymer and corresponds to the glass transition of nylon-6. According to the literature,[19] the peak near the α transition at the lower temperature should be the β transition. However, the positions of the α and β transitions move toward a much higher temperature than the normal positions; this seems to be caused by drawing. The α-transition temperature of run D is about 2°C lower than that of G-1, indicating the low MW star-shaped polymer of run D has more chain ends
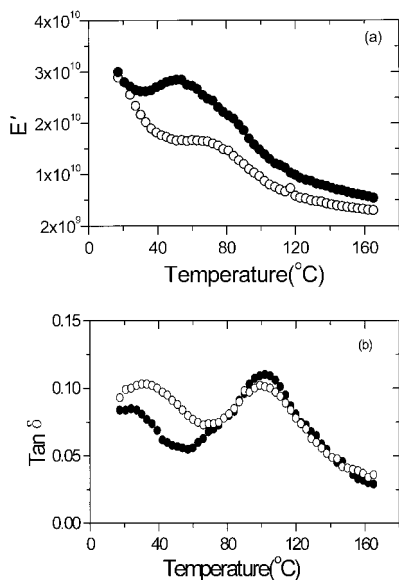
Figure 9 Dynamic mechanical behavior (E' and tan δ vs temperature) of star-shaped and linear-chain PA-6: (●) G-1 and (○) run D (polymerization time = 4 h).

and, therefore, more mobile segments, resulting in a lower α-transition temperature. However, Figure 9(a) shows that the dynamic modulus (E') of run D is always smaller than that of G-1 within the measurement range.

CONCLUSION

From the results, the following conclusions may be made:

1. Different polymerization systems have a similar caprolactam-conversion response to reaction time. The polymerization takes place rapidly at first and then, after several hours, slows down and levels off, leading to an equilibration conversion of about 90%. The increase amount of trimesinic acid inhibits the increase of RV because of the increase of branched chains.

2. The melting point of nylon-6 star-shaped polymer drops with an increasing concentration of trimesinic acid, whereas its crystallization temperature is lower than that of linear-chain nylon-6. As the concentration of trimesinic acid increases, a shoulder peak or a small peak on the left of the original peak in the DSC curve is observed,

demonstrating that there are both linear and branched chains in the polymer.

3. The crystal structure of star-shaped nylon-6 still belongs to the α form as normal linear-chain nylon-6 does. The diffraction intensities of the peaks at 24° in the WAXD patterns of star-shaped nylon-6 with different trimesinic acid concentrations do not show distinct differences, whereas peaks at 20° show that the crystallizability of the star polymer with an elevated amount of trimesinic acid does not seem to be weakened.

4. IR spectra show that the main characteristic bands of run B are blunted. The absorptions in the 1500–500-cm^{-1} region are sharpened as a result of the characteristic absorption of substituted benzene and COOH group. In particular, the absorption at 690 cm^{-1}, whose peak heights are three times as much as those of linear nylon-6, is a combination of characteristic absorptions of 1,3,5-substituted benzene and N—H vibration, indicating the existence of star polymer.

5. Compared with those of linear-chain nylon-6, mechanical properties such as strength, elongation, and initial modulus of the star polymer decrease with an increase concentration of trimesinic acid, but the elasticity of the latter is higher than that of the former. E' and the α-transition temperature of star-shaped nylon-6 are lower than those of linear-chain nylon-6 in our measurement range.

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