

RAPID COMMUNICATION

Smectic structure and glass transition in poly(butylene terephthalate)

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INTRODUCTION

Poly(butylene terephthalate) (PBT) is a semi-crystalline polyester that is used extensively in many engineering materials. PBT has two triclinic crystalline forms, the α -form and the β -form,^{1–4} and a smectic liquid crystalline structure.⁵ The α -form is mainly obtained when PBT is crystallized from molten or glassy states. Recently, we investigated the crystallization of PBT from glass by small-angle X-ray scattering and differential scanning calorimetry (DSC), and revealed that PBT crystallizes through a mesomorphic phase, which has an intermediate structure between crystal and amorphous.⁶ The β -form is produced when the α -form is held under strain, and then reversibly transforms to the α -form on removal of the strain. The main difference between these forms is that the c axis (fiber axis) length of the α -crystalline unit cell (~ 11.6 Å) is shorter than that of the β -form (~ 13.0 Å). The conformations of the four methyl groups in the α - and β -forms are the gauche–*trans*–gauche and all-*trans* conformations, respectively. The smectic structure of PBT is obtained when amorphous PBT is stretched at room temperature and transforms into the α -form with heating.⁵ The length of the smectic periodicity is 11.69 Å, which corresponds to the c axis length of the α -crystalline unit.⁵

Similar smectic ordering has been found in other polyesters^{7–10} and isotactic polypropylene (iPP).^{11–14} For poly(ethylene terephthalate)^{7,8} and poly(ethylene naphthalate),⁹ smectic structures are formed only by stretching glassy state polymers. For poly(butylene naphthalate) (PBN)¹⁰ and iPP,^{11–14} smectic structures are also formed by rapid quenching from the molten state without stretching. In the latter polymers, two glass transition temperatures (T_g) are observed; the T_g of the smectic structure, T_g^{sm} 65 °C for PBN and

1 °C for iPP, is higher than the T_g of the isotropic amorphous liquid, T_g^{am} 45 °C for PBN and –30 °C for iPP.^{10,12} Thus, T_g^{sm} is higher than T_g^{am} for polymers forming the smectic structure by quenching or by stretching the glassy state. In PBT, the value of T_g has not been well established, because the crystallization rate of PBT is much higher than that of poly(ethylene terephthalate), and a complete amorphous state is not formed. Recently, Pyda *et al.*^{15,16} reported the T_g of PBT as 314 K from DSC results. The aim of this study is to clarify T_g for PBT, and discuss the relationship between the observed T_g and smectic structure formation of PBT.

EXPERIMENTAL PROCEDURE

PBT (viscosity average molecular weight $M_v=38\,000$, Sigma-Aldrich Co. Ltd, St Louis, MO, USA) was used as the starting material. PBT was melted at ~ 280 °C for 2 min on a hot plate and then rapidly quenched in ice water. The thickness of the quenched PBT film was ~ 150 μm . The quenched PBT was examined immediately after quenching by one-dimensional wide-angle X-ray diffraction (1D-WAXD) at room temperature. Quenched PBT films that annealed at 40, 60 and 180 °C for 30 min were also examined using 1D-WAXD. The quenched PBT films were uniaxially stretched to four times their length at room temperature. The stretched PBT films were annealed at 40, 60 and 180 °C for 30 min, cooled to room temperature and then examined by two-dimensional WAXD (2D-WAXD). WAXD measurements were performed using a Rigaku Rint 2500 system (Rigaku Corporation, Tokyo, Japan). WAXD patterns were recorded using an imaging plate that covers the q -range from 0.4 to 4 Å^{–1} ($q=4\pi(\sin \theta)/\lambda$, where λ and 2θ are the X-ray wavelength and scattering angle,

respectively). Before DSC measurements (Shimadzu DSC60 (Shimadzu Corporation, Kyoto, Japan), 10 °C min^{–1}, –100 to 250 °C), the quenched PBT was uniaxially stretched to four times its length at 0 °C in ice water and at room temperature, and then annealed in the same way as for the WAXD measurements. The sample histories for DSC measurements are listed in Table 1.

RESULTS AND DISCUSSION

Structures of quenched PBT with and without stretching

Figures 1a–d show WAXD patterns measured at room temperature for the PBT quenched from the melt to 0 °C and the quenched PBT films annealed at 40, 60 and 180 °C for 30 min, respectively. The quenched PBT is identified as the amorphous phase, because of amorphous halo and the absence of crystalline peaks in the WAXD pattern. The α -crystalline peaks at $q=0.64, 1.15, 1.22, 1.46, 1.65, 1.77, 2.05$ and 2.20 Å^{–1} appear for the films annealed at 40 °C and above, and the intensities increase with increasing annealing temperature.

Figures 2a–d show 2D-WAXD images of the as-stretched PBT and the PBT stretched and annealed at 40, 60 and 180 °C, respectively. The WAXD image of the as-stretched PBT has two sharp peaks along the stretching direction and two broad peaks perpendicular to the stretching direction. The position of the sharp peak observed at $q=0.54$ Å^{–1} corresponds to 11.6 Å and is assigned to the periodicity of the smectic phase.⁵ The intensity of this peak decreases with increasing annealing temperature and eventually disappears (Figure 2). On the other hand, the two broad peaks on the equator first split vertically into four peaks (Figure 2b) and then into eight peaks (Figure 2d), and their intensities increase with increasing annealing

Table 1 Sample histories of the PBT specimens for DSC measurements

DSC curve in Figure 3	Stretching temperature	Thermal treatment
A	Without stretching	None
B	Without stretching	40 °C, 30 min
C	Without stretching	60 °C, 30 min
D	0 °C	None
E	Room temperature	None
F	Room temperature	40 °C, 30 min
G	Room temperature	60 °C, 30 min

Abbreviations: DSC, differential scanning calorimetry; PBT, poly(butylene terephthalate).

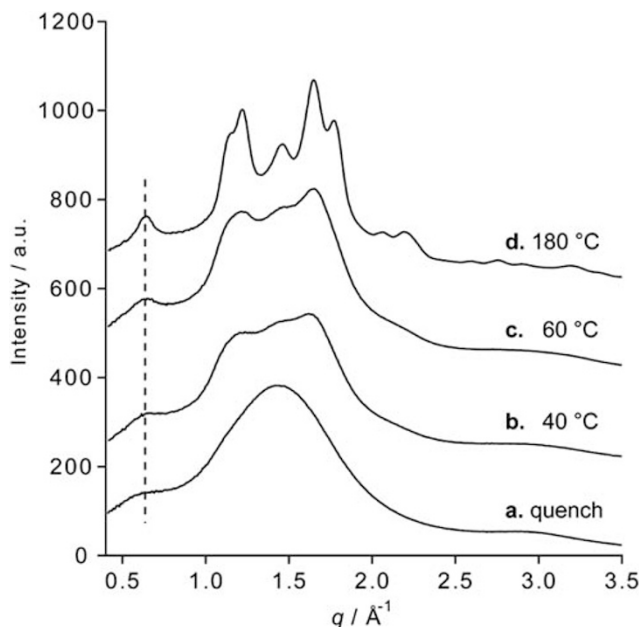


Figure 1 1D-WAXD patterns for quenched PBT (a) without stretching, and PBT annealed at (b) 40, (c) 60 and (d) 180 °C after quenching. The curves for annealed PBT are shifted vertically for comparison. The vertical broken line represents the position of the (001) peak of the α -form at $q=0.64 \text{ \AA}^{-1}$.

temperature. The strong peaks are assigned to the α -crystalline peaks.⁵ Results show that the smectic structure transforms into the α -form on annealing of the stretched PBT. However, in Figure 1, the α -form peak at $q=0.64 \text{ \AA}^{-1}$ is observed, but not the smectic peak at $q=0.54 \text{ \AA}^{-1}$, which indicates that the smectic structure is formed only by stretching of the glass state PBT.

Thermal properties of quenched PBT with and without stretching

Figure 3a shows the DSC curves of PBT without stretching. The DSC curve for amorphous PBT in Figure 3a (curve A) has two endothermic peaks at 25 and 225 °C and an exothermic peak at 40 °C. The endothermic peak at 225 °C is assigned to the melting temperature. For amorphous PBT annealed at 40 and 60 °C (curves B and C, respectively), the lower endothermic peak and the exothermic peak shift to the higher

temperature region with increasing annealing temperature. The exothermic peak is due to crystallization. Cheng *et al.*¹⁷ have reported that the lower endothermic peak $\sim 10\text{--}15 \text{ }^\circ\text{C}$ above the annealing temperature is due to melting. However, the DSC curves of amorphous PBT annealed at both 40 and 60 °C have a small endothermic peak or shoulder at 31 °C, which is independent of the annealing temperature. This small endothermic peak at 31 °C (onset 26 °C) is considered to be related to the T_g of amorphous PBT. When the DSC curve for amorphous PBT (curve A) around T_g is compared with the specific heat C_p data,¹⁵ the maximal value of the peak at 31 °C does not reach the expected value of liquid PBT shown by the broken line.¹⁵ The behavior of curve A around T_g indicates that amorphous PBT starts to crystallize during the change of C_p at T_g with an exotherm.

Figure 3b shows DSC curves for the stretched PBT specimens. The curves for

PBT stretched at room temperature and those that annealed at 40 and 60 °C after stretching at room temperature (Figure 3b, curves E, F and G, respectively) also have a peak at 31 °C, the lower endothermic peak and the exothermic peak, and the melting peak. Figure 3c shows a comparison of the DSC curves for PBT with and without stretching. The peaks of PBT specimens that annealed at 40 and 60 °C with stretching (curves F and G) are located at the same temperatures as those without stretching (curves B and C). In particular, the peak at 31 °C in all the DSC curves, which is considered to be related to the T_g of the amorphous liquid, does not shift by annealing. However, in the DSC curve of PBT stretched at 0 °C (Figure 3b, curve D), the lower endothermic peak, which is absent in the DSC curve of the quenched PBT without stretching (curve A), appears below 31 °C. Figure 3c clearly shows the difference between the initial increases of curves A and D around 30 °C.

The exothermic peak at 40 °C of the sample quenched and stretched at 0 °C (curve D) is smaller than that without stretching (curve A), whereas the effect of stretching on the exothermic behavior of samples annealed at 40 °C (curves B and F) and 60 °C (curves C and G) is negligible. The annealed samples are semicrystalline, with a small fraction of the smectic structure in the stretched samples; therefore, the lower endothermic peak and the exothermic peak correspond to melting and recrystallization, respectively. The quenched sample is glassy (curve A) and the sample that stretched at 0 °C consists of the smectic structure and the amorphous phase; therefore, the difference in the exothermic peak indicates that the enthalpy of transition from the amorphous to the crystalline state is larger than that from the smectic to the crystalline structure.

Relationship between smectic structure and glass transition

Here, we consider the origin of the lowest peak at 25 °C in the quenched PBT by stretching at 0 °C. The quenched and stretched PBT has peaks at 25 and 31 °C, whereas the quenched PBT without stretching has only the peak at 31 °C. According to WAXD results, the PBT stretched in the glass state has the smectic structure, and when quenched PBT with and without stretching is heated, the smectic structure and amorphous phase transform into the α -form. The DSC curves of PBT that annealed at 40 and 60 °C, both with and without stretching, depend only on the annealing

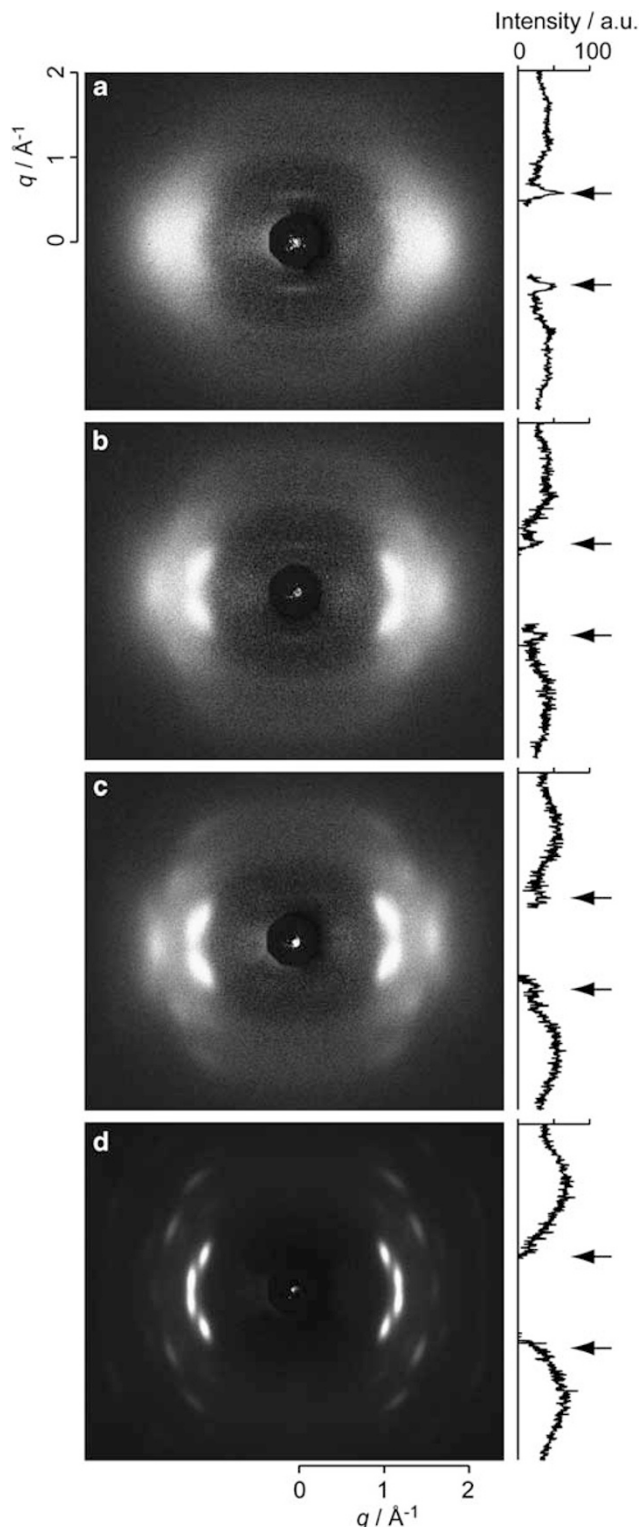


Figure 2 2D-WAXD images of (a) PBT stretched at room temperature after quenching, and the stretched PBT annealed at (b) 40, (c) 60 and (d) 180 °C. The patterns on the right side of the 2D-WAXD images are the intensities in the meridional direction. The arrows in the right figures represent the position of the smectic peak at $q=0.54 \text{ \AA}^{-1}$.

temperature, regardless of stretching, and exhibit the 31 °C peak. The result indicates that the oriented amorphous PBT also has

enthalpy relaxation at 31 °C. The lowest peak at 25 °C is present only in the DSC curve of the quenched PBT by stretching at 0 °C,

which has the smectic structure. Therefore, we propose that the lowest peak at 25 °C (onset 21 °C) for PBT that stretched at 0 °C is the T_g of the smectic structure formed by the stretching of amorphous PBT, and that the T_g of the smectic structure T_g^{sm} and that of the isotropic or oriented amorphous liquid T_g^{am} are 21 and 26 °C, respectively, according to the onset temperatures of the endothermic peak.

We now discuss the reason for the disappearance of T_g^{sm} in the stretched and annealed PBT specimens (Figure 3, curve F and G), in which the smectic structure is still evident from the WAXD result (Figure 2). The WAXD images in Figure 2 show that the smectic structure transforms into the α -form during the annealing process. Therefore, a continuous decrease in the fraction of the smectic structure is the main cause for the disappearance of the T_g^{sm} endothermic peak in Figure 3. Furthermore, there is a possibility that stabilization of a part of the smectic structure by crystallization confines the mobility of the PBT chains and thus increases T_g^{sm} .

From the results of this study, we have confirmed that the smectic structure is formed only by the stretching of amorphous PBT, and determined that PBT has two T_g values: T_g^{sm} at 21 °C and T_g^{am} at 26 °C. Multiple- T_g behavior has been reported for some liquid crystalline polymers,^{18–20} in addition to crystalline polymers.^{10,12} Some liquid crystalline polymers are reported to have T_g^{sm} below T_g^{am} .^{18–20} PBN and iPP, in which T_g^{sm} is above T_g^{am} , form the smectic structure without stretching. In these polymers, the fraction of smectic structure, rather than the crystalline phase, increases at temperatures between T_g^{sm} and T_g^{am} .^{10,12} Chen and Zachmann¹⁸ reported the locations of T_g for a liquid crystalline structure, T_g^{LC} , and an isotropic phase T_g^{iso} with respect to the free volume theory. According to their interpretation, T_g^{LC} should be lower (higher) than T_g^{iso} when the difference between the volumes at T_g^{LC} and T_g^{iso} is larger (smaller) than the volume change on liquid crystallization. We propose the following relationship between smectic structure formation and T_g . A material with T_g^{sm} higher than T_g^{am} forms the smectic structure by simple quenching or annealing above T_g^{am} . On the other hand, a material with T_g^{sm} lower than T_g^{am} forms the smectic structure only by stretching of the glassy state. In the case of PBT, the smectic structure is formed only by stretching of the glassy state, because T_g^{sm} is lower than T_g^{am} . Similar relationships are expected for poly(ethylene terephthalate)^{7,8} and poly(ethylene naphthalate).⁹

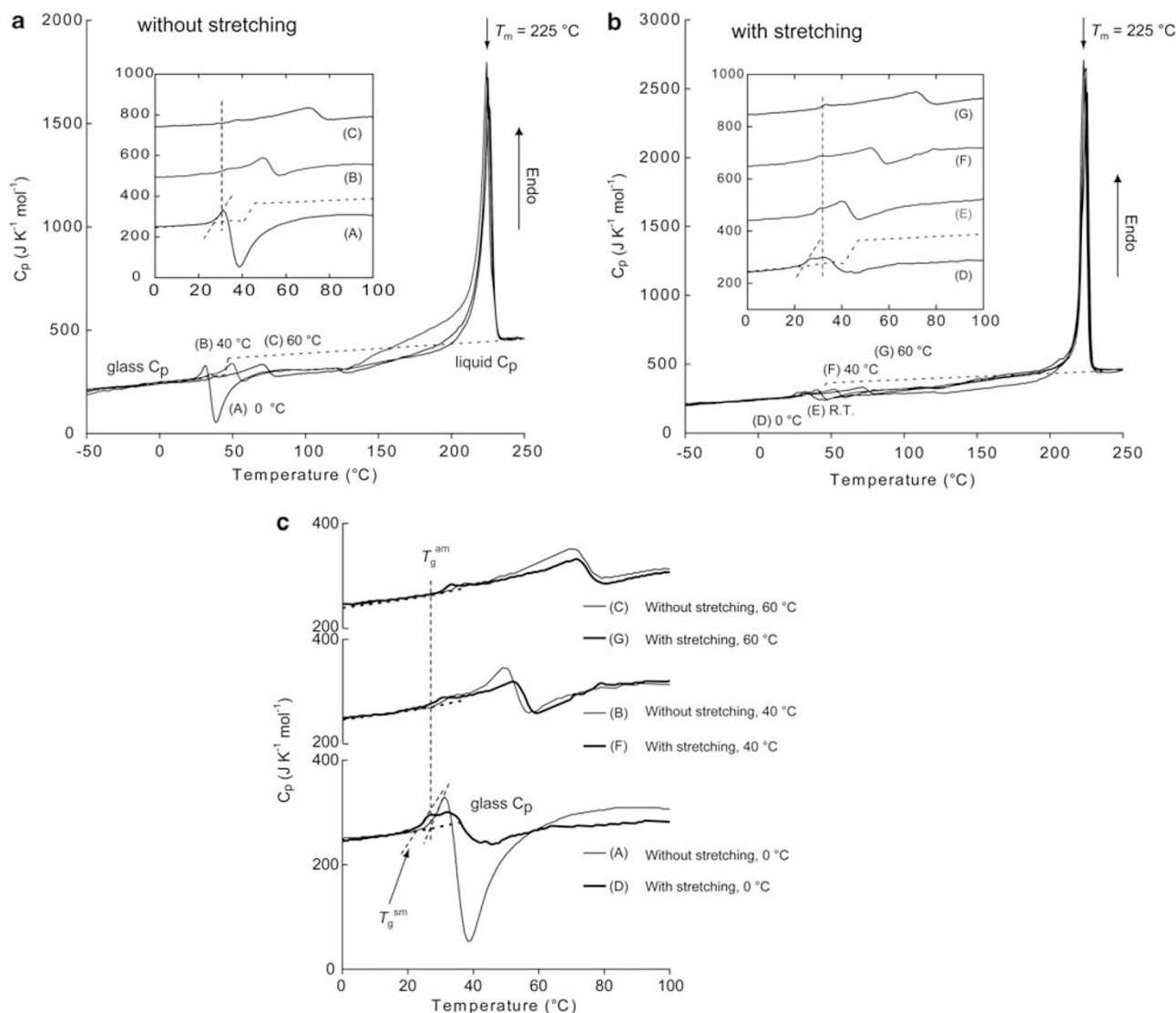


Figure 3 DSC curves for the heating of PBT with and without stretching. (a) PBT quenched to (A) 0 °C without stretching and annealed at (B) 40 and (C) 60 °C after quenching. (b) Quenched PBT stretched at (D) 0 °C and (E) at room temperature, and annealed at (F) 40 and (G) 60 °C after stretching at room temperature. (c) Comparison of the DSC curves for (a) PBT without stretching (thin lines) and (b) PBT with stretching (thick lines) in the range from 0 to 100 °C. The inserts in (a) and (b) are enlarged curves for the range between 0 and 100 °C, which have been shifted vertically. The dotted lines in a-c indicate the specific heat capacity of the liquid and glass states of PBT from Konishi *et al.*¹⁴

CONCLUSION

The smectic structure is observed in quenched PBT only by stretching. The stretched PBT has T_g at 21 °C, in addition to the T_g of the amorphous liquid T_g^{am} at 25 °C. We propose that the T_g at 21 °C for PBT is the T_g of the smectic structure T_g^{sm} . T_g^{sm} is located below T_g^{am} in PBT; therefore, the smectic structure is formed only by stretching after quenching.

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Takashi Konishi and Yoshihisa Miyamoto

Department of Interdisciplinary Environment, Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan
E-mail: t.konishi@kt5.ecs.kyoto-u.ac.jp

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