세그멘트화 블록 코폴리에테르에스테르의 MDSC 분석

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The MDSC Analysis of Segmented Block Copolyetheresters

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1. Introduction

Segmented block copolyetherester has hard segments of polyesters and soft segments of polyethers. The copolyetherester having high hard segment content shows multiple melting behavior which was thought to be due to melting/recrystallization/remelting process.[1] However, the melting temperature can not be determined correctly because of simultaneous melting with recrystallization.

In this study modulated DSC(MDSC) was used in order to separate crystallization exotherms from melting endotherms obtained from isothermally crystallized copolyetherester samples.

2. Experimental

2.1 Synthesis of Copolyetheresters

The copolymer used was prepared from dimethyl-2,6-naphthalate, 1,4-butanediol(BD) and poly(tetramethylene ether)glycol(PTMG) with average molecular weight 2900. The two-stage polymerization was performed on a lab scale polymerization reactor in the melt.

This polymer has hard segment of PBN (poly(butylene-2,6-naphthalate) and soft segment of PTMGN (poly(tetramethylene ether glycol) 2,6-naphthalate).

2.2 Thermal Analysis

The isothermal crystallization was performed using a Perkin Elmer DSC-4. The samples were heated to 260℃, held for 10min in order to melt the crystal completely. They were then quenched to the selected crystallization temperature T_c, and held isothermally for 60min.[2]

The crystallized samples were scanned by MDSC (TA DSC 2910) with a heating rate of 2℃/min. An oscillation amplitude ±0.318℃, and period 60 sec were employed for the MDSC experiments.

3. Result and discussion

3.1 The multiple melting behavior

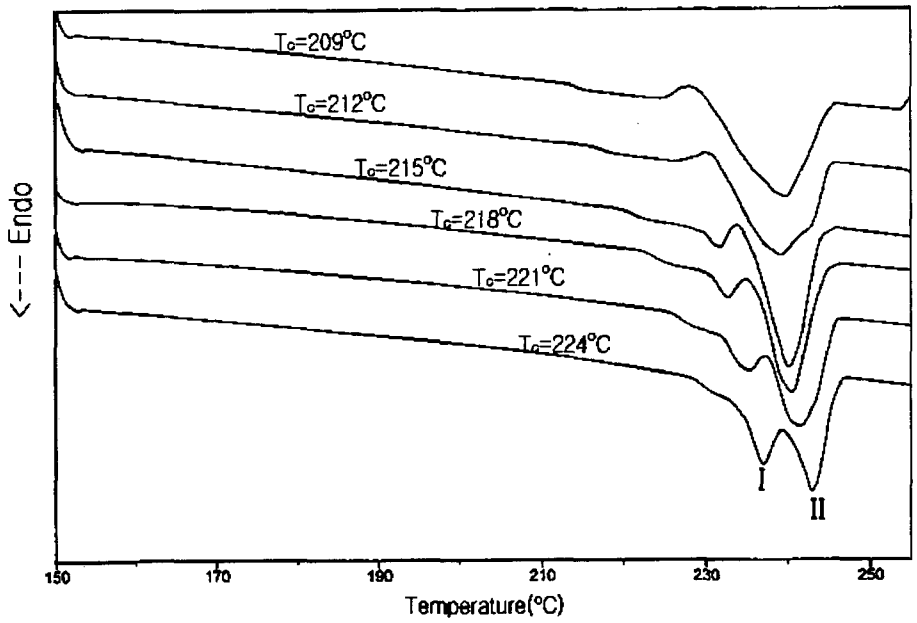

Figure 1. Modulated DSC heating scans at 2℃/min of 4GN/PTMGN2900 (80wt% of hard segment) crystallized for 1hr at various crystallization temperature. All thermograms represent the total heat flow signals.

Figure 1 shows the multiple melting behavior of 4GN/PTMGN 2900(hard segment 80 wt%) crystallized at a series of temperature ranging from 206 to 21 8℃. This exhibits the total heat flow curves which are observed in the results from conventional DSC. The multiple melting peaks are observed obviously in series of scans. The lowest melting temperature (the first peak I) shows strong dependence on the isothermal crystallization temperature, however, the highest melting temperature (the second peak II) does relatively little dependence. This indicates that the multiple melting is due to the melting and subsequent recrystallization followed by remelting. The first melting is due to melting of lamellar crystal formed during the isothermal crystallization. On the other hand,

the second melting peak is due to melting of recrystallized material. [1]

However, the first melting should be often overlaid by recrystallization because of simultaneous melting with recrystallization. So it is difficult to determine the melting and recrystallization temperature. Furthermore the equilibrium melting temperature cannot be calculated exactly. This problem can be solved by using MDSC. The MDSC is very useful in deconvoluting complex transition to obtain the more standard DSC heat flow curves.

3.2 Thermogram of Modulated DSC

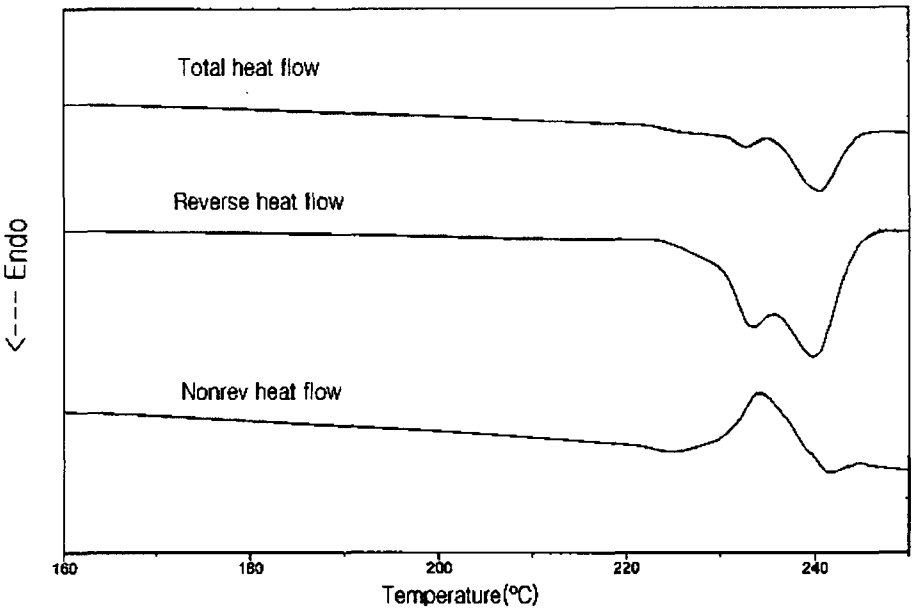

Figure 2. Total, reverse, and nonreverse heat flow signals of 4GN/PTMGN2900 (hard segment 80 wt%) crystallized for 1hr at 218℃.

Figure 2 shows the three signals of Modulated DSC. In the reverse heat flow curve, heat capacity information(melting endotherm) was separated from total heat flow successfully. On the other hand, the nonreverse heat flow curve provides kinetic component(recrystallization). In the reverse heat flow curves precise melting temperature can be determined.

Table 1 shows the isothermal crystallization temperature (T_c), the first (T_{m1}) and the second (T_{m2}) melting temperature of a polymer sample crystallized isothermally in the reverse heat flow curves and the calculated equilibrium melting temperature (T°_m). The equilibrium melting temperature is calculated by the Hoffmann-Weeks plot.

4. Conclusion

Modulated DSC provides not only the same information as conventional DSC, but also special information that can deconvolute multiple endothermic melting behavior.

We were able to determine the first melting temperature from the reverse heat flow curves and calculate the equilibrium melting temperature using the Hoffman-Weeks plot.

Table 1. Melting temperature of polymer samples crystallized for 1hr at various crystallization temperature T_c

Sample	HS wt.* fraction	HS* length	T_c(℃)	T_{m1}(℃)	T_{m2}(℃)	T^o_m(℃)
4GN/ PTMGN2900	0.80	45.9	209	227.2	239.0	274.7
			212	229.1	238.3	
			215	232.3	239.9	
			218	233.7	239.8	
			221	235.8	240.6	
	0.50	12.2	188	214.2	214.2	242.2
			191	217.4	217.4	
			194	218.1	218.1	
			197	219.4	219.4	
			200	220.7	220.7	

* Data were calculated from monomer feed ratio

5. References

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