Journal of Thermal Analysis, Vol. 54 (1998) 605-622

MOLECULAR WEIGHT EFFECTS ON THE REORGANIZATION OF POLY(VINYLIDENE FLUORIDE), POLYAMIDE 12, AND POLY(*p*-PHENYLENE SULFIDE)

L. Judovits[a*], *J. D. Menczel*[b] *and A.-G. Leray*

[a]Elf Atochem North America, Inc., 900 First Avenue, P.O. Box 61536, King of Prussia
PA 19406-0936
[b]Hoechst Celanese, 86 Morris Avenue, Summit, NJ 07901, USA

Abstract

Although reorganization in metastable polymeric crystals has been recognized for over 30 years, the effect of molecular weight on the reorganization process has not been widely investigated. In this work three polymeric systems were studied: poly(vinylidene fluoride), polyamide 12, and poly(*p*-phenylene sulfide). For the polymers investigated, the lowest molecular weight sample was found to reorganize the most and, conversely, the highest molecular weight sample was found to reorganize the least. Comparisons of each system show that independent of molecular weight the reorganization rates among the three systems could be differentiated with the polyamide showing the greatest reorganization and the poly(phenylene sulfide) the least. Both conventional differential scanning calorimetry (DSC) and temperature-modulated DSC (TMDSC) were used in this study to investigate the reorganization process.

Keywords: DSC, MDSC, polyamide 12, poly(*p*-phenylene sulfide), poly(vinylidene fluoride), reorganization, TMDSC

Introduction

Reorganization in polymeric crystals during melting has been recognized to occur since the 1960's [1]. Reorganization is a process in which improvements or perfections of the initial metastable crystal occurs [2]. However, the molecular weight effects on the reorganization processes have not yet been studied to any extent nor the processes been compared between various systems. In this study three different polymers were investigated which have had their molecular weights characterized and have been noted previously to exhibit reorganization. The systems under investigation for this study are poly(vinylidene fluoride) (PVDF), polyamide 12 and poly(*p*-phenylene sulfide) (PPS).

In an early study on PVDF, Nakagawa and Ishida [3] noted the double endotherms typically seen for reorganization. Based on work on other polymeric

---

[*] Author to whom all correspondence should be addressed.

1418-2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

systems, they ascribed the lower temperature melting peak to the melting of the crystals originally present while the upper temperature peak was associated with melting of the reorganized crystals. Both electron microscopy and heating rate studies were performed. Electron microscopy showed that for the melt-quenched samples only one crystal population could be noted, although, depending upon the heating rate applied, two melting peaks could be seen. DSC experiments carried out with varying heating rates showed a classical response in that a double endotherm was recorded with the lower temperature peak being more pronounced for the faster heating rates while the higher temperature peak being more pronounced for the slower heatings.

The major effort in the literature to study the irreversible melting of polyamides has been directed to polyamide 6 [1, 4]. In a study on drawn polyamide 6 fibers Todoki and Kawaguchi [5] were able to demonstrate extensive reorganization. They annealed various fiber samples at different temperatures. After the annealing and prior to reheating, the amorphous regions were slightly crosslinked by γ-irradiation in acetylene. Upon reheating melting peaks can be noted at the annealing temperatures which were not noted if not crosslinked. Thus, the reorganization for polyamide 6 is so rapid that it is difficult to detect by DSC within the usual heating rates used. Illers [6] also found reorganization to occur for polyamides containing between six to fifteen carbons per repeat unit which he denoted as secondary cold crystallization.

The reorganization process in PPS is not as well studied as that of polyamides or PVDF. However, Cheng *et al.* [7], have noted reorganization in PPS by using a two-step isothermal crystallization. Additionally, observation of reorganization by non-isothermal crystallization was not as clearly noted, but could be seen as low-temperature shoulders for various cooling rates.

The effect of molecular weight on the reorganization processes in PVDF and Polyamide 12 (PA-12) have not been studied extensively and not at all for PPS [8]. Past investigations do exist of molecular weight studies of these systems but were concerned with the effect on other properties such as crystallization, for example [9–11]. It is therefore the purpose of this study to find how molecular weight affects reorganization and compare these effects among the different polymeric systems.

Temperature-modulated differential scanning calorimetry (TMDSC) provides a useful tool in the study of reorganization. In TMDSC a specimen is exposed to a linear ramp which has a superimposed sinusoidal temperature oscillation which results in a cyclic heat flow [12]. Through the use of such a modulation the reversing and non-reversing heat flow can be separated. It has been shown that new crystallization events that occur upon heating, such as cold crystallization can be separated into the non-reversing heat flow [12]. However, quantification of thermal events taking place during melting may be difficult due to loss of steady state [13]. Additionally, selection of wrong parameters may result in an incorrect separation and phantom peaks may result [14]. Therefore, an evaluation of the modulated heat flow for its consistency and correlation to the various heat flow should be made. Since TMDSC provides an additional tool for the thermal analyst to study crystallization effects upon heating, it should provide additional insight into the reorganization process even though data obtained may only be useful in a qualitative fashion.

Experimental

Materials

Four PVDF, two PA-12, and five PPS samples were investigated. The PVDF samples used were made using a polymerization process which results in 5% reversed repeat units [11]. The molecular weights of all three systems are given in Table 1. The PVDF analyses were performed on a Waters 150C GPC coupled with an on-line high-temperature viscometer operating at 90°C. The polyamide analysis was performed on a Waters GPC ambient temperature system by the method of Mourey and Bryan [15] using a mixture of dichloroacetic acid/dichloromethane as the eluent. The molecular weights of the PPS samples were supplied by Hoechst Celanese and were measured by high temperature GPC.

Table 1 Average molecular weight characterization

Sample	$\overline{M}_w$	$\overline{M}_n$	D
PVDF A	128000	75000	1.7
PVDF B	173000	78000	2.2
PVDF C	204000	97000	2.1
PVDF D	284000	113000	2.6
PA-12-L	31000	16000	2.0
PA-12-H	130000	60000	2.0
PPS#1	16100	6700	2.4
PPS#2	24200	5830	4.2
PPS#3	34000	9030	3.8
PPS#4	48200	16000	3.0
PPS#5	79700	43700	1.8

Calorimetry

To study reorganization by conventional DSC a multiple heating rate profile is usually used. In this study heating rates between 2 to 20°C min^{-1} were investigated for conventional DSC runs. For TMDSC slow underlying heating rates of either 2 or 5°C min^{-1} were used. Comparisons of conventional DSC and TMDSC runs for the same thermal history and heating rate showed no differences between the scans.

Table 2 Modulated DSC parameters

Polymer	Rate/ °C min^{-1}	Period/ s	Amplitude/ °C	Modulation type
PVDF	2	40	±0.210	heating with zero heating
PA-12	2	60	±0.318	heating with zero heating
PPS	2	40	±0.16	always heating

TMDSC measurements were made using either a TA Instruments 2910 or 2920 DSC. Conventional DSC was performed using either a TA Instruments 910 or 2920. Nitrogen was used as the purge gas and all specimens were crimped in standard aluminum pans. For all TMDSC measurements, small masses of between 4 to 6 mg were used. Experimentally, the optimum TMDSC conditions were found to be different. Therefore, the parameters for each system were different and noted in Table 2. The modulation parameters were chosen to result in heating with zero heating or always heating. Comparison with additional TMDSC scans which showed modulation of heating rates only (no cooling) and specifically TMDSC which had a minimal heating rate of zero were found to show little difference for PVDF and PA-12 for all parameters chosen. Thermal conditioning of the samples before reheating consisted of a relatively fast and slow coolings from the melt. For PVDF and PA-12 cooling rates of 1 and 10°C min^{-1} were chosen. However, higher cooling rates up to 40°C min^{-1} were found necessary for PPS.

Results

Poly(vinylidene fluoride), PVDF

Figures 1 to 8 show the conventional DSC heating curves recorded at different heating rates for samples which had been cooled relatively fast and slow, 1 and 10°C min^{-1}, respectively, prior to analysis. The heat flows were adjusted for heating rate to allow superposition. Figures 9 and 10 are the TMDSC overlays for different molecular weights for the 1 and 10°C min^{-1} coolings, respectively.

For a PVDF sample cooled at 10°C min^{-1} and reheated at various rates, a classical reorganization behavior can be seen in the conventional DSC traces (Figs 1 to 8). On heating a double melting peak can be observed with the ratio of the heights of the two peaks being heating rate dependent. Figure 11 show that the reorganization process decreases with increasing molecular weight or slower cooling (thermal history) when curves of similar heating rates are compared. A slower cooling should result in better crystal perfection and, hence, reduce the reorganization process. Comparisons of the non-reversing heat flow curves for the fast coolings (Fig. 10) show a relative decrease of an apparent exothermic process with increasing molecular weight.For the slow coolings (Fig. 9), the highest molecular weight sample showed very little change in peak temperature. Conversely, the lowest molecular weight sample shows some reorganization at

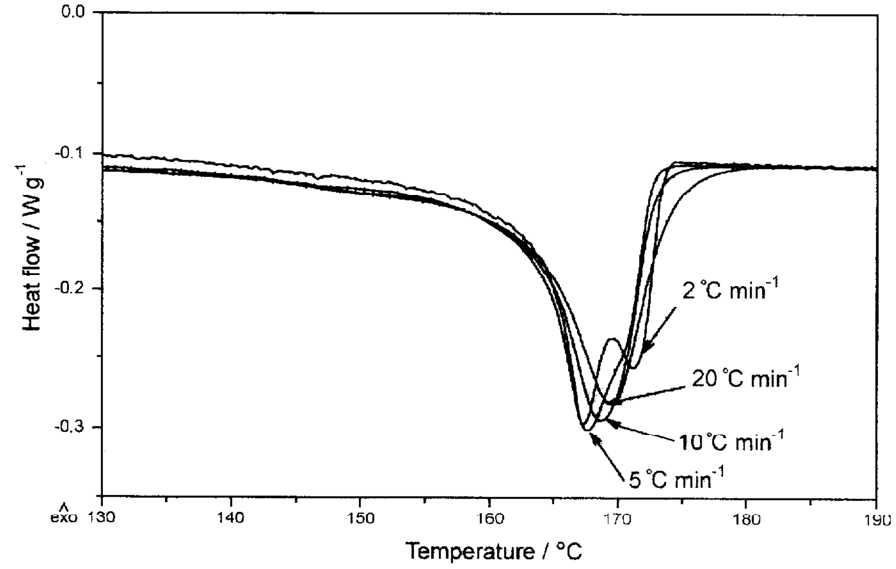

Fig. 1 Overlays of PVDF A cooled 1°C min^{-1} from the melt and reheated at various rates, curves were adusted for heating rate

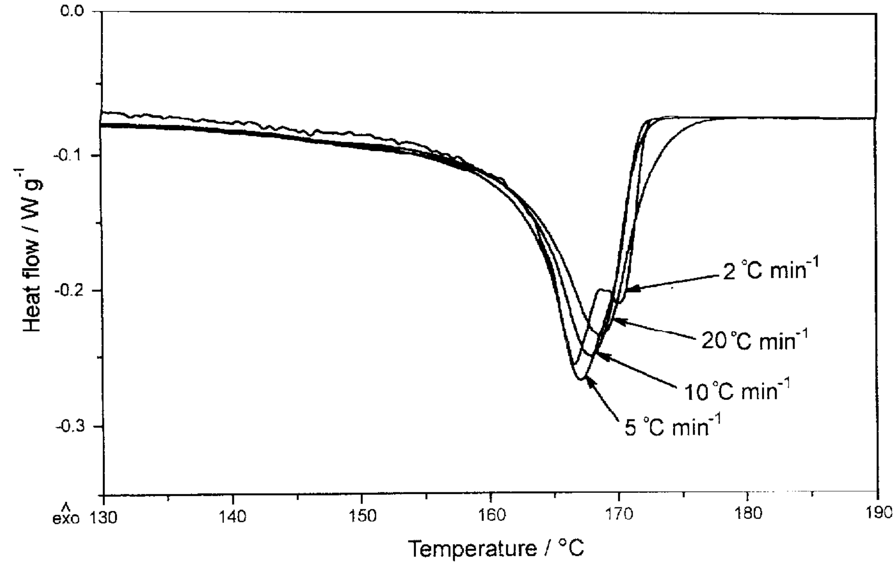

Fig. 2 Overlays of PVDF B cooled 1°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

the slow heating rates. However, at faster heating rates a single peak is formed and an increase in peak temperature with heating rate is observed. This effect is also noted for other molecular weight PVDF samples in this study. This suggests

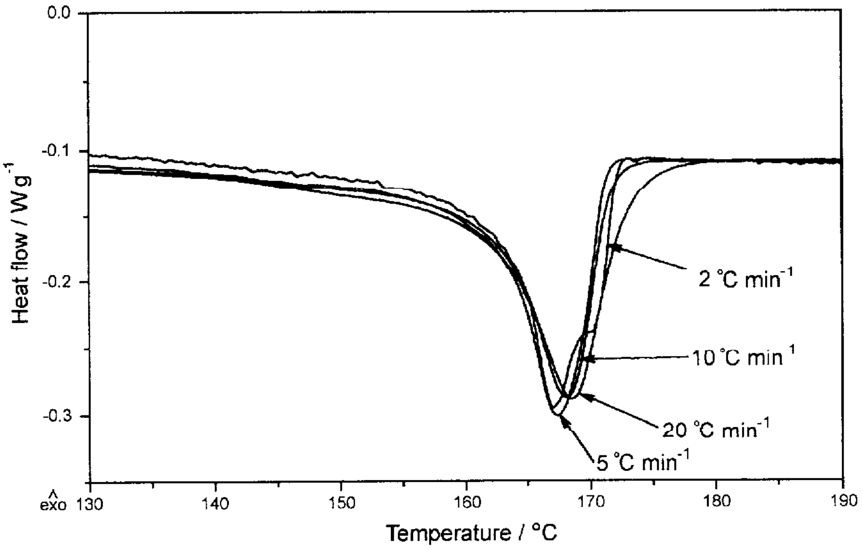

Fig. 3 Overlays of PVDF C cooled 1°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

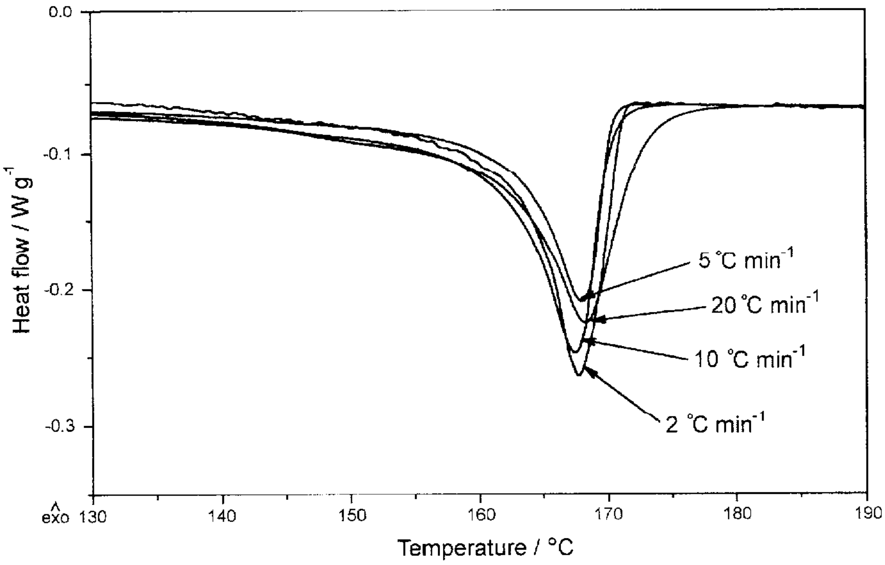

Fig. 4 Overlays of PVDF D cooled 1°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

the presence of a second process which may be the superheating of zero entropy production melting. That is, the sample has reached a level of perfection so that it cannot reorganize within the time allotted and instead, superheats. In addition,

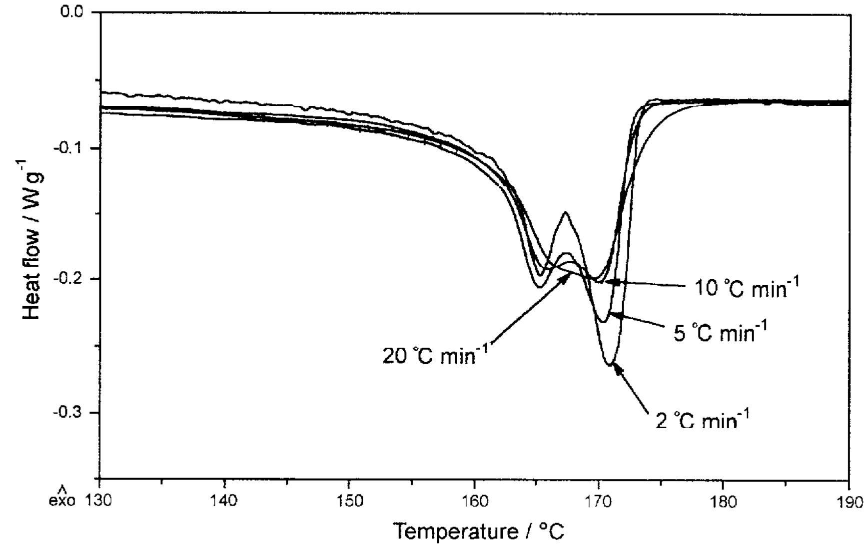

Fig. 5 Overlays of PVDF A cooled 10°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

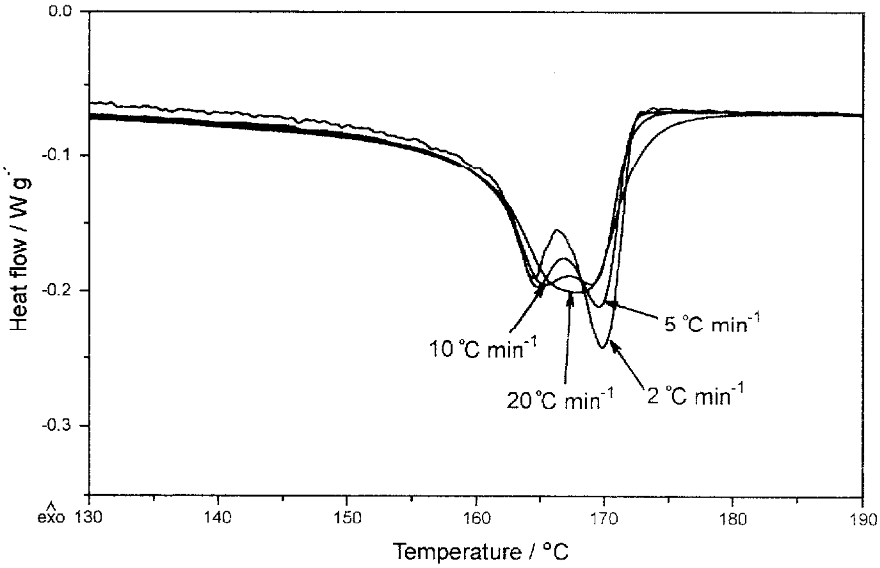

Fig. 6 Overlays of PVDF B cooled 10°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

a two-stage process seems to be present in the non-reversing heat flow curve (Figs 9 and 10) where a broad shallow exotherm preceding the double endothermic peak and another exotherm within the main endotherm were recorded. Also

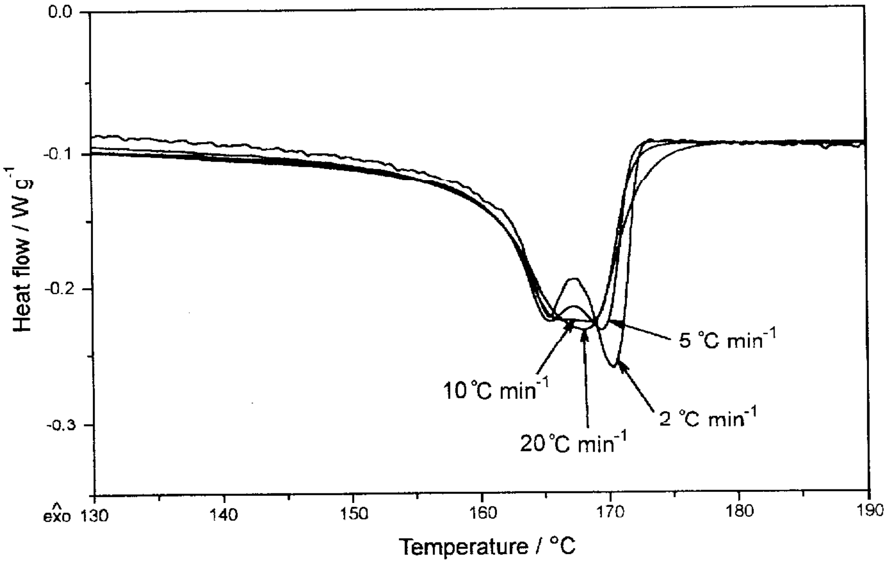

Fig. 7 Overlays of PVDF C cooled 10°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

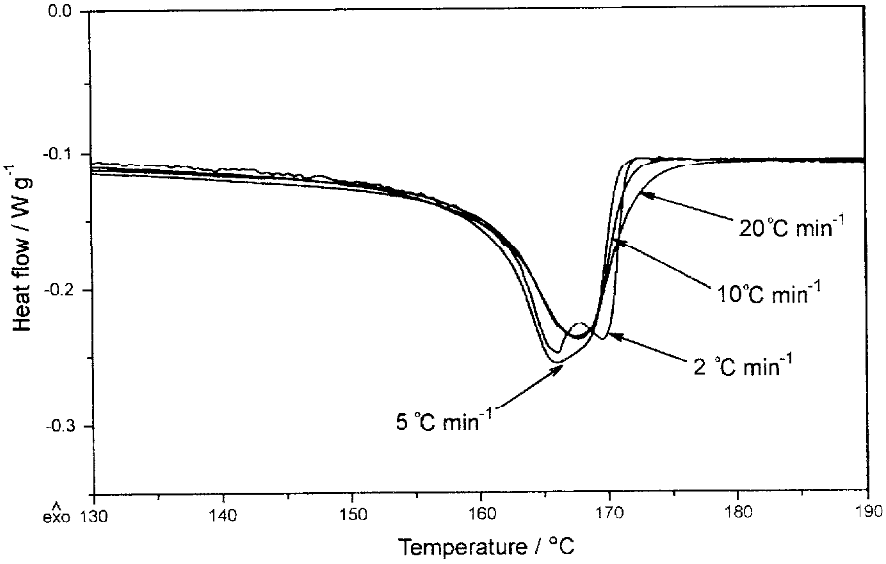

Fig. 8 Overlays of PVDF D cooled 10°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

of interest is what appears to be a two-stage process in the non-reversing heat flow (Figs 9 and 10). However, the second exothermic process appears to be reduced with both reduction in cooling rate (during thermal conditioning and increase in molecular weight.

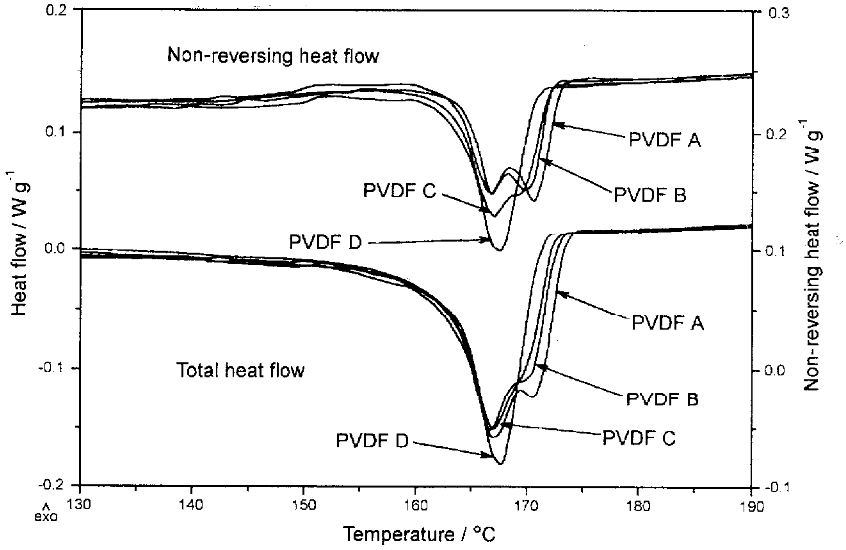

Fig. 9 TMDSC overlays of molecular weight effects on the reorganization in PVDF (1°C min^{-1} coolings)

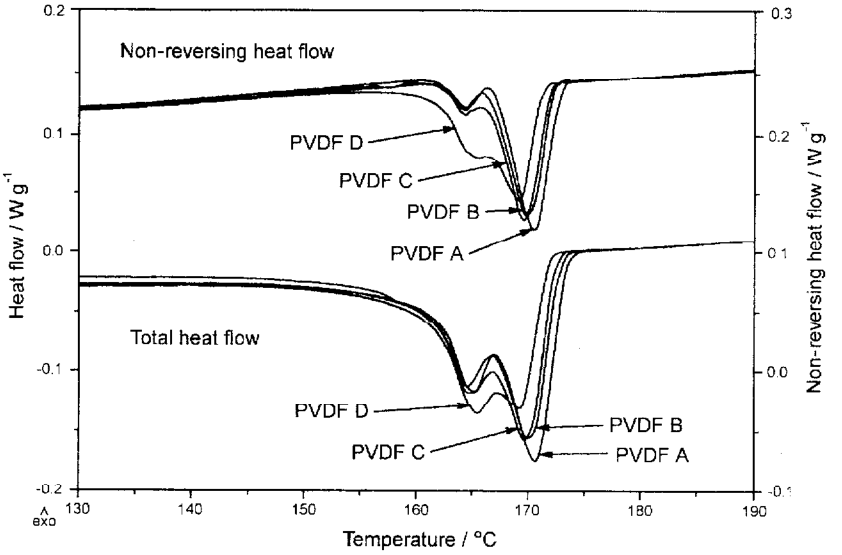

Fig. 10 TMDSC overlays of molecular weight effects on the reorganisation in PVDF (10°C min^{-1} coolings)

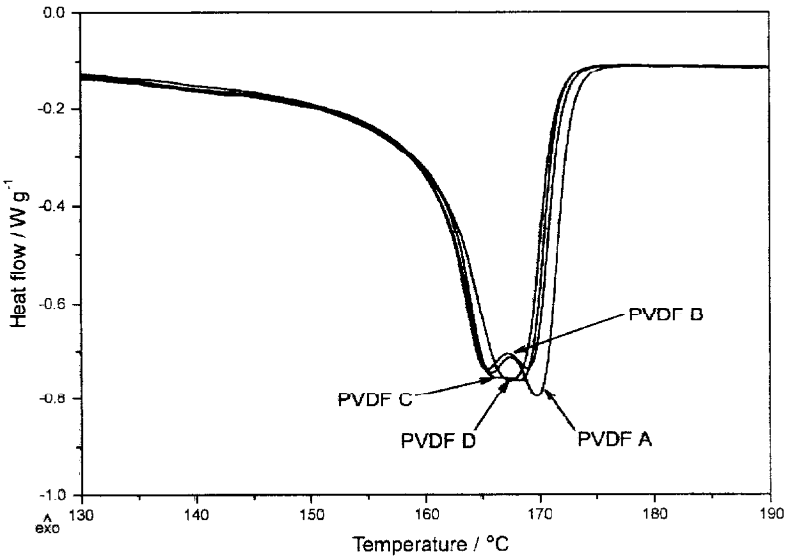

Fig. 11 Overlays of PVDF samples of different molecular weight cooled and reheated 10°C min^{-1}

Polyamide 12, PA-12

The melting of PA-12 for similar cooling and heating conditions shows a much different behavior than that of PVDF as seen in Figs 12 to 15. For the relatively fast coolings, double endothermic peaks were not seen instead, an exotherm before the main melting can be noted. As mentioned in the Introduction, polyamides show considerable reorganization between the glass transition and the main melting peak. Additionally, the density and reversibility of the hydrogen bonds should also complicate the reorganization process by acting as both nucleation sites and a crystallization barrier. Slow cooling experiments, show a reorganization effect somewhat similar to that of PVDF. This is especially true for the high molecular weight sample where double endothermic peaks at slow heatings are seen.

Only a low temperature shoulder could be observed in the low molecular weight samples. Analysis of the TMDSC traces shows a different response than what was obtained for the PVDF samples. Whereas the PVDF non-reversing curves exhibited an exothermic response only within the major melting peak, PA-12 shows a considerable exothermic response before the major melting peak. This is suggestive of a greater reorganization response for PA-12 than for PVDF. This process can be further highlighted by comparing the raw modulated signal between PVDF and PA-12. In the raw signal, the PA-12 exotherm can be clearly noted. The higher degree of reorganization for the lower molecular weight from that of the higher molecular weight polyamide can be discerned in Fig. 16. A relatively greater exothermic process was observed in the non-reversing curve

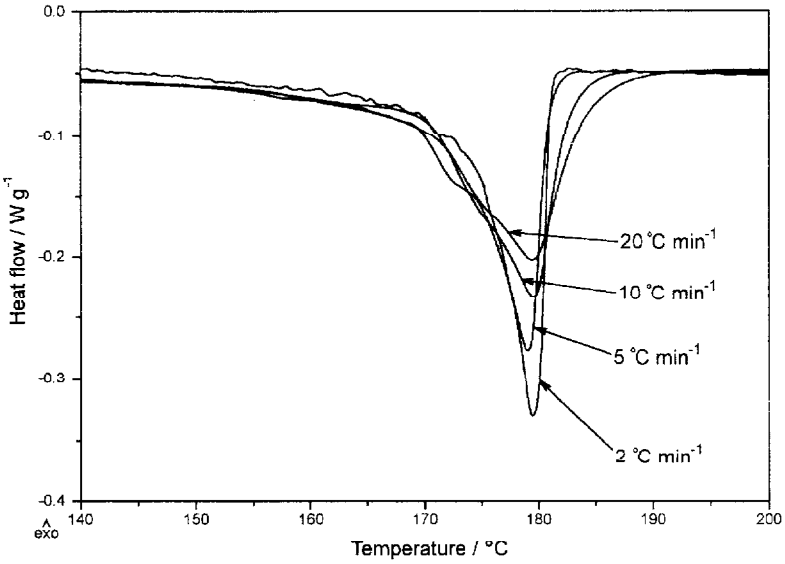

Fig. 12 PA-12-L specimens cooled 1°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

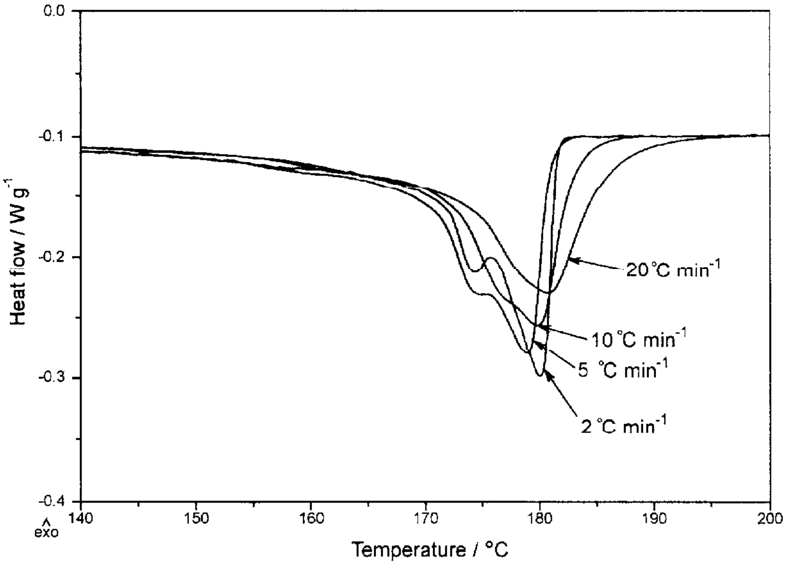

Fig. 13 PA-12-H specimens cooled 1°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

for the lower molecular weight sample. Additionally, a two-stage process can also be noted which becomes more evident in the higher molecular weight sample.

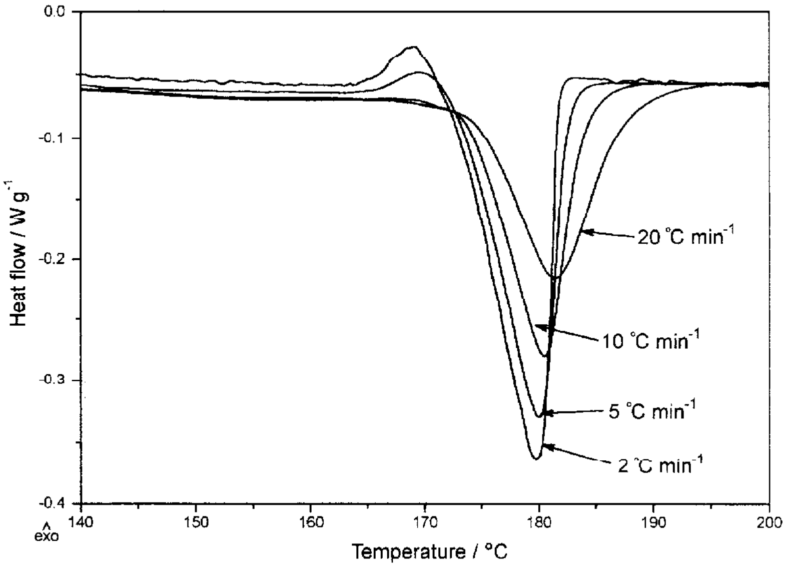

Fig. 14 PA-12-L specimens cooled 10°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

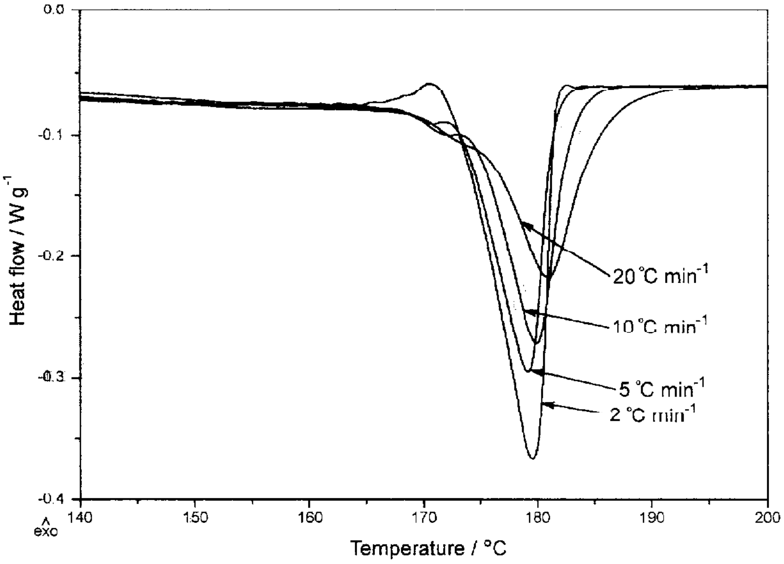

Fig. 15 PA-12-H specimens cooled 10°C min^{-1} from the melt and reheated at various rates, curves were adjusted for heating rate

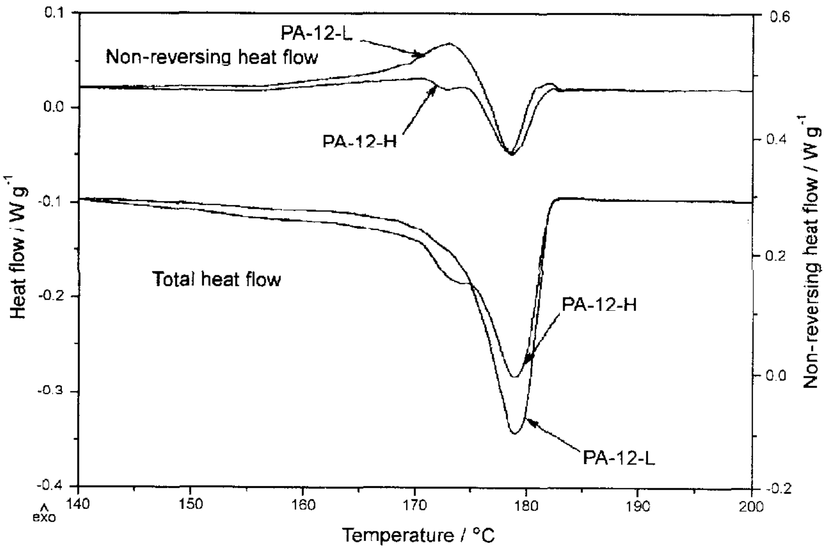

Fig. 16 TMDSC showing the effect of molecular weight on the reorganization in Polyamide 12. The specimens were cooled 1°C min^{-1} from the melt and then reheated. The scan is phase corrected

Poly(p-phenylene sulfide), PPS

A reorganization response was observed for PPS, similar but not as well defined to that of PVDF (Fig. 17). Figure 17 shows that the ratio of the peak heights of the two endotherms changes with heating rate, with only the upper temperature peak apparent for the fastest heating rate for a 20°C min^{-1} cooling from the melt followed by multiple heating rates. As seen in Fig. 18 much higher cooling rates are needed to detect the reorganization process in that when the samples are crystallized at for a 20°C min^{-1} cooling, only the lowest molecular weight sample (PPS# 1) exhibits a double melting peak at the slowest heating investigated (of 2°C min^{-1}). Even after a 40°C min^{-1} cooling, only the two lowest molecular weight samples reorganized (Fig. 19). As with PVDF and PA-12, the non-reversing peaks become less exothermic with increasing molecular weight (Fig. 20). In general, the heating curves for the 20°C min^{-1} coolings are less exothermic than the heating curves for the 40°C min^{-1} coolings. As with PVDF, a two-stage reorganization process can be seen for the lowest molecular weight PPS on the non-reversing heat flow which may indicate the presence of two distinct reorganization processes.

Discussion

At first glance PVDF and PA-12 show similar melting characteristics. For similar thermal histories (10°C min^{-1} coolings through the melting), both differ slightly by approximately 10°C in peak temperature and 10 J g^{-1} in their heats of fusion. However, comparisons of their thermal histories show very different thermal behaviors for similar molecular weights. As can be seen in Fig. 21, upon

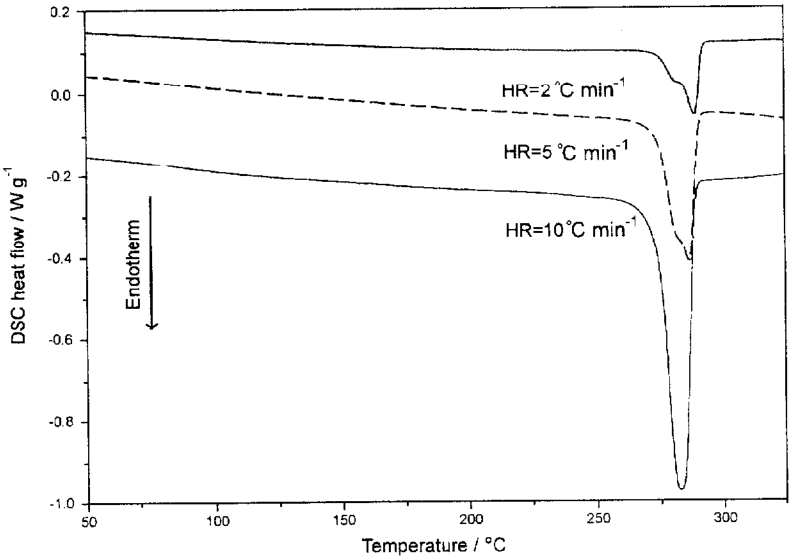

Fig. 17 Overlays of PPS#1 cooled 20°C min^{-1} from the melt and then reheated at various rates

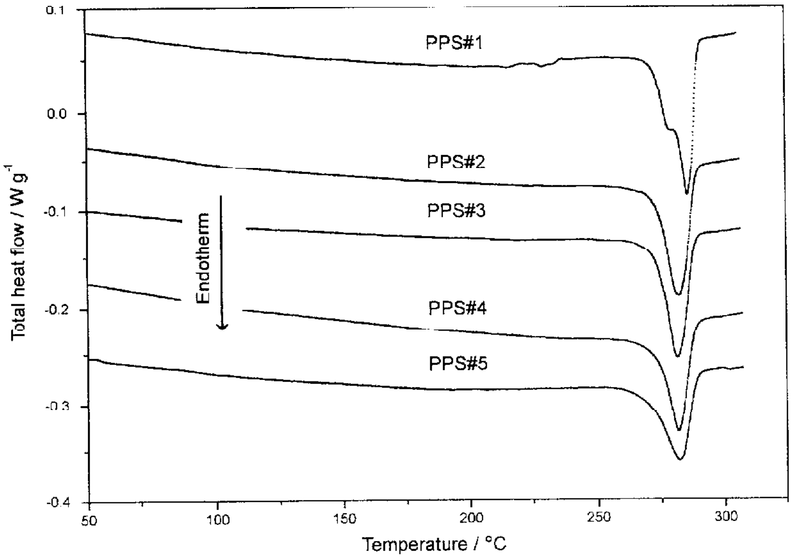

Fig. 18 Comparisons of PPS samples of different molecular weights cooled 20°C min^{-1} from the melt and reheated 2°C min^{-1}

heating the fast cooled PA-12 sample a more pronounced melting peak develops than for the slowly cooled sample, whereas for PVDF the slowly cooled sample

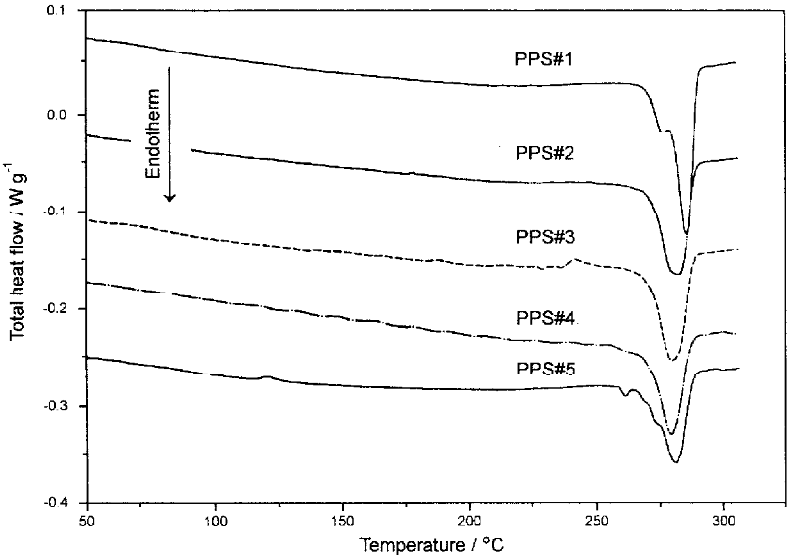

Fig. 19 Comparisons of PPS samples of different molecular weights cooled 40°C/min from the melt and reheated 2°C min^{-1}

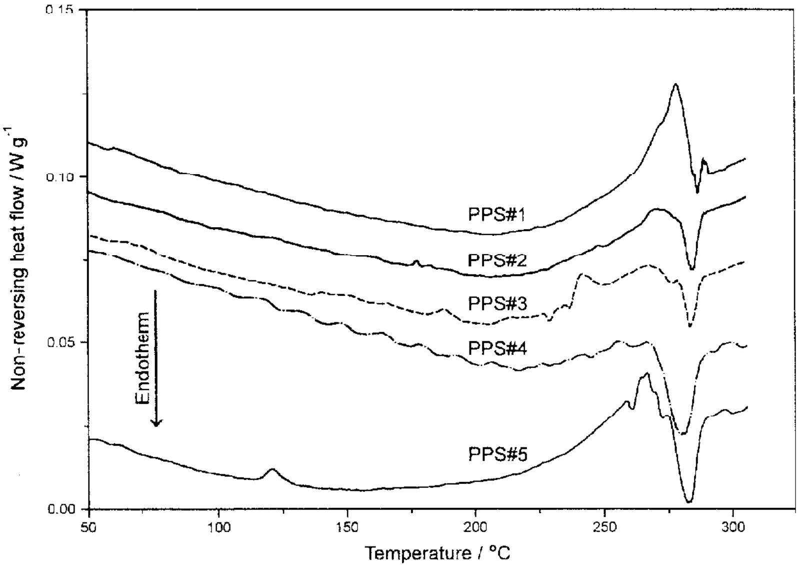

Fig. 20 Non-reversing heat flow curves of PPS samples of different molecular weights for a 40°C min^{-1} cooling followed by a 2°C min^{-1} heating

showed the most pronounced peak. The cause for this is the higher rate of reorganization in the PA-12 system.

All three polymer systems studied can be found to exhibit reorganization, but to varying degrees. The PA-12 sample was found to be more prone to reorganization than the PVDF sample, which in turn was more prone to reorganization than the PPS sample. The degree of reorganization between the polymer systems is sufficiently different that no apparent overlap was observed within the molecular weight ranges studied for similar thermal histories. That is, based on the peak height ratio of the components of the double melting peaks noted or premelting exotherms, clear differences can be qualitatively noted. For the case of the 10°C min^{-1} cooling from the melt followed by a 10°C min^{-1} heating one can observe the differences in behavior in that for the PA-12 a premelting exotherm was discerned, for the PVDF samples a doublet peak could be noted and only a single melting peak was observed for the PPS. To see a double melting peaks for PPS much higher coolings rates needed to be employed.

The sluggish reorganization for the PPS system may be explained by its rigid backbone structure, but why is the polyamide more prone to reorganization than PVDF? Upon crystallization polyamides normally crystallize to approximately 25% while PVDF crystallizes to approximately 50% [16, 17]. Although the hydrogen bonds can act as nucleation sites, they also can act to inhibit crystallization since the forming crystal has to incorporate repeat units which have to overcome the hydrogen bonding. Upon heating, additional energy cannot only

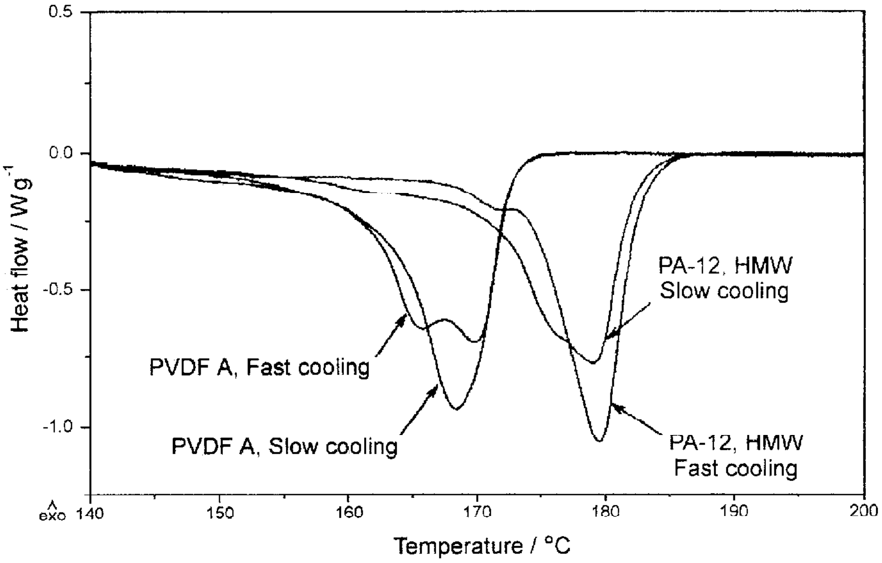

Fig. 21 Conventional DSC comparisons between PVDF and PA-12 having similar molecular weights. Both 1 and 10°C min^{-1} coolings from the melt were employed followed by 10°C min^{-1} reheatings

melt the small crystallites formed, but disrupt the hydrogen bonding, allowing the reorganization process to proceed. Since PVDF is in no way inhibited and crystallizes to a higher degree, its reorganization is therefore relatively slower.

TMDSC of both PVDF and PPS as noted in the Results shows what appears to be a two-stage process in that one can observe a broad exotherm followed by a sharper exotherm within the main melting peak. The PA-12 samples also show this behavior, but only for the slowly cooled sample.

Generally, a preexothermic peak is observed, an indication of a higher degree of reorganization for that thermal history. A possible interpretation of this two-stage process would be lamellar thickening followed by a melting, recrystallization, and remelting process.

Conclusions

The melting of polymers is far more complicated than that of small molecules due in part to reorganization which is frequently observed for polymers during melting. Until now this process was best followed by conventional DSC using varying heating rates. Now with the advent of TMDSC this process can be directly monitored and further understanding of the reorganization process can be obtained. In this study both DSC and TMDSC were used to study the reorganization process. In all three polymer systems studied the lowest molecular weight showed the fastest reorganization. This is probably due to differences in segmental motion between molecular weights. Classical reorganization processes were found for all three systems, but different thermal conditioning was necessary to obtain the double endothermic, heating rate dependent response. The reorganization process in PA-12 was found to be much quicker and a pre-exotherm could be noted in the relatively fast cooling thermal histories. The slowest reorganization was noted for PPS which can be attributed to its more rigid backbone. Although conventional DSC provided data at fast heating rates, the additional use of TMDSC allowed for a further characterization of the reorganization process. A two-stage exothermic process could be noted in each polymer system depending on the thermal history selected.

* * *

A special thanks to Dr. R. Perrinaud for measuring the molecular weights of PVDF and PA-12.

References

1 B. Wunderlich, Macromolecular Physics, Vol. III, Crystal Melting, Academic Press, 1980.
2 B. Wunderlich, Thermal Analysis, Academic Press, 1990.
3 K. Nakagawa and Y. Ishida, J. Polym. Sci.: Polym. Phys., 11 (1973) 2153.
4 F. N. Liberti and B. Wunderlich, J. Polym. Sci.: Part A-2, 6 (1968) 833.
5 M. Todoki and T. Kawaguchi, J. Polym. Sci.: Polym. Phys., 15 (1977) 1067.

6 K.-H. Illers, Polymer, 18 (1977) 551.
7 S. Z. D. Cheng, Z. Q. Wu, and B. Wunderlich, Macromolecules, 20 (1987) 2802.
8 A. G. Leray and L. Judovits, Proc. of the 25th North American Thermal Analysis Society Conference, September 7–9, McLean Virginia 1997, p. 72.
9 J. D. Menczel and G. L. Collins, Polym. Eng. Sci., 32 (1992) 1264.
10 G. L. Collins and J. D. Menczel, Polym. Eng. Sci., 32 (1992) 1270.
11 S. Roussel, K. L. McElroy and L. H. Judovits, Polym. Eng. Sci., 32 (1992) 1300.
12 M. Reading, A. Luget, and R Wilson, Thermochim. Acta, 238 (1994) 295.
13 T. Ozawa and K. Kanari, Thermochim. Acta, 253 (1995) 183.
14 L. Judovits, NATAS Notes, 29 (1997) 31.
15 T. H. Mourey and T. G. Bryan, J. Chromatography A, 679 (1994) 201.
16 R. Greco and L. Nicolais, Polymer, 17 (1976) 1049.
17 A. J. Lovinger, in Developments in Crystalline Polymers, D. C. Basset, Ed., Vol. 1, Applied Science, London, 1982, Chap. 5, p. 195.