Thermoluminescence study of the crystal modifications of polypropylene fibres

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Polypropylene fibres with different crystal modifications were investigated using thermoluminescence (TL). Unirradiated, ultraviolet-irradiated and γ-ray-irradiated fibre specimens were studied from room temperature to 200°C. It was found that the glow curves obtained for fibres with both monoclinic and pseudohexagonal modifications have a sharp peak at the melting temperature, but the glow intensities for the fibres with the pseudohexagonal modification were much stronger than for the monoclinic ones. The TL glow peak at the melting temperature for the specimens with the pseudohexagonal modification was found to extend to a temperature as low as 100°C, suggesting that the characteristic molecular motion may occur during the transition of the crystal modifications. In addition, a weak TL peak was detected at about 65°C for the γ-ray-irradiated specimens, which corresponds to the temperature at which polypropylene achieves its maximum crystallization rate constant.

(Keywords: thermoluminescence; monoclinic; pseudohexagonal; crystal modification; polypropylene fibre)

INTRODUCTION

Isotactic polypropylene (iPP) is one of the most commercially important polymer materials and its molecular structure and processing properties have been studied extensively. Depending on the spinning conditions, two different crystal modifications in polypropylene fibre will usually be obtained in melt spinning, the monoclinic modification and the pseudohexagonal modification[1–4]. Since the crystal modification of a fibre correlates directly with the crystallization conditions during its melt spinning, the formation of the different crystal modifications in as-spun fibres has been used to demonstrate the role of molecular orientation-induced crystallization of polymers, which is an important feature of polymer crystallization in melt spinning[5]. The behaviour of molecular orientation-induced crystallization in melt spinning, however, has not been fully elucidated, partly because of the complexity of molecular structures of polymers and also because of the lack of experimental evidence. Therefore, a fundamental and dynamic investigation of the different crystal modifications of polypropylene fibres is desirable.

The thermoluminescence (TL) technique has been demonstrated to be a powerful tool for detecting the characteristic molecular motion and structure transitions in polymers[6–12]. A vast amount of molecular information about the excited or trapped electronic states has been obtained through the study of the luminescence behaviour of small organic molecules. This molecular information, which forms the basis for analysing the characteristic molecular motion of polymers, is correlated both to the means of dissipating electronic excitation energy and to molecular motion in its environment[13,14]. A thermoluminescence glow curve of polymers detects characteristic molecular motion[8,10,11]. For this reason, the TL technique has been applied widely in the investigation of molecular motion accompanying fine structure changes in polymers.

The authors are interested in acquiring molecular motion information from TL glow curves of polypropylene fibres with the monoclinic and the pseudohexagonal modifications. In the present report, the TL of the γ-ray-irradiated and ultraviolet-irradiated as well as unirradiated PP fibres is presented.

EXPERIMENTAL

Specimens

Two types of isotactic polypropylene (Ube Industry Ltd; PP-SI15MV and PP-SI30MV) with molecular weights of 185 000 and 135 000, respectively, were used. By selecting suitable spinning conditions, slightly oriented monoclinic, slightly oriented pseudohexagonal, and highly oriented monoclinic fibres were obtained[5]. The main spinning conditions and the crystal modifications obtained as well as the specimen numbers adopted in this study are shown in *Table 1*.

The TL of a polymer depends very sensitively on its thermal history. For this reason, fibres spun about 3 years earlier (series A) (stored at room temperature) and fibres spun within 1 week (series B) were measured for comparison.

Irradiation of specimens

^{60}Co γ-ray irradiation of the specimens was carried out at liquid nitrogen temperature for 30 min so that the total dose of irradiation reached 0.5 Mrad (dose rate 1 Mrad min^{-1}). The irradiated specimens were kept at

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liquid nitrogen temperature until TL measurements were performed.

To study the possible mechanism of TL of the unirradiated specimens, the ultraviolet irradiation was effected by applying a Cacenon lamp at room temperature for 2 h for the series B fibres. TL for the Cacenon lamp-irradiated specimens was then measured immediately.

TL measurements

The apparatus employed for the TL measurements was designed and manufactured in the laboratory of Tokyo Institute of Technology[10]. The light intensity emitted from the specimens was recorded as glow curves when the specimens were warmed from room temperature to 200°C, with a heating rate of 5°C min^{-1}. Specimens were weighted with about 40 mg and subsequently fixed uniformly on a 2 × 2 cm^2 sample table in the apparatus with clips. All the measurements were carried out under high vacuum. In order to facilitate comparison, the glow curves presented in this report have been normalized.

Table 1 Specimens and their crystal modifications

Specimen	Crystal modification	Molecular weight
A-1	Non-oriented pseudohexagonal	135000
A-2	Oriented pseudohexagonal	135000
A-3	Non-oriented monoclinic	185000
A-4	Oriented monoclinic	185000
A-5	Oriented monoclinic	135000
B-1	Non-oriented monoclinic	135000
B-2	Oriented pseudohexagonal	135000
B-3	Oriented monoclinic	135000

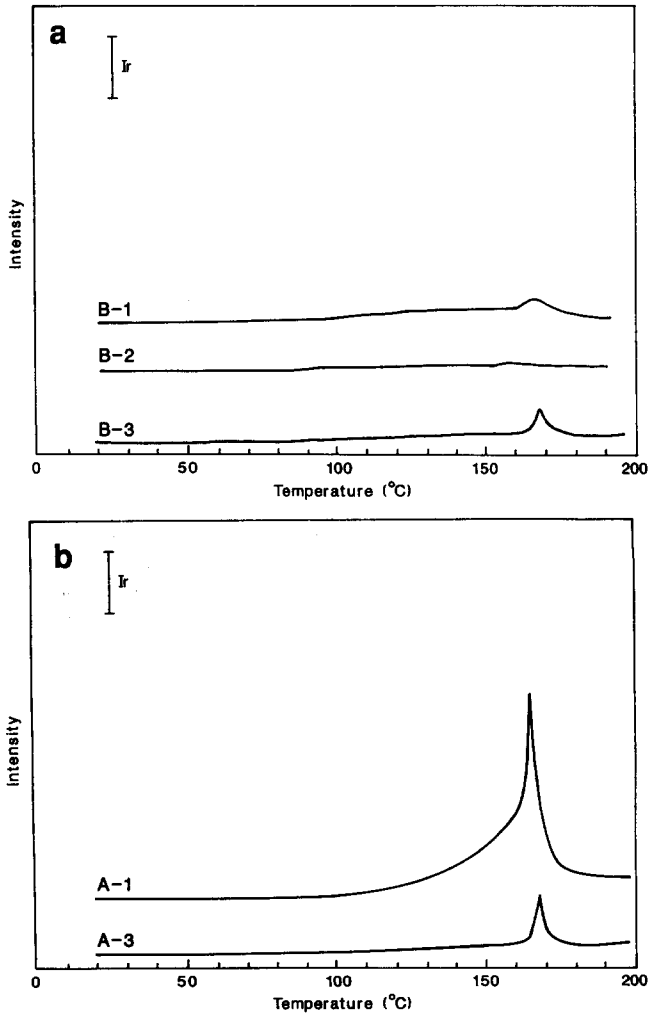

Figure 1 Thermoluminescence curves of unirradiated (a) series B fibres and (b) series A fibres

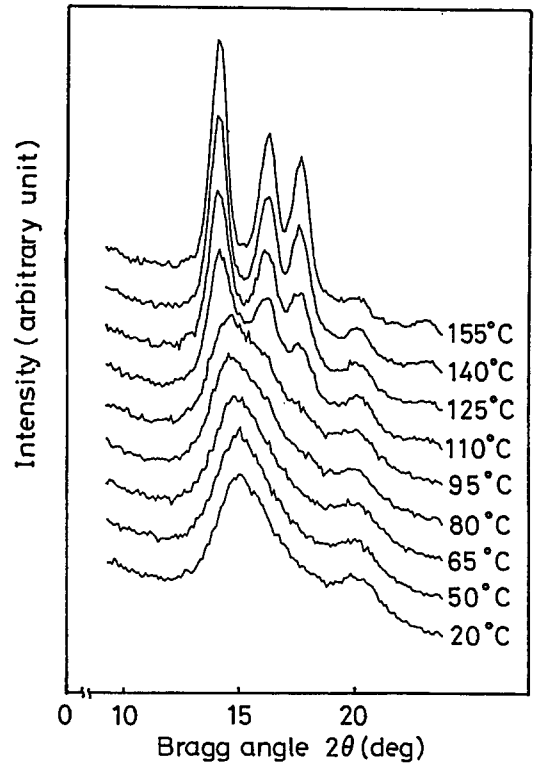

Figure 2 Changes of equatorial wide-angle X-ray diffraction profile with increasing temperature for fibre with pseudohexagonal modification

RESULTS AND DISCUSSION

Thermoluminescence for unirradiated specimens

Figure 1a presents the glow curves for the unirradiated series B samples. Curve 1 and curve 3 are the glow curves for the specimens with the monoclinic modification. A very small peak near 170°C was observed in each case. In contrast, no TL was observed for the fibre with the pseudohexagonal modification over the whole temperature range investigated.

The glow curves for the unirradiated series A fibres are shown in *Figure 1b*. Specimen A-1 had a non-oriented pseudohexagonal modification and specimen A-3 had the monoclinic modification. It can be seen from *Figure 1b* that

1. The glow peak intensities for all the specimens were particularly strong near 170°C.
2. The glow intensities for fibres with the pseudohexagonal modification were much stronger than for fibres with the monoclinic modification.
3. The peak near 170°C in the glow curves of the fibres with the pseudohexagonal modification was rather asymmetrical and protruded to about 100°C.

The results of differential scanning calorimetry measurements suggest that the peak near 170°C could be due to crystal melting[4]. This implies that the violent molecular motion during crystal melting may release trapped electrons at a much more rapid rate than at other temperatures. The protruding tail of the peak at 170°C,

on the other hand, could be due to the molecular motion caused by the transition of the crystal modification from pseudohexagonal to monoclinic. To confirm this suggestion, the wide-angle X-ray diffraction results[5] using PSPC thermal analysis (Position Sensitive Proportional Counter, Rigaku Denki Co.) were re-presented in *Figure 2*. The equatorial profiles of the X-ray diffraction for the specimen with pseudohexagonal modification were recorded as the specimen was warmed at a heating rate of $5°C\,min^{-1}$. It can be seen from the figure that the fibre kept the pseudohexagonal modification until 95°C. The diffraction peaks of the monoclinic modification appeared as the specimen was warmed above 95°C, and these peaks increased in intensity with increasing temperature. Thus this observation provides positive support for the suggestion that the protruding tail corresponded to molecular motion caused by the transition of the crystal modifications.

Thermoluminescence for γ-ray-irradiated specimens

Figure 3a shows the glow curves for the γ-ray-irradiated series A fibres with the pseudohexagonal modification. Note that the intensity axis is set 1.5 times greater than in the previous figures. It can be seen that ^{60}Co γ-ray irradiation greatly enhanced the glow intensities. As expected, the peak near 170°C corresponding to the crystal melting was detected and it protruded down to about 100°C. This TL behaviour is consistent with the series A unirradiated specimens with the pseudohexagonal modification. In addition, a new peak near 65°C appeared in the glow curves.

The glow curves for the series A fibres with the monoclinic modification are shown in *Figure 3b*. Compared with *Figure 3a*, it is clear that the glow intensities were much weaker than those for the specimens with the pseudohexagonal modification. A small peak at 65°C and a strong peak near 170°C were observed for the series A specimens as well. The glow curves between the 65°C peak and the 170°C peak were not very smooth.

In this filament, *a**-axis and *c*-axis oriented crystals coexist. PSPC study has revealed that *a**-axis oriented crystals experience relaxation but *c*-axis oriented crystals do not in this temperature range[5]. Therefore this 'unsmooth' TL curve could reflect the *a**-axis relaxation.

Figure 3c presents the glow curves for the γ-ray-irradiated series B fibres, of which B-2 was the specimen with the pseudohexagonal modification and the others had the monoclinic modification. It can be seen that the glow curve of the pseudohexagonal specimen showed a stronger intensity than the curves of the monoclinic modification specimens. On the other hand, the protruding tail was not as clear as that observed in the previous figures. The peak near 65°C was detected for all specimens.

Based on Magill's experimental data[15], Ziabicki formulated the crystallization rate constant of polypropylene, suggesting that the crystallization rate constant reaches a maximum at 65°C without consideration of the effect of molecular orientation-induced crystallization[16]. This suggestion leads us to believe that the 65°C peak may correspond to the characteristic molecular motion at the maximum crystallization rate constant temperature. However, this maximum crystallization rate temperature for polypropylene has yet to be proved experimentally, simply because crystallization is too fast to be experimentally measured in the temperature range. The TL

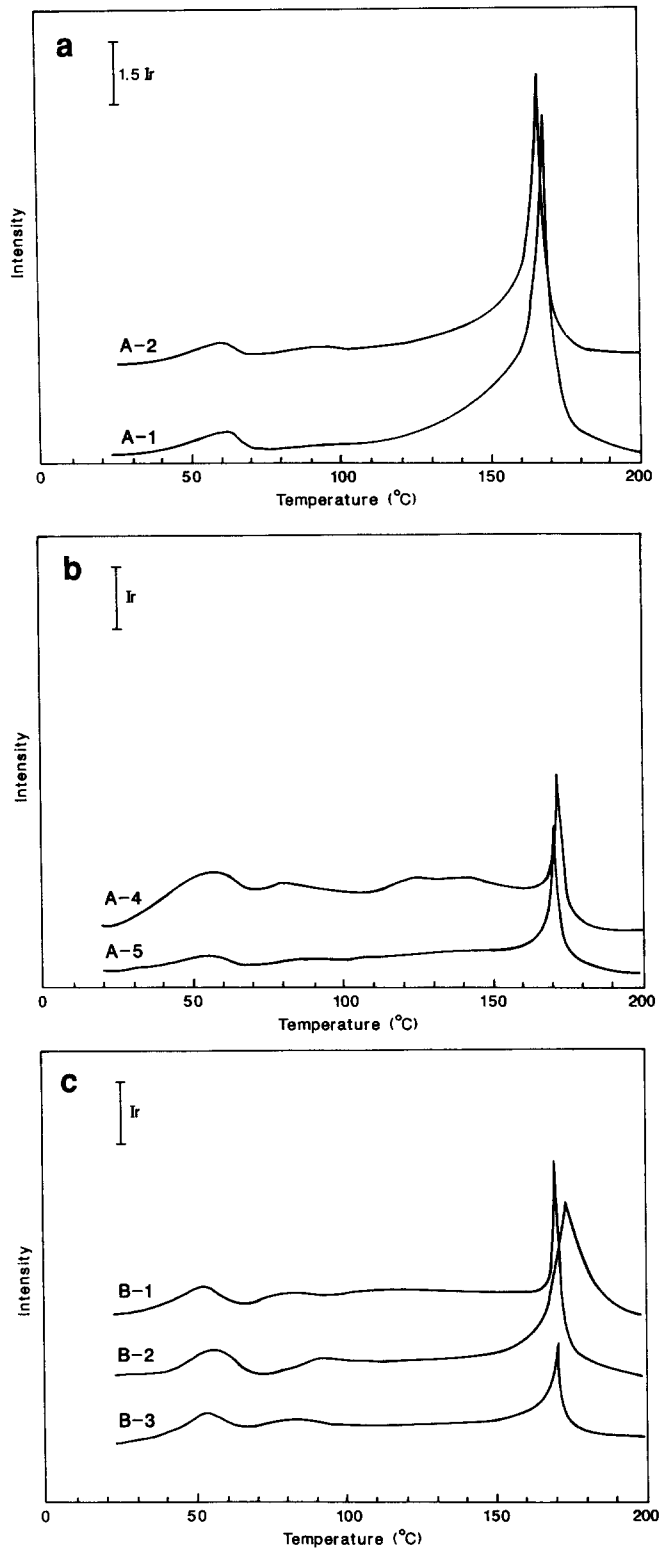

Figure 3 Thermoluminescence curves of (a) γ-ray-irradiated pseudohexagonal series A fibres (b) γ-ray-irradiated monoclinic series A fibres and (c) γ-ray-irradiated series B fibres

results have probably provided indirect evidence for the maximum crystallization rate constant temperature of polypropylene.

Thermoluminescence for ultraviolet-irradiated specimens

Figure 4 shows the glow curves of the Cacenon lamp-irradiated specimens, where B-2 was the fibre with the pseudohexagonal modification and B-3 that with the

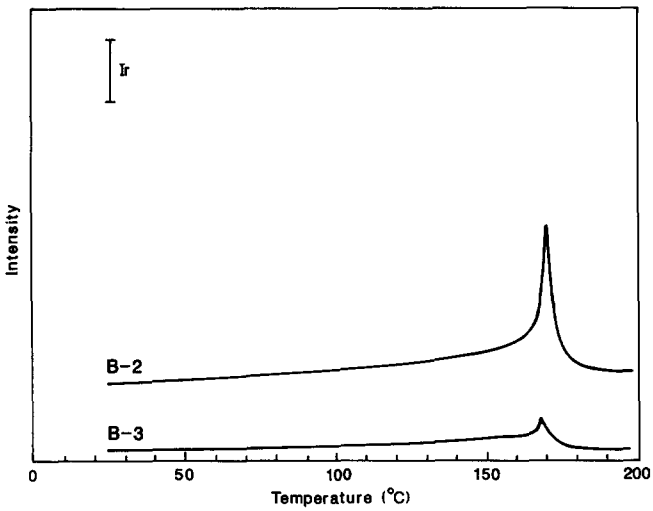

Figure 4 Thermoluminescence curves of ultraviolet-irradiated series B fibres

monoclinic modification. It can be seen from the figure that the glow intensity of the B-2 specimen was much stronger than that of the B-3 fibre. No peak near 65°C was found for either the B-2 or the B-3 fibre. The protruding tail of the glow peak near 170°C seemed to extend to a lower temperature than those observed in the unirradiated old fibres with the pseudohexagonal modification. In spite of these differences, the glow curves for the Cacenon lamp-irradiated specimens are, however, quite similar to those observed for unirradiated series A fibres (*Figure 1b*).

Discussion

Because all the luminescence measurements were taken under vacuum, it is not necessary to consider the possibility of oxidation luminescence. The violent molecular motion during melting could lead to a rapid release of trapped electrons from their trap sites. Therefore, the spinning process seems to play the role of resetting trapped electrons. This explains why the unirradiated series B fibres (both monoclinic and pseudohexagonal modifications) showed no obvious TL peak in their glow curves. The similarity between the glow curves of the unirradiated old fibres and the Cacenon lamp-irradiated new fibres, however, lends support to the assumption that the TL glow behaviour detected from the unirradiated old specimens was, partially or wholly, caused by adventitious irradiation of the short wavelength light of daylight etc.

It was found that the fibres with the pseudohexagonal modification showed much stronger glow intensities than the fibres with the monoclinic modification. One reason could be that the poor perfection of the pseudohexagonal modification resulted in more stable electron trap sites. This explanation seems consistent with the fact that the pseudohexagonal modification is only thermally metastable. On the other hand, it was the high energy of the ^{60}Co γ-rays that excited more electrons, resulting in stronger glow curves and producing a new small peak near 65°C, which did not appear in the glow curves of the ultraviolet-irradiated and unirradiated specimens.

CONCLUSION

The TL glow curves of the polypropylene fibres showed that the fibres with the pseudohexagonal modification had much stronger glow intensities than the monoclinic ones, suggesting that the poor perfection of the pseudohexagonal modification produced more electron trap sites. A strong TL peak was detected at the melting temperature, and for the fibres irradiated by ^{60}Co γ-rays a weak peak was found near 65°C, which corresponds to the temperature at which the crystallization rate constant for iPP reaches its maximum. In addition, TL was also observed during the transition of the pseudohexagonal modification to the monoclinic modification. These observations should be the subject of further studies.

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