

# Melting and Crystallization Behavior of Poly(tetrafluoroethylene). New Method for Molecular Weight Measurement of Poly(tetrafluoroethylene) Using a Differential Scanning Calorimeter

TAKESHI SUWA, MASAOKI TAKEHISA, and SUEO MACHI,  
*Takasaki Radiation Chemistry Research Establishment, Japan Atomic  
Energy Research Institute, Takasaki, Gunma, 370 Japan*

## Synopsis

Melting and crystallization behavior of virgin polytetrafluoroethylene have been studied using a differential scanning calorimeter. Following quantitative relationship was found between number average molecular weight of polytetrafluoroethylene and the heat of crystallization in the molecular weight range of  $5.2 \times 10^5$  to  $4.5 \times 10^7$ :  $\bar{M}_n = 2.1 \times 10^{10} \Delta H_c^{-5.16}$ , where  $\bar{M}_n$  is number average molecular weight and  $\Delta H_c$  is the heat of crystallization in cal/g. The heat of crystallization is independent of cooling rate ranging from 4 to 32 °C/min. This relationship provides a simple rapid and reliable method for measuring the molecular weight of polytetrafluoroethylene.

## INTRODUCTION

As is well known, since poly(tetrafluoroethylene) is insoluble, the usual method for measuring molecular weight from solution viscosity is not applicable. Sperati et al.<sup>1,2</sup> presented a practical method for the measurement by using the specific gravity of poly(tetrafluoroethylene). The test method of the standard specific gravity (SSG), is, however, rather complicated, and sometimes the sample prepared has voids which result in low specific gravity.

In the course of the study on melting and crystallization behavior of poly(tetrafluoroethylene), we found that the heat of crystallization of the polymer melt is closely related to its molecular weight. Based on the observations, this paper presents a simple and reliable method for measuring the molecular weight from the heat of crystallization which can be obtained from a differential scanning calorimeter curve.

## EXPERIMENTAL

Most poly(tetrafluoroethylene) samples were prepared in our laboratory by radiation-induced emulsion and suspension polymerization, and some

samples were commercial "virgin" polymers which were never at elevated temperatures. The molecular weights of the samples were determined from standard specific gravity according to the relation reported by Sperati et al.<sup>1,2</sup> Standard specific gravity was measured according to ASTM D-1457-62T.

Melting and crystallization experiments were carried out using a Perkin-Elmer Model 1B differential scanning calorimeter (DSC). About 5 mg polymer was used for each experiment. Heating and cooling rates of the samples were 4°, 8°, 16°, and 32°C/min. Heats of fusion and crystallization were calculated from their peak areas which were calibrated using benzoic acid as standard compound.

## RESULTS AND DISCUSSION

Figure 1 shows DSC curves for the radiation-polymerized poly(tetrafluoroethylene) of  $17.5 \times 10^6$  molecular weight at three different heating and cooling rates. It can be seen that the virgin polymer has two melting peaks in the temperature range from 320° to 350°C, while the sample crystallized from the melt shows a single melting peak at much lower temperature than the virgin polymer. The heat of fusion of the virgin polymer was shown to be larger than the sample crystallized from the melt. These facts indicate that the polymer has high crystallinity as polymerized because of its entirely linear structure<sup>3,4,5</sup> and that the sample cooled from the melt has lower crystallinity because the polymer chains of very high molecular weight cannot completely crystallize during the process, and part of the polymer chains remains in the amorphous state. It can also be seen that the melting peak shifts to higher temperature as the heating rate increases, and the crystallization peak shifts to lower temperature as the cooling rate increases. On the other hand, the area of crystallization peak, that is, the heat of crystallization, is independent of the cooling rate (see also Fig. 4) in the range of 4° to 32°C/min.

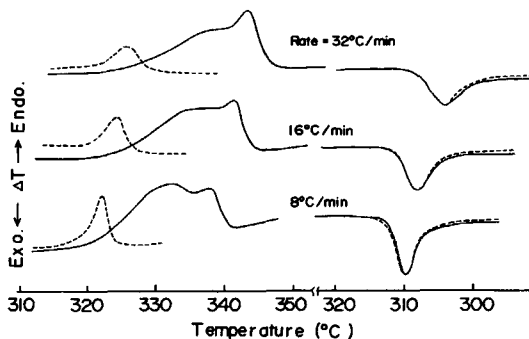


Fig. 1. DSC curves of poly(tetrafluoroethylene) at various heating and cooling rates, Sample 11 in Table I: solid line, melting of virgin polymer and first crystallization from the melt; dotted line, melting of sample crystallized in first run, and second crystallization.

TABLE I  
Heat of Crystallization of Poly(tetrafluoroethylene)<sup>a</sup>

Sample no.	Standard specific gravity	$\bar{M}_n \times 10^{-6}$ <sup>b</sup>	Heat of crystallization, cal/g
1	2.282	0.49	7.36
2	2.280	0.52	7.59
3	2.280	0.53	8.56
4	2.277	0.59	8.32
5	2.275	0.64	7.76
6	2.270	0.78	7.61
7	2.260	1.15	6.42
8	2.254	1.50	6.31
9	2.246	2.00	5.80
10	2.207	9.60	5.13
11	2.192	17.5	3.93
12	2.172	38.5	3.50
13	2.168	45.0	3.24

<sup>a</sup> Samples 10, 12, and 13 are commercial poly(tetrafluoroethylene); other samples were prepared by radiation polymerization.

<sup>b</sup> Determined from SSG using Sperati's relation.<sup>1,2</sup>

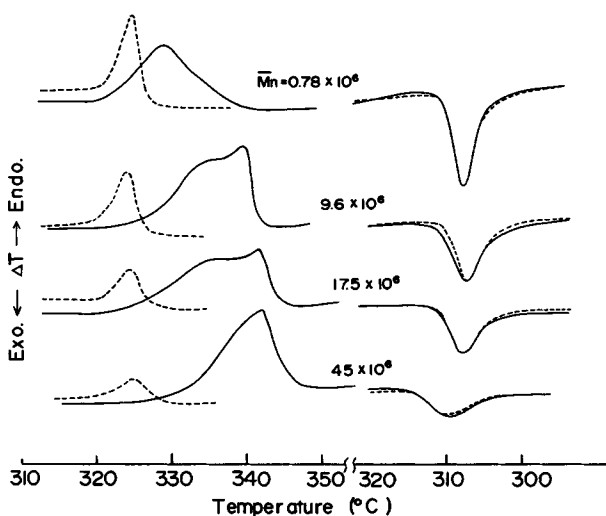


Fig. 2. Effect of molecular weight on DSC curve of poly(tetrafluoroethylene). Heating and cooling rate is 16°C/min; solid and dotted lines, identical to Fig. 1.

Typical DSC curves for poly(tetrafluoroethylenes) of various molecular weights are shown in Fig. 2, and the results are summarized in Table I. Figure 2 indicates that the larger the molecular weight, the higher is the melting temperature for the virgin polymers. This can be explained by the superheating of the virgin polymer which is more pronounced with larger molecular weight.<sup>6</sup>

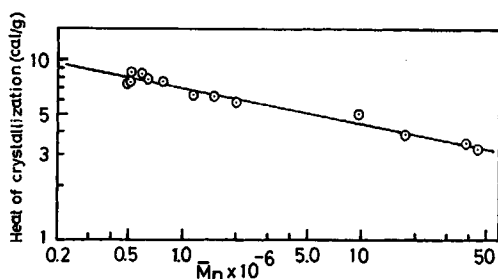


Fig. 3. Relation between number-average molecular weight and heat of crystallization for poly(tetrafluoroethylene).  $\bar{M}_n$  was calculated from SSG.

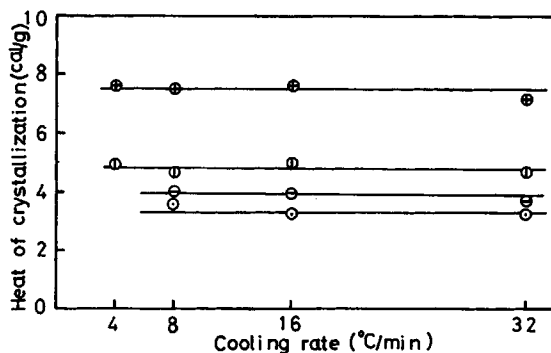


Fig. 4. Effect of cooling rate on heat of crystallization for various poly(tetrafluoroethylenes): (⊕) sample 6; (⊙) sample 10; (⊖) sample 11; (⊗) sample 13 in Table I.

The crystallization peak is shown to be remarkably affected by the polymer molecular weight. The larger the molecular weight, the smaller and broader is the crystallization peak. In other words, a higher molecular weight polymer, when crystallized from the melt, gives a lower level of crystallinity. This is explained by considering that the longer polymer chain has greater difficulty in the regular rearrangement or orientation during the solidification because of smaller mobility and greater intra- and intermolecular entanglement.

In Table I, the heat of crystallization calculated from the DSC curves for 13 samples of different number-average molecular weight ranging from  $5.2 \times 10^5$  to  $4.5 \times 10^7$  is listed. The heat of crystallization is plotted in Fig. 3 against the number-average molecular weight on a logarithmic scale. A straight line was obtained, which is expressed by the following equation:

$$\bar{M}_n = 2.1 \times 10^{10} \Delta H_c^{-5.16}$$

where  $\bar{M}_n$  is number-average molecular weight and  $\Delta H_c$  is the heat of crystallization in cal/g.

As shown in Fig. 4, the effect of the cooling rate on the heat of crystallization was investigated for various samples of different molecular weight.

The heat of crystallization was found to be independent of the cooling rate from 4° to 32°C/min, though it may be rate dependent in the range of extremely slow and rapid cooling rates.

The advantages of this method for molecular weight measurement are: simple and rapid method, small amount of sample required, and high reproducibility. A more detailed study on the melting and crystallization behavior of poly(tetrafluoroethylene) is in progress.

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### References

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