

Effect of a Chain Extender on the Crystallization Behavior of Nylon 66

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Received 29 September 2001; accepted 15 May 2003

ABSTRACT: The crystallization behaviors and crystalline morphologies of initial and chain-extended nylon 66 samples were studied with differential scanning calorimetry and polarizing microscopy, respectively. The crystallization rate increased and the size of the spherulites decreased with chain-extension. In addition, a two-peak behavior was observed in chain-extended nylon 66. These results showed

that for the chain-extended nylon 66, there was heterogeneous nucleation during crystallization. Therefore, the chain extender possibly functioned as a nucleating agent at the same time. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 68–71, 2004

Key words: chain; nylon; crystallization; nucleation

INTRODUCTION

High-molecular-weight (or high-viscosity) nylon 66 is prepared mainly by solid-phase polycondensation^{1,2} or chain-extending reactive extrusion.^{3–9} Based on the coupling reaction between a chain extender, with at least two functional groups, and the amino groups or carboxyl groups of nylon 66, the latter method increases the molecular weight of nylon 66 within an extruder and has the advantages of speed and high efficiency. Organic phosphite ester,^{3,4} bisoxazoline,⁵ bisoxazolone,⁶ biscalprolactam and bislauro lactam,⁷ epoxy resin,⁸ and benzoxazine⁸ have all been used as chain extenders to increase the molecular weights of nylon and polyester. We have also used epoxy resin as a chain extender to produce high-viscosity nylon 66.⁹ In this report, we mainly discuss the effect of a chain extender on the crystallization behavior of nylon 66. Although the crystallization behaviors of nylon and polyester have been extensively investigated in previous works,^{10–13} the behavior of chain-extended nylon 66 has not been covered until now. Using differential scanning calorimetry (DSC) and polarizing microscopy (PLM), we made a detailed study of initial and chain-extended nylon 66 samples with respect to their crystallization behavior and crystalline morphologies.

EXPERIMENTAL

Raw materials

Sample 1 (101L) was pure nylon 66 from the DuPont Co. (Wilmington, DE). The chain extender was a bisphenol A epoxy resin (E618), with two epoxide groups, from Jingdong Chemical Plant (Tianjin, China).

Preparation of samples 2–5

Sample 1 and various amounts of the chain extender (0.5, 1.0, 1.5, and 1.8% based on the weight of sample 1) were mixed in a high-speed blender and were then processed in a WPZSK ϕ 25 twin-screw extruder (Werner and Pfleider, Stuttgart, Germany) to give four different products. The rotational speed of the extruder was 300 rpm, and the temperatures of its four sections, from the charging hole to the ram head, were 230, 240, 240, and 230°C. The four products were pelletized and dried at 100°C for 2 h in a vacuum drying oven. Finally, the residual chain extender in the four products was extracted by acetone in a Suo extractor (Vas Lab. Supplies Co., Tianjin City, China) for 24 h, and this yielded samples 2–5. The relative viscosities of samples 1–5 were 2.28, 2.63, 3.81, 5.06, and 5.58, respectively, as measured by a Ubbelohde viscometer (Vas Lab. Supplies Co.) with formic acid as a solvent.

Instruments

A WPZSK-25 reaction twin-screw extruder (Werner & Pfleider Co.), a DSC-7 differential scanning calorime-

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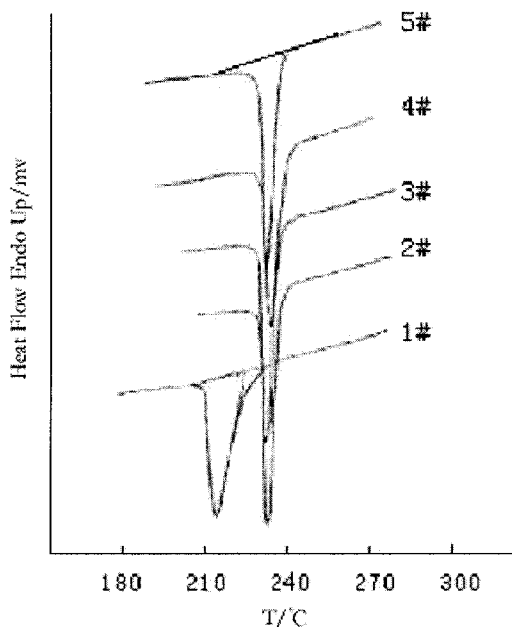


Figure 1 DSC curves of samples 1-5 during cooling from 300°C.

ter (PerkinElmer Co., Wellesley, MA), and an SM-LUX polarizing microscope (Leitz Co., Wetzlar, Germany) were used.

Property testing

DSC conditions

DSC was performed with a PerkinElmer DSC-7 apparatus. The five samples were heated for the first time at 10°C/min to 300°C, kept at that temperature for 5 min, and then cooled at 10°C/min to the ambient temperature. Subsequently, the five samples were heated for a second time at 10°C/min to 300°C. After 5 min, for isothermal crystallization, the samples were cooled rapidly to 240°C and kept there for 15 min. The environment was nitrogen in all the experiments.

In addition, to obtain the necessary accuracy, we carried out a calibration of the heat capacity by running a standard sapphire sample. The melting peak temperature and cell constant were calibrated with indium, and we established the base line by running an empty pan. In all the thermograms, the endothermic signals were pointing upward.

TABLE I
Crystallization Parameter 3 During Cooling from 300°C

Sample	1	2	3	3	5
T_c (°C)	215.3	232.8	232.0	232.2	229.9
ΔW (°C)	7.8	3.6	3.8	4.4	3.8
ΔH_c (J/g)	54.30	40.59	40.27	38.03	41.16

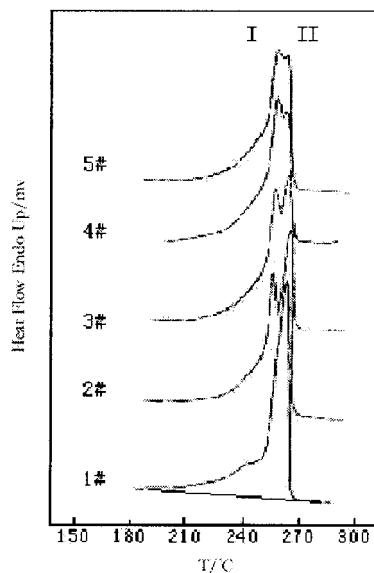


Figure 2 DSC traces of samples 1-5 during the second heating.

Morphology

Lamellae of samples 0.5 mm thick were obtained between two cover glasses via heat pressing at 280°C and were kept at 240°C for 40 min in a vacuum drying oven. The morphology of the five samples of lamellae was observed with PLM.

RESULTS AND DISCUSSION

Influence of the chain extender on the isothermal cooling crystallization behavior of nylon 66

Figure 1 shows the DSC curves of five samples cooling at 10°C/min from 300 to 20°C. The data for the crystallization temperature (T_c), the enthalpy of crystallization (ΔH_c), and the semipeak width (Δw) are listed in Table I. T_c of chain-extended nylon 66 (samples 2-5) increased about 14.5-17.5°C compared with T_c of pure nylon 66 (sample 1); this indicated that the rate of crystallization of the chain-extender samples increased markedly. Δw of chain-extended nylon 66 became much smaller than that of the pure sample, and this showed that the lamellar thickness distribution tended to be uniform. However, the T_c and Δw data for samples 2-5 showed only slight differences. The crystallization rate is known to consist of two parts: the rate of crystal nucleus formation and the rate of crystal grain growth. In general, the latter should decrease with an increase in the relative viscosity, which is contrary to this case. Thus, it was deduced that the former was the main factor here. We suppose that the chain extender acted as a nucleating agent at the same time. When the polymer melt was cooled to crystallize, the chain extender acted as crystal nuclei and

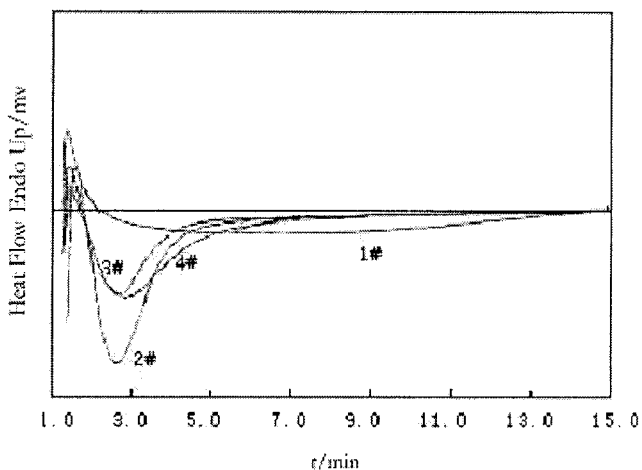


Figure 3 Isothermal crystallization curves of samples 1-4.

induced the other sections of chain to grow on it. The number of crystal nuclei increased with an increase in the quantity of the chain extender, and so the rate of crystal nucleus formation also increased. However, as the molecular chain of nylon 66 became longer with an increase in the relative viscosity, the active capacity of the chains decreased, and this restrained the chain segment from moving and arranging to form crystal nuclei; therefore, the rate of crystal grain growth decreased. The cooperative phenomena of the extender and nucleation led to a decrease in ΔH_c with an increase in the relative viscosity. No remarkable differences were observed for ΔH_c and T_c of extended nylon 66 because of the cooperative phenomena of the extender and nucleation.

Influence of the chain extender on the isothermal crystallization behavior of nylon 66

Figure 2 shows thermograms of the five samples heated to 300°C at 10°C/min after cooling. The shapes of the peaks changed greatly after the nylon 66 was chain-extended, and the two-peak behavior became more obvious. The strength ratio of peak I at a low

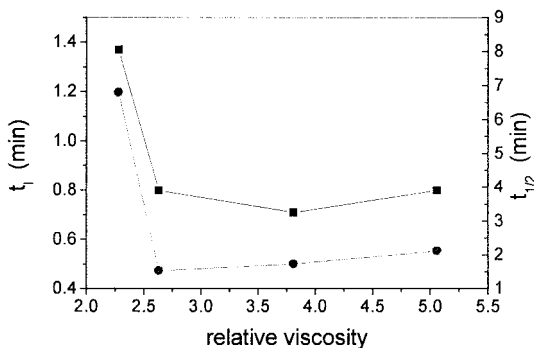
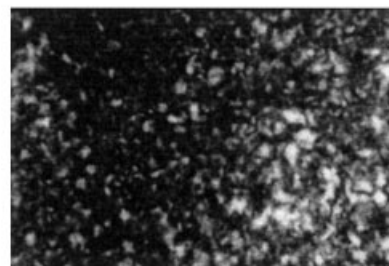


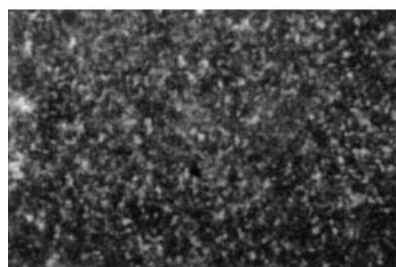
Figure 4 Variation of t_l and $t_{1/2}$ with the relative viscosity.



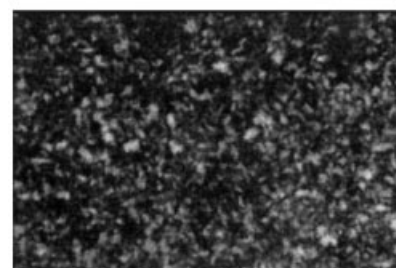
1#



2#



3#



4#

Figure 5 PLM photographs of initial and chain-extended nylon 66 samples.

temperature to peak II at a high temperature increased with the increasing relative viscosity of nylon 66. This two-peak behavior has been found in other systems. Bell¹³ believed that the high-temperature peak and low-temperature peak of two-peak melting might be attributed to the melting of folded-chain crystal and extended-chain crystal, respectively. Robert and Holdworth^{11,12,14} proposed a theory of structural rear-

TABLE II
Average Crystal Radius of Pure and Chain-Extended Nylon 66 Samples

Sample	1	2	3	4
Average crystal radius (μm)	43.0	<10	<10	<10

range: they claimed that peak I was the melting result of imperfect crystals and peak II was the melting peak of crystallization, which was caused by the recrystallization of imperfect crystals during heating. This theory of structural rearrangement is now widely accepted as an explanation for the phenomenon of two-peak melting. According to this theory, under the same conditions, the greater the viscosity is of a sample, the more difficult it is for the molecular chains to move. Therefore, more imperfect crystals form, and recrystallization is more difficult, and so the intensity of peak I becomes higher as the viscosity increases, whereas that of peak II becomes lower.

Figure 3 shows isothermal crystallization curves of samples 1–4 at 240°C. Figure 4 shows the relationship of the induction period of crystallization (t_i) and the semicrystallinity time ($t_{1/2}$) with the relative viscosity of the samples. Both t_i and $t_{1/2}$ of chain-extended nylon 66 decreased markedly compared with those of pure nylon 66, and this indicated that the rate of isothermal crystallization increased with the addition of the chain extender. This supported the idea that the chain extender acted as a nucleus agent.

Crystalline morphologies of pure and chain-extended nylon 66

Figure 5 shows PLM photographs of nylon 66 samples 1–4. Using a objective lens micrometer, we measured the radii of spherulites and worked out the actual average radius of every sample; they are listed in Table II.

Figure 5 shows that, for pure nylon 66, the spherulites were perfect, the black-cross extinction patterns were clear, the spherulite radius was larger, and the

average radius was about 43 μm . In comparison with pure nylon 66, chain-extended nylon 66 had much smaller spherulites; moreover, they were more uniform, and the average radius was about 10 μm . Figure 5 also shows that with an increase in the amount of the added chain extender, spherulite interference occurred; they became imperfect, and black crosses became blurred but still visible. The decrease in the spherulite radii proved that the chain extender also functioned as a nucleating agent, making the chain-extended nylon 66 crystallize more easily and more quickly.

CONCLUSIONS

The crystallization behavior of nylon 66 chain-extended by epoxy resin was very different from that of pure nylon 66. The results showed that the crystallization rate increased markedly, an obvious two-peak behavior was observed, and the spherulites became much smaller after nylon 66 was chain-extended. We deduced that there existed a process of heterogeneous nucleation in the crystallization of chain-extended nylon 66, in which the chain extender functioned as a nucleating agent as well.

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