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CRYSTAL PERFECTION OF POLY(*p*-PHENYLENE SULFIDE) DURING COOLING USING TEMPERATURE-MODULATED DSC

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Abstract

Temperature-modulated DSC (TMDSC) was used to enhance the perfection of crystals of different poly(*p*-phenylene sulfide) samples formed during slow cooling from the melt. The sample preparation was made with modulated cooling using a cool-heat mode. Re-heating the samples prepared by slow conventional and modulated coolings indicated that the melting point of the samples prepared by modulated cooling is considerably higher than the melting point of the samples crystallized with conventional cooling. Thus, the perfection of crystallites can be improved if the outer layers just deposited on their surface are re-melted and re-crystallized immediately.

Keywords: crystal perfection, poly(*p*-phenylene sulfide), TMDSC

Introduction

TMDSC is one of the newest thermal analysis techniques. In this technique, a sinusoidal modulation is superimposed on the linear temperature-time ramp. Up to now, TMDSC was mainly used in quasi-isothermal or heating modes. The quasi-isothermal mode is the preferred method to accurately measure the heat capacity. Several different modulation techniques exist in the heating mode. In the heat-only mode, the modulation conditions are chosen such that the sample is always heated, of course, with continuously varying heating rate. In the heat-with-zero-heating mode, the modulation is chosen such that it reduces the heating rate to zero. In the heat-cool mode, the sample is heated in the first part of modulation, and then partially cooled until the end of the modulation period. In all of these modulation modes the underlying rate is positive, meaning heating.

In this work modulated cooling performed in the cool-heat mode is used to perfect the crystallites developed in melt crystallization.

Experimental

The DSC measurements were carned out using a TA Instruments 3200/2920 MDSC with a mechanical cooling accessory. The sample mass was always 4–5 mg.

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As described in Results and discussion, the cooling experiments were performed in the modulated mode at an underlying cooling rate of 2°C min^{-1} (the modulation conditions were changed until the optimum results were obtained). The re-heating of the cooled samples were done in the conventional DSC mode at a heating rate of 10°C min^{-1}. The DSC experiments were carried out under the constant flow of dry nitrogen. The melting point (T_m,) was taken as the last, highest temperature point of the melting endotherm. The peak temperature of melting (T_{mp}) is also given in addition to the melting point, and the heat of fusion (ΔH_f) was measured to characterize the crystallinity of the samples.

Table 1 Average molecular mass of the PPS samples

Sample	M_w	M_n	*D**
PPS #1	16100	6700	2.4
PPS #2	24200	5830	4.2
PPS #3	34000	9030	3.8
PPS #4	48000	16000	3.0
PPS #5	79700	43700	1.8

*polydispersity

Fortron poly(*p*-phenylene sulfide) (PPS) samples of Hoechst Celanese of different molecular masses were used. The molecular masses of these samples are summarized in Table 1.

Results and discussion

Although there are some exceptions [l, 2], crystallization of polymers takes place in conditions far from equilibrium. Therefore, the crystallites are small and defec-

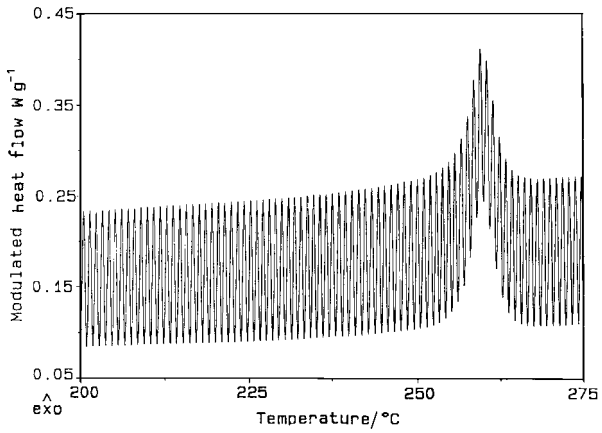

Fig. 1 The modulated heat flow *vs*. temperure curve for moduleted cooling experiments

tive, and often crystal perfection takes place during the heating of such samples. Reference [3] describes how to use the TMDSC technique to study crystal perfection during heating. From that work it is clear that the imperfect crystallites formed during melt crystallization are able to perfect themselves during the subsequent re-heating when the mobility of the segments becomes sufficient.

TMDSC should provide an opportunity to achieve this crystal perfection during cooling. For this purpose, the just deposited outer layers of the crystals should be re-melted and re-crystallized again (Fig. 1). For PPS-samples studied in this work, at an underlying cooling rate of 2°C min^{-1}, a ±1°C/60 s modulation condition proved to be effective to improve the perfection of the crystallites.

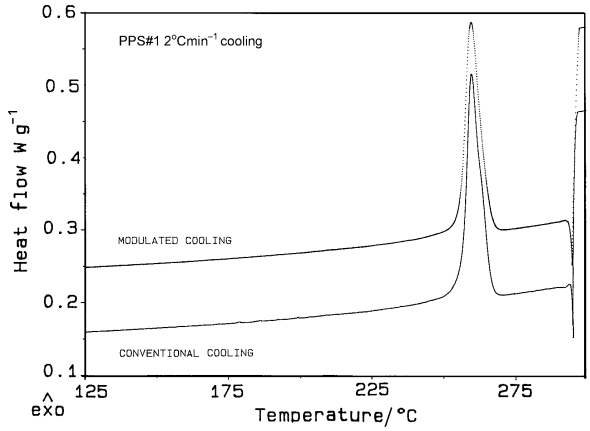

Fig. 2 The crystallization curves (total heat flow and heat flow *vs*. temperature) for PPS #1 at a cooling rate and underlying cooling rate of 2°C min^{-1}

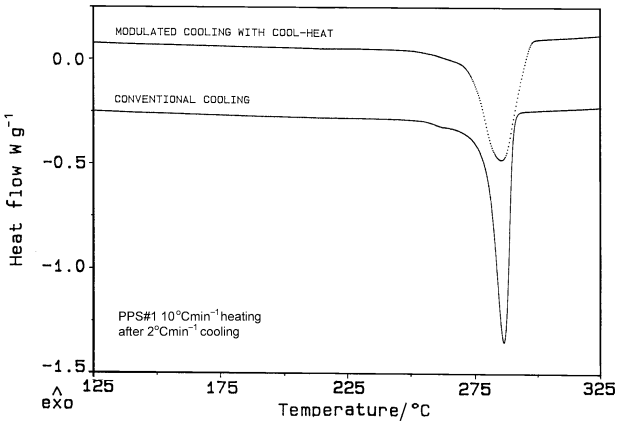

Fig. 3 The melting curves of the PPS #1 samples cooled by conventional and modulated cooling. Conventional heating, heating rate=10°C min^{-1}

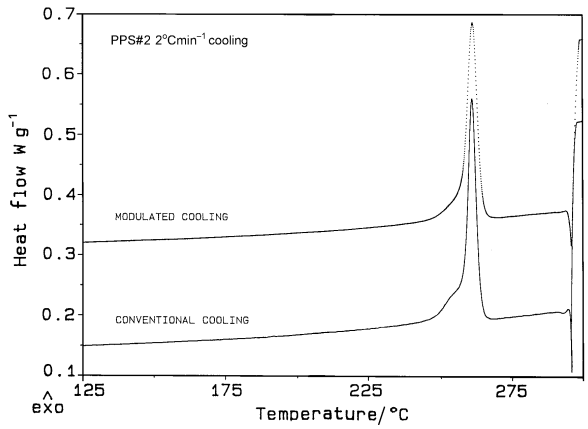

Fig. 4 The crystallization curves (total heat flow and heat flow *vs*. temperature) for PPS #2 at a cooling rate and underlying cooling rate of 2°C min^{-1}

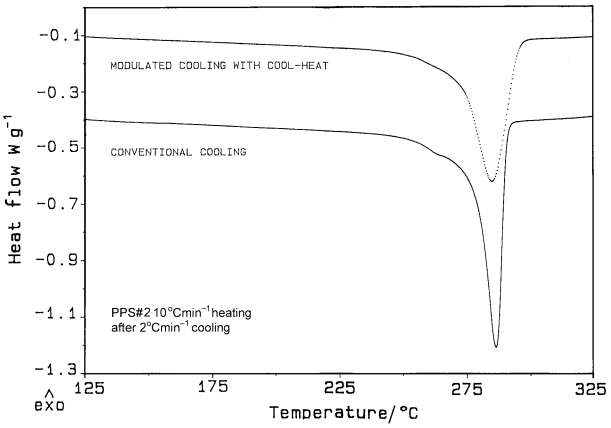

Fig. 5 The melting curves of PPS #2 samples cooled by conventional and modulated cooling. Conventional heating, heating rate=10°C min^{-1}

Figures 2, 4, 6 and 8 compare the crystallization curves (total heat flow *vs*. temperature for modulated cooling and heat flow *vs*. temperature for conventional cooling) for the PPS samples l, 2, 4 and 5. As can be seen, the amplitude of the crystallization exotherm recorded in the conventional mode, is always larger (i.e. the peak is sharper) than that recorded in the modulated mode. This is an expected result, since the crystallization-remelting process in the modulated mode will broaden the crystallization curve. The samples prepared by cooling in the two cooling modes were reheated at a rate of 10°C min^{-1} by conventional DSC, and these melting curves are shown in Figs 3, 5, 7 and 9. The characteristic temperatures of the melting endotherms and the heat of fusion of the samples cooled in the conventional and modulated modes are summarized in Table 2. The first number in each column refers

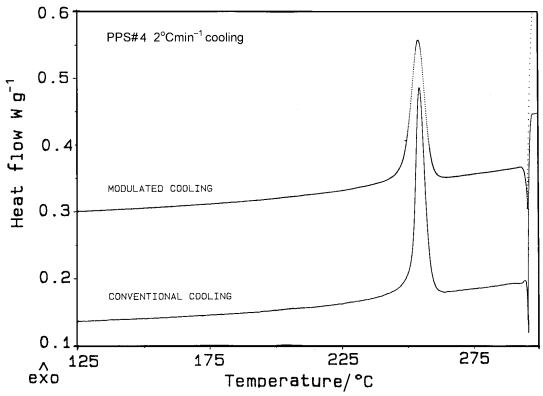

Fig. 6 The crystallization curves (total heat flow and heat flow *vs*. temperature) for PPS #4 sample at a cooling rate and underlying cooling rate of 2°C min^{-1}

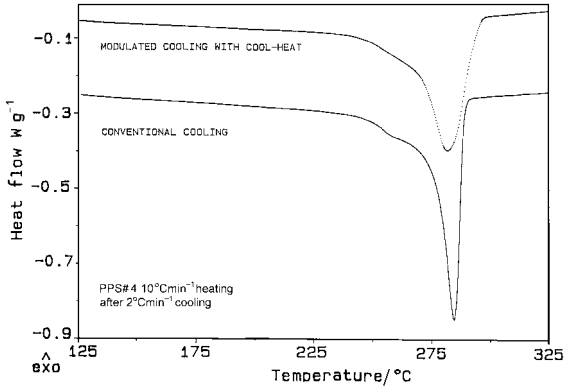

Fig. 7 The melting curves of the PPS #4 samples cooled by conventional and modulated cooling. Conventional heating, heating rate=10°C min^{-1}

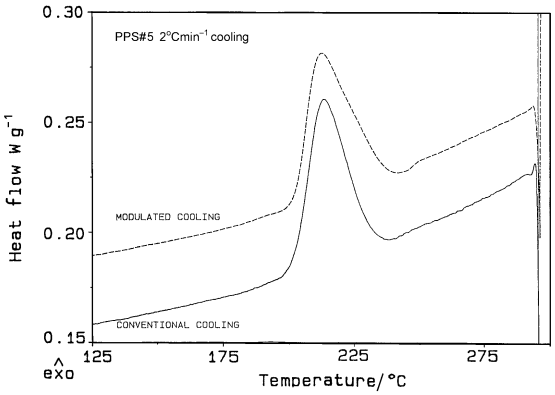

Fig. 8 The crystallization curves (total heat flow and heat flow *vs*. temperature) for PPS #5 samples at a cooling rate and underlying cooling rate of 2°C min^{-1}

Table 2 Comparison of the effect of conventional and modulated coolings on the melting parameters of PPS samples of different molecular masses; cooling rate=2°C min^{-1}, heating rate=10°C min^{-1}

Sample	T_{mp}*/°C	T_m*/°C	ΔH_f*/J g^{-1}
PPS #1	286.5/285.5	294.5/300.5	52.5/52.9
PPS #2	286.5/284.5	295.0/300.0	50.4/50.8
PPS #3	285.5/283.0	293.5/298.5	46.6/45.9
PPS #4	284.5/282.0	292.5/299.0	41.4/41.4
PPS #5	277.0/277.0	290.5/295.5	35.2/34.5

* The first number in each column refers to a sample obtained by conventional cooling, while the second number is the result of modulated cooling

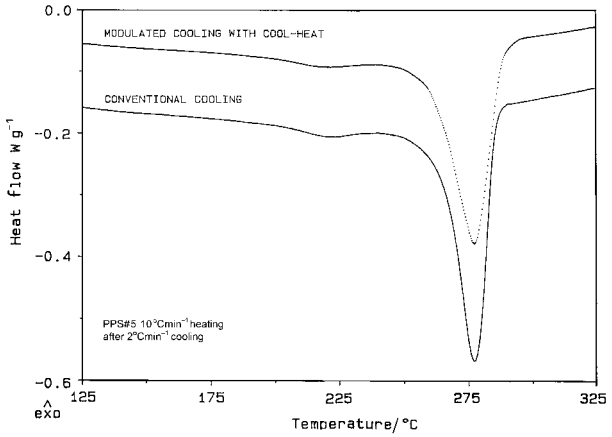

Fig. 9 The melting curves of the PPS #5 samples cooled by conventional and modulated cooling. Conventional heating, heating rate=10°C min^{-1}

to the samples cooled in the conventional mode, while the second number reflects the properties of the samples cooled in the modulated mode.

As can be seen, the crystallinity of the samples is not influenced by the mode of cooling, it depends only on the molecular mass: it decreases with increasing molecular mass, as expected under the above conditions. The peak temperature of melting decreases as a result of modulating the cooling, but the melting point shows a considerable increase of 5–7°C. Even visual comparison of the melting curves presented in Figs 3, 5, 7 and 9 suggests that considerable crystal perfection takes place for the part of the samples. At the same time, it has to be mentioned that the melting curves of the samples cooled by modulated cooling is broadened not only into the direction of the higher temperatures, but also into the direction of the lower temperatures, meaning that in the lower temperature region the crystallites may become less perfect due to modulation during cooling. Also, the efficiency of the crystal perfection

during cooling seems to decrease with increasing molecular mass, but this could be overcome with changing the modulation conditions, i.e. with finding the right modulation condition for each sample.

Conclusions

l. The crystallites of poly(*p*-phenylene sulfide) formed during melt crystallization can be considerably perfected during cooling by overlaying a cool-heat sinusoidal modulation on the linear temperature-time cooling. The melting point of the samples increases considerably due to the modulated cooling. For the samples used in this work, the optimum modulation at a 2°C min^{-1} underlying cooling rate is 1°C/60 s, but these conditions need to be determined for every polymer separately.

2. The crystallinity of the melt-crystallized PPS samples is a function of the underlying cooling rate and the molecular mass of the polymer, and it did not exhibit any dependence on the modulation conditions.

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