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ORIGINAL PAPER

Pulsed magnetic field as a new technique to control the crystallization and orientation of poly(trimethylene terephthalate)

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Abstract Magnetic influence on the crystallization and orientation of poly(trimethylene terephthalate) (PTT) were studied by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimeter (DSC), and X-ray diffraction (XRD) during isothermal crystallization at 195 °C under pulsed magnet. The results showed that the crystallization properties of PTT are changed under the influence of pulsed magnetic field. It should be emphasized that the pulsed magnetic field can be applied as a new method to control the crystallization and orientation of polymers.

Keywords PTT · Pulsed magnetic field · Crystallization · Orientation · XRD

Introduction

Poly(trimethylene terephthalate) (PTT) was firstly synthesized by Whinfield and Dickson in 1941 [1]. The chemical structure of PTT is similar to polyethylene terephthalate. It is a promising material for textile fiber, carpet, film, and engineering plastic due to its excellent physical and mechanical properties [2, 3]. A great many of studies on morphology, chain conformation, packing of PTT crystals, crystallization, and melting behavior have been reported in recent years [4]. But the crystallization of PTT under pulsed magnetic field was seldom researched.

The influence of magnetic field on state of aggregation of polymer has studied since 1986. Stupp [5] put forward that magnetic field could make polymer molecule

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a line in his paper. Later, magnet was applied to form specific polymer structures, especially in the field of making liquid crystal production. Since 1997, Kimura [6] successively reported that some common polymers, for example, poly(ethylene 2,6-naphthalate), *i*-polystyrene, *i*-polypropylene, and poly(ethylene terephthalate) can come into static magnetic orientation near the melting point. The effect of strong static magnetic field on melting orientation of polymer had already been proved.

In this article, we introduced pulsed magnetic field during isothermal crystallization of PTT and studied the magnetic influence on crystallization. We chose FTIR to characterize the crystalline content of samples, DSC to study thermal and crystalline characteristics, XRD to study crystal orientation.

Experimental section

Sample preparation and pulsed magnet measurement

PTT pellets were got directly from commercial products. Figure 1 shows a schematic diagram of the furnace used to prepare samples heat-treated in a pulsed magnet (strength of 2 T and frequency of 4 times/min). As is shown in Fig. 2, sample was melted at 260 °C for 15 min, cooled rapidly to 195 °C, and subjected to the isothermal crystallization for 25 min, then quenched to room temperature.

The process was completely carried out in pulsed magnetic field and in argon atmosphere to prevent samples from oxidation. The start of the crystallization process was defined as the point where the temperature reached the given crystallization

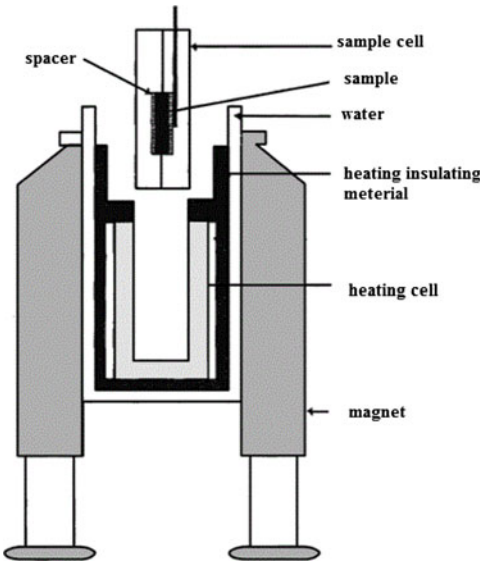

Fig. 1 Schematic figure of the furnace used for sample preparation in pulsed magnet (strength of 2 T and frequency of 4 times/min)

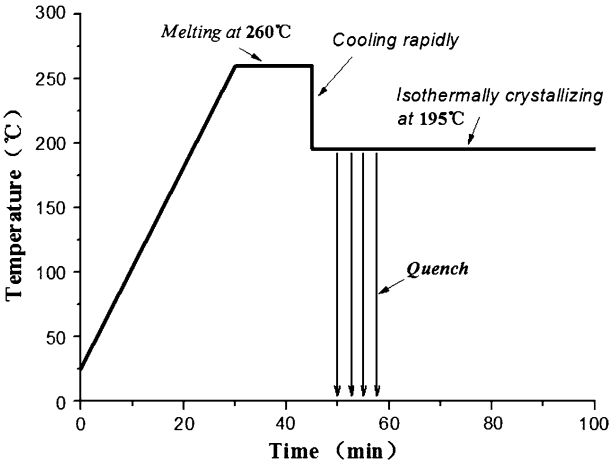

Fig. 2 Thermal history applied for the preparation of samples

temperature. The magnetic field was applied from the beginning, before the heating from the room temperature until the completion of the experiment. For comparison, exactly the same procedure was taken outside the magnet as well.

Differential scanning calorimeter

A NETZSCH DSC 200PC is used for differential scanning calorimeter with a heating rate of 10 °C/min.

X-ray diffraction

XRD is carried by using a DLMAX-2200 and operating at 40 kV and 200 mA to generate a Ni-filtered Cu K_α X-ray beam, the 2θ scan range is from 10° to 90°.

Infrared measurements

A NICOLET 380 is used for Fourier transform infrared (FTIR) measurements with a resolution of 4 cm^{-1}.

Results and discussion

Infrared measurements

Figure 3 shows the infrared spectra of the samples crystallized outside and inside magnet, which refer to curve a-1 and a-2, respectively. The assignments of main peaks given in Table 1 [7–10] are used for the structure analyses. We chose 1505 cm^{-1} as internal standard whose intensity had no change after annealing

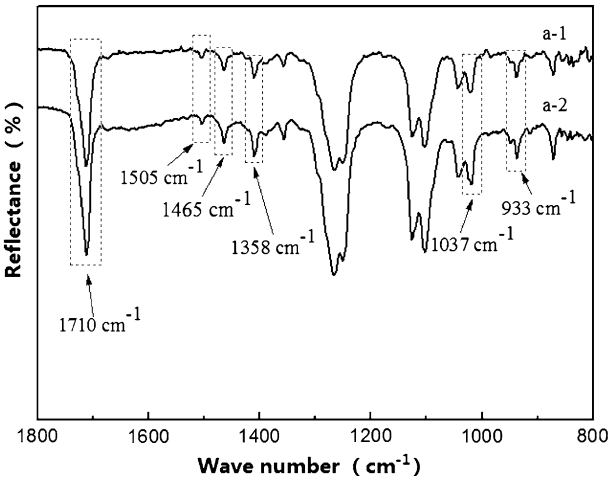

Fig. 3 Infrared spectra of PTT samples: (*a-1*) outside pulsed magnet, (*a-2*) inside pulsed magnet

Table 1 PTT IR band assignments

Wave number (cm^{-1})	Assignment	Phase	I/I_{1505}	
			a1	a2
933	CH_2 rocking of glycol residue	Crystalline	1.90	2.43
1037	Ag C–C stretching	Crystalline	2.36	3.32
1358	Bu CH_2 wagging	Crystalline	1.36	1.67
1465	Benzene ring C–C stretch	Crystalline	1.64	2.37
1505	Benzene ring C–C stretch	Internal standard	–	–

according to Kim's result [6], meanwhile, 933, 1038, 1358, and 1465 cm^{-1} as crystalline peaks, intensity of whom increased after annealing [7–9]. The relative intensity of crystalline peaks of 933, 1038, 1358, and 1465 cm^{-1} increases after the treatment of magnet which illustrates that pulsed magnetic field increases the content of crystalline part of PTT.

Thermal behavior measurements

Samples were scanned from 50 to 260 °C with the heating rate of 10 °C/min, and the melting curves see in Fig. 4. The crystallinity of polymers was calculated by the following equation:

$$x\% = \Delta H_m/\Delta H_0 \times 100\% \quad (1)$$

ΔH_m is the melting enthalpy while ΔH_0 refers to the melting enthalpy with crystallinity of 100% which value is 30 ± 2 kJ/mol [11]. So we could compare the crystallinity through the change of melting enthalpy and results showed in Table 2. The melting temperature, melting enthalpy, and crystallinity increased after the

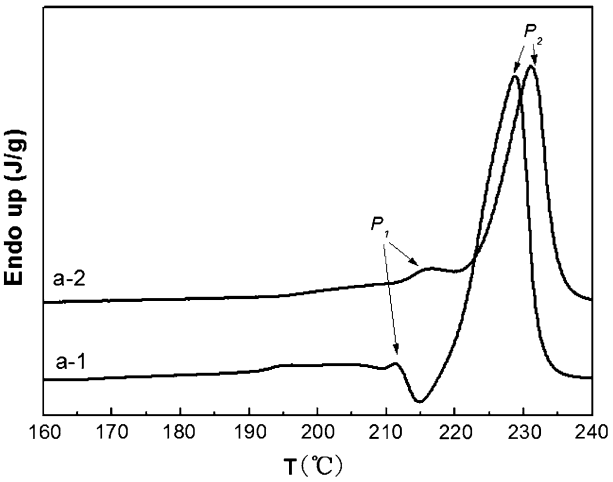

Fig. 4 DSC curves of PTT samples: (*a-1*) outside pulsed magnet, (*a-2*) inside pulsed magnet

Table 2 DSC data from melting curves

Sample	P_1 (°C)	P_2 (°C)	ΔH_m (J/g)
a-1	211.4	228.8	45.7
a-2	216.0	231.0	47.8

The enthalpy of recrystalline have been taken into account by using the software of DSC device

treatment of magnet which is consistent with results from FTIR. As is shown in Fig. 4, two melting peaks is observed, which are marked as P_1 and P_2, respectively. P_1 is of grainy imperfect crystal aggregates, and P_2 is the main melting peak of PTT [12]. Both melting peaks transfer to higher temperature location, among which P_1 increases from 211.4 to 216.0 °C and P_2 from 228.8 to 231.0 °C. These results illustrate that pulsed magnetic field perfects the crystallization of PTT.

XRD measurement

Figure 5 show X-ray diffraction patterns of specimens prepared inside (a2) and outside (a1) pulsed magnetic field. XRD peaks assignment [13] are shown in Fig. 5.

Compared sample a1 with sample a2, no change is found in the Bragg angle position of (010), $(0\bar{1}2)$, (012), $(102/10\bar{3}/112)$, and $(1\bar{1}3)$ plane, which means that there is no difference in crystal form. And the crystallinity of each samples was calculated, 40.4% for sample a1 while 58.0% for sample a2 which accord closely with the results of FTIR and DSC.

We can notice that there are some changes in the intensity of peaks between a1 (top) and a2 (top).The intensity of $(102/10\bar{3}/112)$ plane is a little difference with $(1\bar{1}3)$ plane in sample a1 (top) while the intensity of $(102/10\bar{3}/112)$ plane is much higher than that of $(1\bar{1}3)$ plane in sample a2 (top). Besides, the relative intensity of

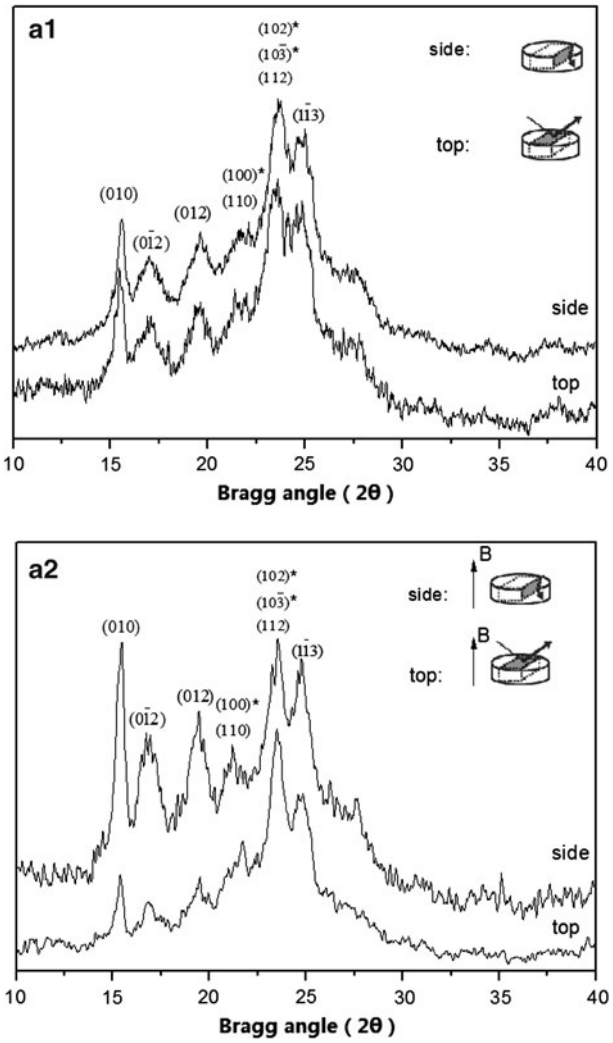

Fig. 5 XRD patterns of PTT samples **a1** outside pulsed magnet and **a2** inside pulsed magnet, **a2** (*side*) the plane in the direction parallel to pulsed magnet, **a2** (*top*) the plane in the direction is perpendicular to pulsed magnet. *The asterisk* indicates the major reflection in the diffraction peak

(010) with $(102/10\bar{3}/112)$ is 0.72 in Sample a1 (top) but 0.34 in sample a2 (top). Above all, crystal texture of PTT induced by the pulsed magnetic field is observed.

In order to further prove crystal texture, we did not only top but also side scan of both samples as shown in Fig. 5. For sample a1, there is no change between top scan and side scan, while in sample a2, situation became different. As shown in Fig. 5(a2) side, the relative intensity of (010) with $(102/10\bar{3}/112)$ is 0.99, which is higher than that in Fig. 5(a1) top. Besides, the relative intensity of $(0\bar{1}2)$, (012) with (100/110) is higher in top than in side of sample a2. We estimated the

Table 3 The "*P* values" of a1 and a2 in two scan planes

	$P_{(h00)}$ (a.u.)	$P_{(0k0)}$ (a.u.)	$P_{(00l)}$ (a.u.)
a1			
Top	0.60	0.62	0.71
Side	0.62	0.61	0.73
a2			
Top	0.69	0.53	0.72
Side	0.52	0.67	0.68

orientation of each crystal axis by the "*P* values" which is defined by the following equations:

$$P_{(h00)} = \left(I_{(h00)} + I_{(hk0)} + I_{(h0l)} + I_{(hkl)}\right) \Big/ \sum I \tag{2}$$

$$P_{(0k0)} = \left(I_{(0k0)} + I_{(hk0)} + I_{(0kl)} + I_{(hkl)}\right) \Big/ \sum I \tag{3}$$

$$P_{(00l)} = \left(I_{(00l)} + I_{(h0l)} + I_{(0kl)} + I_{(hkl)}\right) \Big/ \sum I \tag{4}$$

where, $\sum I$ is the summation of the intensity values of all the crystal planes in one curve.

These equations express the scales of the distribution intensities of crystal axis normal to the scan face and calculation results showed in Table 3.

The data proved that the distribution density of *b*-axis which is normal to (0*k*0) decrease in the direction perpendicular to the top plane when *c*-axis (00*l*) and *a*-axis (*h*00) increase in the sample crystallized inside the magnet. These changes can be easily intuited in Fig. 6. It is obvious that the distribution intensities of *a*-axis and *b*-axis are anisotropic in sample a2, and the *a*-axis is oriented obviously in the direction of magnetic field.

The phenomenon of crystal orientation in our study is coincided with the literature reported by Kimura and Florian [14, 15]. It can be explained according to the following formula:

$$V|x_a|B^2/2\mu_0 > kT \tag{5}$$

where V is the volume of a particle, μ_0 is permeability of vacuum, B is the magnetic flux density, and x_a is the anisotropic diamagnetic susceptibility.

The difference in magnetic energy between the two alignment states, parallel and perpendicular to the field direction, is the driving force of the alignment. In a condensed phase, this difference in magnetic energy competes with the thermal energy kT that disturbs alignment.

Magnetically anisotropic crystal particles are usually oriented in the direction of the lowest energy in a static magnetic field [16], which means that the axis with the largest diamagnetic susceptibility is always oriented perpendicular to the magnetic field, and the direction of this axis is random within the plane normal to the magnetic field and the axis with the smallest diamagnetic susceptibility tends to be aligned along the magnetic field.

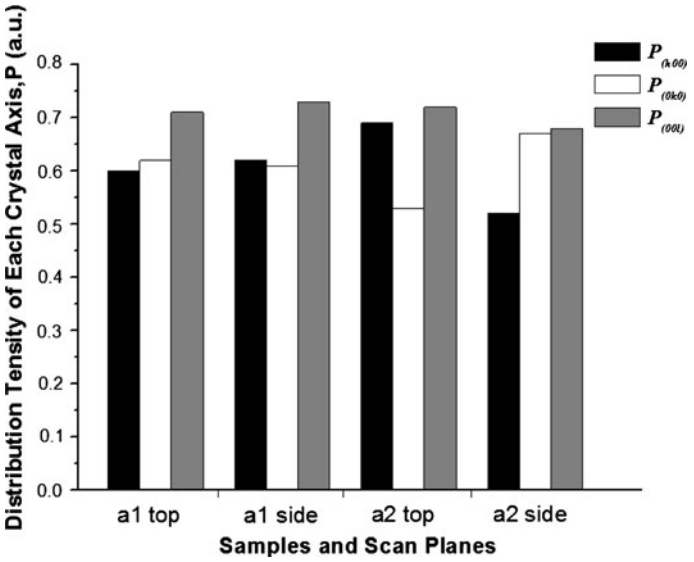

Fig. 6 *P* values of different samples and scan planes

Conclusions

The influence of PTT isothermal crystallization at 195 °C by pulsed magnetic field (4 T, 4 times/min) has been researched in this study. From the experiments, we can conclude that the pulsed magnetic field perfects crystals and enhance crystallinity. XRD orthotropic-plane-scans patterns showed that crystal texture existed in PTT samples treated by pulsed magnet. In pulsed magnetic field, polymer crystal orientation can be produced as reported in strong static magnet. The *a*-axis which is aligned along the magnetic field should be with the smallest diamagnetic susceptibility and the confirmation of this speculation depends on the mensuration of the anisotropic diamagnetic susceptibility of PTT in the future. We proposed that the pulsed magnetic field is a promising processing method of controlling the crystallization and microstructure of polymer.

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