Keywords: differential scanning calorimetry, melting, thermoplastic polymers

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ABSTRACT

DSC step annealing is used to study the fine molecular structure of poly(vinylidene fluoride) (PVDF) homopolymers and copolymers. The melting pattern, obtained after step annealing, is a characteristic "fingerprint" for small variations in structure. This "fingerprint" detects variations in the polymerization process, the molecular weight of the polymer, the fraction and the nature of the co-monomer.

INTRODUCTION

Molecular structure of a polymer largely determines its final material properties. For this reason characterization of variations in molecular structure is an important issue. For poly(vinylidene fluoride) (PVDF) homopolymers small variations in polymerization conditions can result in noticeable differences in chain heterogeneity and hence in physical properties. Moreover the average molecular weight and molecular weightdistribution of the polymer chains are important processing characteristics. For PVDF copolymers the properties are dependent upon the type and fraction of the co-monomer. It is important to have a technique for detection of small batch-to-batch variations or homopolymer contamination of copolymer for quality control of the PVDF polymerization process. DSC is an ideal candidate for this purpose as it is robust, easy to implement and generate accurate results rapidly.

A key element in establishing relationships between structure and properties is the characterization of the length of crystallizable segments. Segregation techniques using DSC for stepwise fractionation according to crystallizability have been described in literature for several types of polymers. Judovits used Stepwise Isothermal Segregation Technique (SIST) to study PVDF copolymers (1). Arnal and coworkers developed a Successive Self-nucleation/Annealing (SSA) procedure to characterize the short chain branching distribution in ethylene/α-olefin copolymers (2). This research group also studied functionalized polyolefins, crosslinked polyethylene as well as crystallizable blocks within triblock copolymers with SSA. The basis for SSA was conceived by Fillon who used it to define an efficiency scale for nucleating additives for polypropylene (PP) (3). Heyez "fingerprinted" isotactic PP by using SSA (4). 2 TA300

In this study, DSC step annealing (or SSA) is applied to PVDF homopolymers and copolymers (5). SSA is preferred over SIST because of the shorter experimental time involved. The influence of polymerization conditions, molecular weight, type and fraction of co-monomer on the DSC thermal curve after SSA segregation is studied.

EXPERIMENTAL

Solvay's PVDF homopolymers and copolymers were investigated. For the first series of homopolymers (two batches of Solef® 1010), polymerization conditions varied slightly. For the second set (Solef® 6008 and 6020), the intrinsic viscosity in dimethylformamide (DMF) is between 6 and 20 mL/g. The copolymers are based on vinylidene fluoride and hexafluoropropylene (HFP) or vinylidene fluoride and chlorotrifluoroethylene (CTFE). The co-monomer fraction is 10 to 15 % (Solef® 21008, 21508, 31008). All copolymers have viscosities of 8 mL/g in DMF.

The DSC measurements are performed on a TA Instruments™ DSC with Tzero™ technology. This technology offers significant advantages for the study of step annealed polymers, including a flat baseline and superior resolution.

Crystallization of the PVDF samples is performed in the DSC. The thermal history is first erased by heating the sample well above its melting region (250 °C for 5 min for the homopolymer, 220 °C for 5 min for the copolymer). The sample is then cooled to well below its crystallization region (e.g., -20 °C) at 10 °C/min to create a common thermal history. This is referred to as "standard" crystallization. Subsequently step annealing is applied to provide molecular segregation. For the homopolymer the step annealing program consists 60 min at each of 4 consecutive temperature (170, 175, 165, and 155 °C). For the copolymer the temperatures of 145, 135, 125, and 115 °C are used. Finally the material is cooled to –20 °C, and the effect of the step annealing on the melting pattern is studied by heating at 10 °C/min up to 250°C. For comparison, the melting pattern after standard crystallization is also measured. The time-temperature program for both series of experiments (step annealing versus standard crystallization) is shown in Figure 1. Details on the choice of temperatures for the isothermal platforms are found in (2).
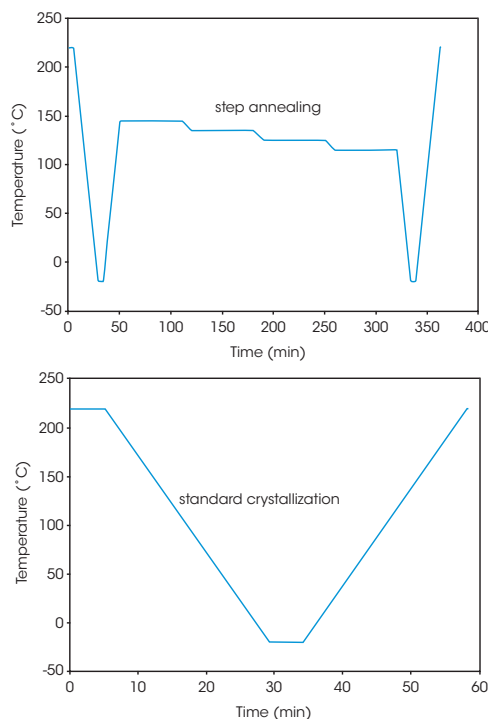

Figure 1. Time-Temperature Programs for PVDF Copolymers

RESULTS AND DISCUSSION

Figure 2 compares the melting of two PVDF homopolymers with slightly different polymerization conditions. For the curves at the left, standard crystallization is applied prior to melting the samples, while for the curves at the right step annealing is applied. After standard crystallization, there is little difference observed between the thermal curves, while after step annealing a clear distinction in the melting pattern is found. For batch 2 the highest peak is at slightly higher temperature (181.1 versus 179.9°C) and contains more of the total melting area (35.5 versus 25.8%). This conforms to a higher ratio of the longer crystalline sequences for batch 2.

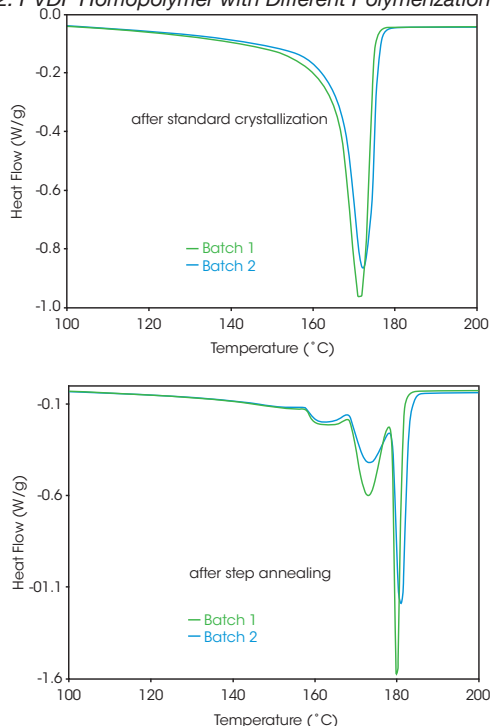*Figure 2. PVDF Homopolymer with Different Polymerization Conditions*

Figure 3 compares two PVDF homopolymers with different molecular weight. Only the melting pattern after SSA is shown, since again the melting after standard crystallization shows little differentiation. A very clear distinction between the grades with different molecular weight can be made. Only the homopolymers with a low molecular weight have long sequences with a melting point near 179.3 °C. This is probably related to the higher mobility for crystallization in less viscous systems.

Figure 3. PVDF Homopolymer with Different Molecular Weight Following
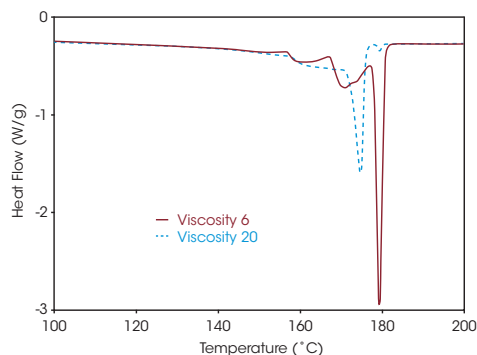

SSA

Figure 4 shows melting curves after SSA for PVDF copolymer with 10 % HFP or CTFE co-monomer, as well as 15 % HFP co-monomer. It is clear that the introduction of HFP co-monomer dramatically reduces the maximum melting temperature. A clear distinction in melting pattern is seen for the polymers with different type of co-monomer. For the HFP co-monomer an increase of 5 % of its fraction reduces the amount of longer crystalline sequences with melting point near 148.7 °C (from 39.5 % of the total area to 3.4 %).
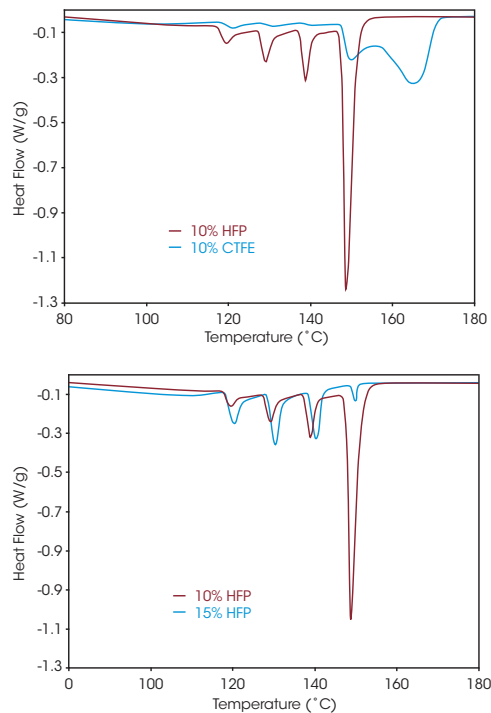

Figure 4. PVDF Copolymers with Different Type and Fraction of Co-monomer Following SSA

To use DSC step annealing for quality control purposes, the experimental time involved needs to be minimized. One way to do this is to minimize the time of the isothermal steps. Figure 5 shows the effect of reducing the time from 60 down to 5 min. A "fingerprint" with all the relevant peaks present is obtained after 5 min, but at least 30 min is required to obtain an image that is independent of the isothermal hold time.

Another way to reduce experimental time is by increasing the heating rate of the final heating step. Figure 6 shows the melting pattern obtained at heating rates ranging from 10 to 100 °C/min. In order to facilitate direct comparison of the curves at different heating rates, heat capacity units are plotted. This is possible since the DSC allows direct measure of heat capacity (8). Even at the very high heating rate of 100 °C/min the multiple peaks fingerprint is still clearly established, and the ratio of the different peaks remains essentially unchanged. This is made possible by the extremely good resolution obtained by employing Advanced Tzero™ DSC technology (7).
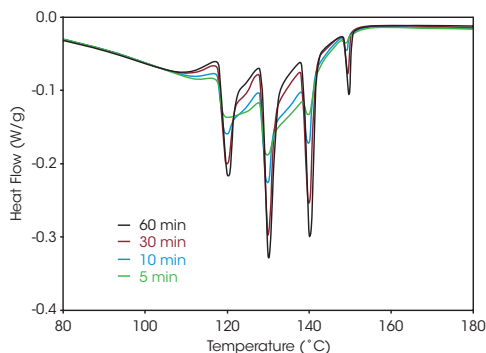
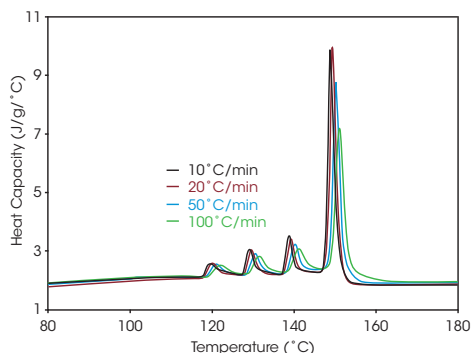*Figure 5. Effect of Isothermal Hold times in the SSA of PVDF Copolymer*

Figure 6. Effect of Heating Rate on PVDF Copolymers Following SSA

CONCLUSION

The step annealing DSC technique yields a very sensitive tool to detect small variations in the molecular structure of PVDF. The experimental time for step annealing measurements is sufficient fast that the technique can easily be implemented for quality control (batch to batch variation) purposes.

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