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The effect of electric field on the crystallization of polyamide-6,6 by rheological measurement

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The effect of the electric field on crystallization behaviour of polyamide-6,6 (PA-6,6) was investigated by a rheological measurement. The crystallization kinetics were estimated by monitoring the changes in the absolute value of complex viscosity during crystallization. In both isothermal and nonisothermal crystallization experiments, it is observed that the crystallization rate of PA-6,6 decreases with increasing the applied electrical field. This phenomenon is explained by the orientation of dipole moments in amide groups under the electric field. In the PA-6,6, dipoles of amide groups are aligned antiparallel to each other to yield a stable crystal structure. The external electric field disturbs the antiparallel orientation of dipoles and thus prevents the chain packing during crystallization. Copyright © 1996 Elsevier Science Ltd.

(Keywords: electric field; crystallization; rheological measurement)

Introduction

The mechanical and physical properties of crystalline polymers are influenced by the crystallization process[1-5]. Information on the kinetics of crystallization are required for optimizing the polymer processing conditions and are commonly obtained from dilatometry, optical microscopy, and differential scanning calorimetry (d.s.c.)[6-8]. The rheological measurement can also be used for examining the crystallization behaviour by monitoring the changes in rheological properties, i.e. the absolute value of complex viscosity ($|\eta^*|$), elastic shear modulus, etc. As the crystallization proceeds, the viscosity is increased due to the increasing friction between the growing crystallites. During the crystallization process, the nuclei formed will act like physical entanglements, hence increasing the modulus of the melt. Recently Rudin *et al.*[9] investigated the crystallization behaviour of polypropylene, polyethylene and their blends by monitoring the changes in elastic shear modulus.

There have been several reports about the effects of electric field on the crystallization behaviour of polar crystallizable polymer[10,11]. These studies used the optical microscopy method for measuring the crystallization kinetics. However, attempts to investigate the crystallization behaviour by a rheological measurement are lacking. In the present study, we investigate the effect of electric field on the crystallization behaviour of polyamide-6,6 (PA-6,6) by means of rheological measurement.

Experimental

The commercial PA-6,6 ($M_n = 23\,000\,\mathrm{g\,mol^{-1}}$) was obtained from Tongyang Nylon Co., Korea, and used without further purification. All samples were dried prior to use in a vacuum oven at 80°C for at least 3 days. The PA-6,6 pellets were compression-moulded into a disc of 2 mm thickness and 25 mm diameter by a hot press at 300°C for 5 min.

The absolute value of complex viscosity of compression-moulded specimens was measured by Rheometrics Mechanical Spectrometer (RMS-800) with a parallel plate fixture. The sample was heated in the parallel plate fixture at 280°C for 5 min to ensure complete melting and purged by nitrogen gas to minimize thermo-oxidative degradation. The absolute value of complex viscosity was measured by using a strain of 5% at a frequency of 1 rad s^{-1}. The reason for choosing a low value of strain and frequency was to ensure that the dynamic shearing would not disrupt or disturb the crystallization process[9]. The measurement was carried out to the largest extent of crystallization before the torque exceeded the maximum value limited by the transducer. The sample was isothermally crystallized by quenching the specimen from 280°C to the crystallization temperature of 230°C under the electric field. The nonisothermal crystallization studies were performed by cooling the specimen at constant cooling rate from 280°C to 180°C under the electric field. The cooling rates used were 2, 5, 10, and 20°C min^{-1}.

A special apparatus was designed to allow the application of d.c. electric fields to the PA-6,6 melts. A Teflon insulator of 20 mm thickness and 40 mm diameter was inserted between the transducer and parallel plate fixtures, and another Teflon insulator was placed between motor and parallel plate fixtures to avoid the electric shock. The polymer specimens were placed between the parallel plate fixtures. The parallel plate fixture was coiled with a metal spring. The spring was linked with heat-resistant wire which was connected with

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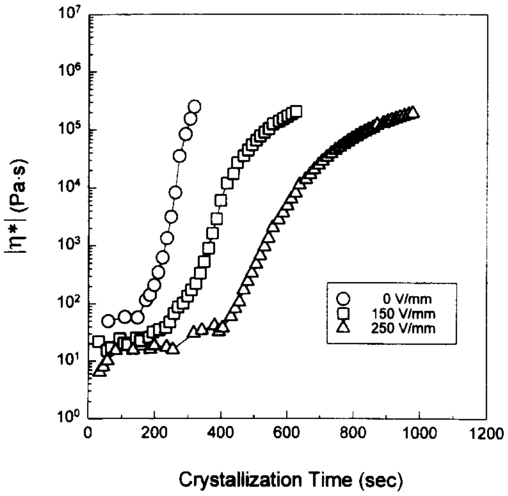

Figure 1 The change of the absolute value of complex viscosity with the crystallization time when the sample is isothermally crystallized at 230°C under various electric fields

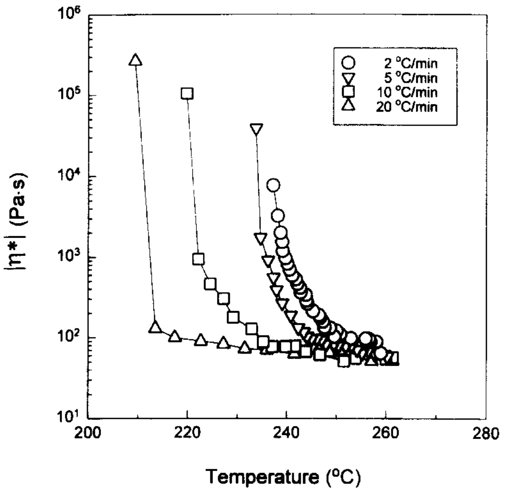

Figure 2 Effect of the cooling rate on the absolute value of complex viscosity under no electric field

d.c. electric field supply. A high voltage power supply (Keithley model 247) was used to apply the d.c. electric fields to the PA-6,6 melts. The applied electric fields were 0, 50, 150, and 250 V mm^{-1}. The temperature controller chamber was made of Teflon sheets of 2 mm thickness.

Results and discussion

Figure 1 shows the change in the absolute value of complex viscosity of PA-6,6 with the crystallization time when the samples are isothermally crystallized at 230°C under various electric fields. The absolute value of complex viscosity increases with the crystallization time, and the increasing rate becomes slower as the applied electric field increases. This means that the crystallization of PA-6,6 is retarded when the external electric field is applied. If the time when the absolute value of complex viscosity increases from 10^2 to 10^4 Pa · s is used as an arbitrary measure of crystallization rate[9], the isothermal crystallization rate (161 s) under 250 V mm^{-1} is approximately three times slower than that (56 s) under no electric field. The decrease of the crystallization rate seems to be closely related to the dipole alignment of amide groups in PA-6,6 as will be discussed later.

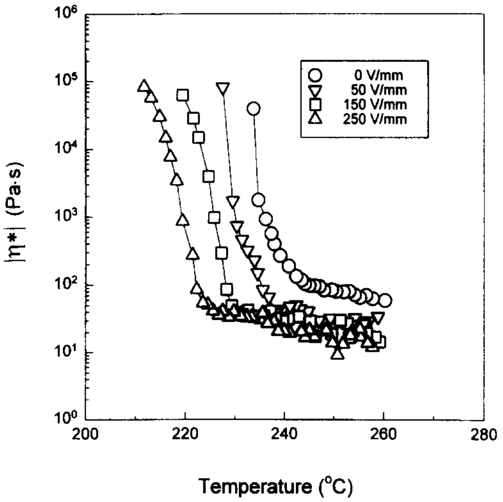

Figure 3 Effect of the electric field on the absolute value of complex viscosity during nonisothermal crystallization at a constant cooling rate of 5°C min^{-1}

Figure 2 shows the effect of cooling rate on the absolute value of complex viscosity of PA-6,6 when the sample is nonisothermally crystallized. Somewhat arbitrarily, the onset crystallization temperature ($T_{c,onset}$) is taken as the intersecting point of the slopes of both curves in the melt and in the crystallization. It is observed that the absolute value of complex viscosity increases as the nonisothermal crystallization proceeds and that the $T_{c,onset}$ becomes lower with increasing the cooling rate.

Figure 3 shows the effect of the strength of electric field on the absolute value of complex viscosity when the PA-6,6 is nonisothermally crystallized at a constant cooling rate of 5°C min^{-1}. Here the $T_{c,onset}$ is also determined as described above. It is observed that the $T_{c,onset}$ decreases with increasing the electric field, indicating that the crystallization of PA-6,6 is retarded when the electric field is applied. More specifically, the $T_{c,onset}$ under the field of 250 V mm^{-1} is about 20°C lower than that under no electric field. This result may be also related to the orientation of dipole moments of amide groups as explained by the following discussion.

The results of both isothermal and nonisothermal crystallization show that the crystallization of PA-6,6 is retarded under the electric field. This phenomenon could be explained by the molecular structure of PA-6,6. In polyamides, hydrogen bonding, which is many times stronger than van der Waals bonding, controls the chain packing. In PA-6,6, the molecules are in the form of extended planar zig-zags joined together in hydrogen-bonded sheets[12-15]. The two crystal structures, α- and β-form, contain hydrogen-bonded sheets of fully extended planar zigzag chains and differ only in the side-by-side packing of the sheets. In α-form, successive planes are displaced in the c direction whereas in the β-form the hydrogen-bonded sheets have alternating up and down displacements. *Figure 4* shows the orientation of dipole moments of amide groups in PA-6,6. The arrows in *Figure 4* indicate the dipole moments in the hydrogen bonds. The dipoles of amide groups are aligned antiparallel to each other and thus form a stable crystal structure. If the strong external electric fields are applied to PA-6,6, during crystallization from

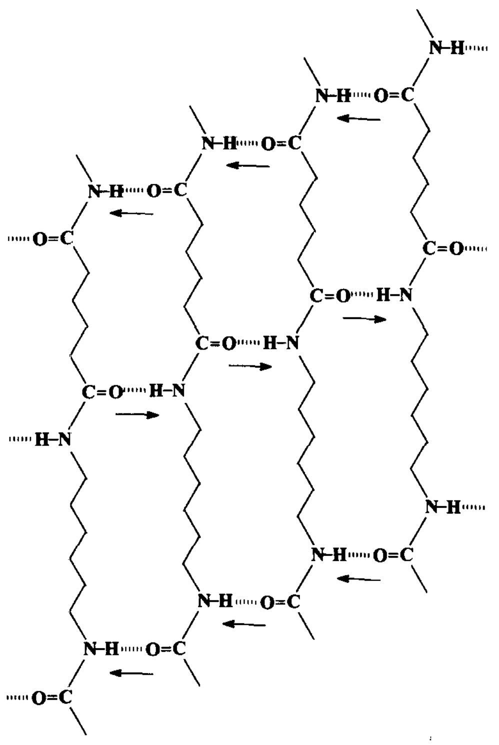

Figure 4 Schematic representation of the orientation of dipole moments in hydrogen bonding of PA-6,6

the melt, the dipoles will tend to align parallel in the direction of the fields. Therefore the electric field disturbs to some extent the antiparallel orientation of dipoles which gives the stable crystal structure. In summary, the electric field has an unfavourable effect on the packing of crystal structure and thus retards the crystallization of PA-6,6.

Conclusions

The effects of electric field on the crystallization behaviour of PA-6,6 have been examined by a rheological measurement. In isothermal crystallization experiments, it is observed that the crystallization rate decreases with increasing the applied electric field. In nonisothermal crystallization experiments, the onset temperature of crystallization under the electric field is lower than that under no electric field, indicating that the crystallization is retarded under the electric field. It is suggested that these phenomena are closely related to the orientation of dipole moments of amide groups. In PA-6,6, the dipoles of amide groups are aligned antiparallel to each other and thus form a stable crystal structure. However, when the electric field is applied to PA-6,6 during crystallization, the field disturbs the antiparallel orientation of dipoles of amide groups and thus prevents the chain packing to some extent. Consequently, the crystallization of PA-6,6 is retarded under the electric field.

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