polymer reports

Thermal behaviour of poly(ethylene oxide) as revealed by differential scanning calorimetry

Yuko Kambe
Showa College of Pharmaceutical Sciences, Tsurumaki, Setagaya-ku, Tokyo, Japan
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Many results have been reported for melting and crystallization of poly(ethylene oxide) (PEO). The effect of molecular weight on the melting transition and the relation of crystallization temperature to fusion have been studied by using low-angle X-ray scattering and dilatometry[1–3]. The end-group effect of PEO with low molecular weight on fusion[4,5] has been reported. A compressibility pressure–temperature cycle has been developed to determine the melting point of PEO[6]. The thermoanalytical method has been applied to measure the entropy of fusion[7,8]. Systematic research on the melting behaviour of low molecular weight PEO fractions has been done using differential scanning calorimetry (d.s.c.)[9]. The thermal history of the sample has a significant effect on the data when the transition of PEO is investigated by thermal analysis. Effect of annealing on the thermomechanical properties of PEO has been reported with regard to the second order transition[10]. In the present report, we use d.s.c. to demonstrate that a PEO sample of molecular weight 4000 shows two endothermic melting peaks, and an exothermic recrystallization peak between them, after thermal treatments.

PEO samples were commercial materials (Nakarai Chemicals Co.). The number-average molecular weight, $\bar{M}_n$, was measured by means of a Knauer Vapour Pressure Osmometer in ethanol solutions at 45°C and also in benzene solutions at 37°C. The melting temperature, T_m, and the crystallization temperature, T_c, were defined as extrapolated onset points (*Figure 1*). According to the nomenclature[11] for differential thermal analysis curves (International Confederation for Thermal Analysis), the extrapolated onset is defined as the point of transition, because the point of intersection shown in *Figure 1* gives the most reproducible value which is experimentally independent of the operator. For thermal analysis of the d.s.c. curves, the same treatment is useful. The melting or crystallization points obtained by dynamic methods are not equal to the isothermal transition point obtained at the thermodynamic equilibrium. The d.s.c. melting curves may be affected by: (i) sample weight; (ii) cooling speed; (iii) heating range; (iv) heating scan speed; and (v) annealing. The peak area of d.s.c. curves and, therefore, the maximum point of the peak, is dependent on sample weight. The heating scan speed has an effect on the shape of d.s.c. curves and the transition point. The extrapolated value of T_m at heating scan speed = 0 can be used[9] at least for stable crystals. In experiments with an unstable PEO sample, the melting transition is very sensitive to the time kept after crystallization. In this experiment, conditions (i) and (ii) were constant; by changing the combination of (iii) and (iv), the existence of less stable solid states monitored after some annealing (v) effects was monitored by d.s.c. The results are shown in *Table 1*. Measurements were carried out using a Perkin–Elmer DSC-1B in N_2 atmosphere. The sample was refined by reprecipitations from ether–methanol or acetonitrile–methanol mixtures. The five samples with different molecular weights gave melting curves as shown in *Figure 2*, where d.s.c. measurements were carried out from 303K to 343K. After the first heating run up to 343K, the samples in the d.s.c. pan were cooled down immediately at 2 K min^{-1} to room temperature. In this cooling run, exothermic crystallization peaks were observed. The crystallization temperature T_c was defined as in *Figure 1*. The temperature was kept constant at T_c until the exothermic crystallization peak was finished. Then the sample was crystallized under isothermal conditions. The crystallization was completed within 3 or 4 min depending on the sample weight in these experimental conditions. However, T_c could not be observed for No. 2000 and No. 1540, because T_c for these samples with lower molecular weights may be situated below 303K and not easily measured under these conditions.

The second and third heating runs were conducted after being kept at definite time intervals at T_c. The dotted line in *Figure 2* is an example of the second heating run for No. 4000 after 4 min at T_c = 303K. The melting curves were changed significantly when measured within an hour of cooling down to T_c; i.e. after the second and third heating runs, two endothermic peaks and an exothermic peak between them were observed for this sample. Endothermic peaks observed at the second run are, respectively, peaks A and B. Peak B appeared at the same temperature as the melting peak during the first run of the original sample. The exothermic peak

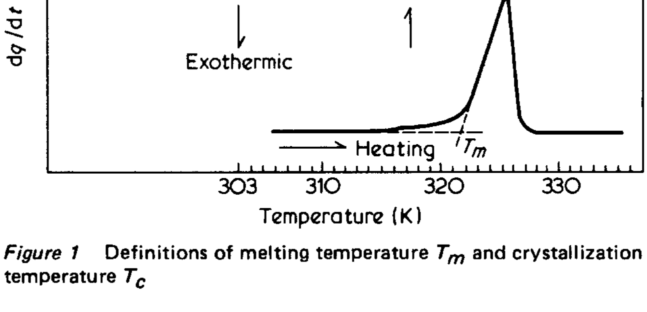

Figure 1 Definitions of melting temperature T_m and crystallization temperature T_c

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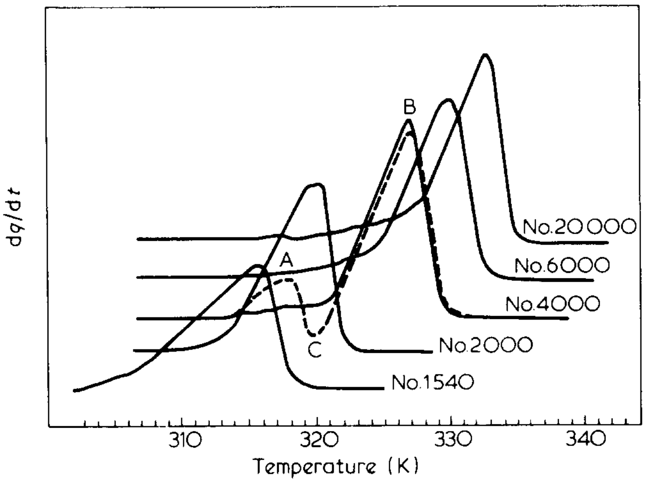

Figure 2 D.s.c. heating curves for poly(ethylene oxide) with different molecular weights. Heating range = 16 mcal s^{-1}, scan speed = 8 K min^{-1}, and sample weight = 0.0119 ~ 0.0124 g. The dotted line is obtained at the second heating run of No. 4000, kept 4 min, isothermally, at T_c = 303K after cooling from 343K

observed in the second run is designated peak C. The area under peak A changes with the period at T_c. Peak A disappeared when the sample was kept at room temperature for one day. Buckley *et al.* reported[9] that PEO H4000 ($\bar{M}_n$ = 3900) crystallized at T_c = 42.9°C in one folded chain form shows absence of any exothermic peak in d.s.c. curves at different heating rates and chain unfolding does not involve large-scale melting followed by recrystallization. In the experiment for No. 4000 crystallized at T_c = 303K, the exothermic peak of recrystallization was observed between two endothermic peaks. The most important difference in these two experiments is the time at T_c. Melting endotherms obtained by Buckley were for the sample kept 2.5 h at T_c.

The d.s.c. curves for No. 4000 (*Figure 3*) were obtained within several minutes after cooling was finished. The new peak A obtained during the second run for sample No. 4000 and the exothermic peak C revealed after peak A are considered as follows. The greater part of the PEO molecules form extended chain crystals at T_c = 303K and melt at T_m. According to the investigation on effects of molecular weight on crystallization[12], a molecular weight of 4000 is said to be the highest limit for which extended chain morphology predominated in mature crystals of PEO. But some PEO No. 4000 does not make extended chain monomole-

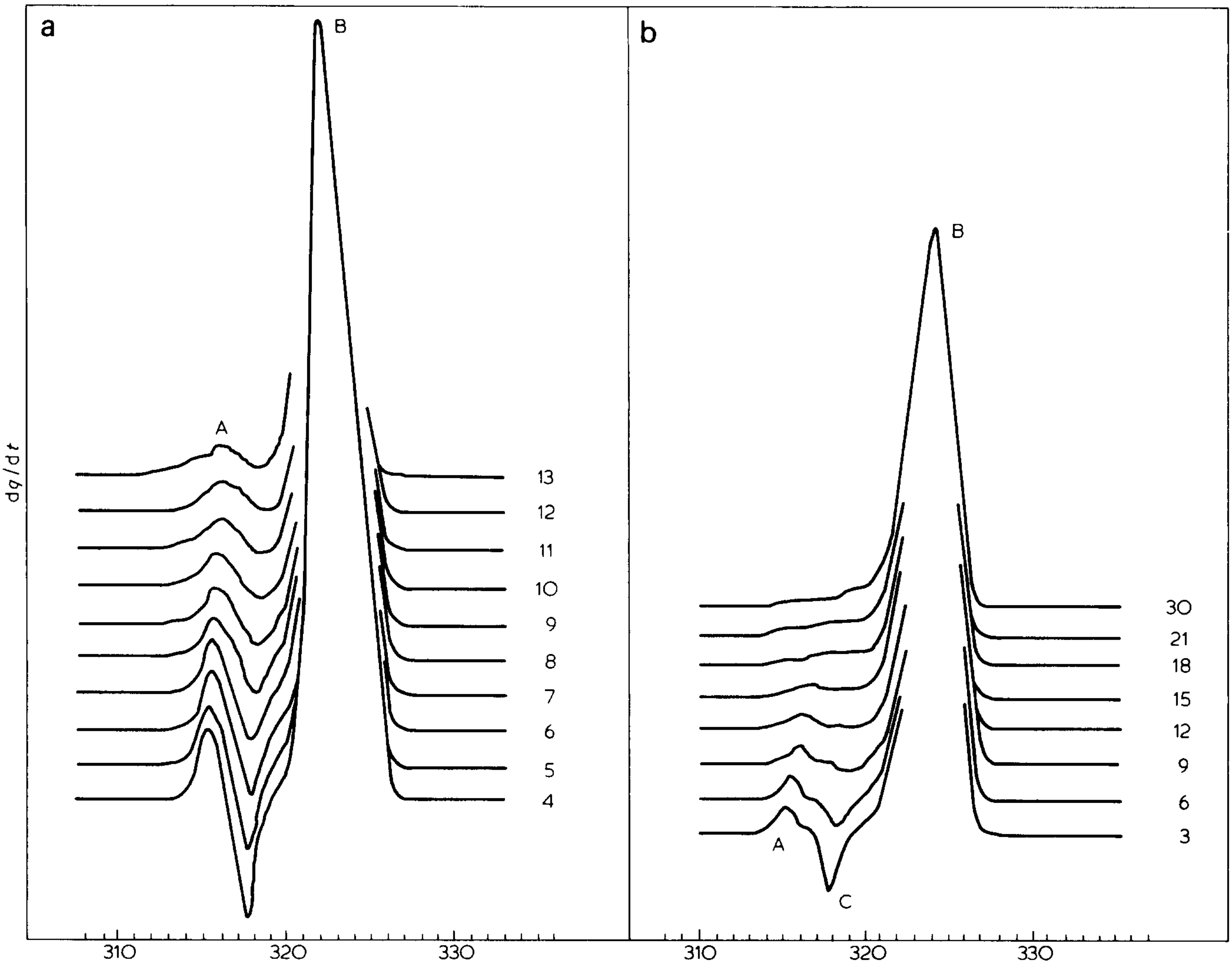

Figure 3 Examples of dependence of melting curve on the period (min) kept at T_c for sample No. 4000. Sample weight = 0.0124 g, scan speed = 4K min^{-1}, T_c = 303K. a, range = 4 mcal s^{-1}; b, range = 8 mcal s^{-1}

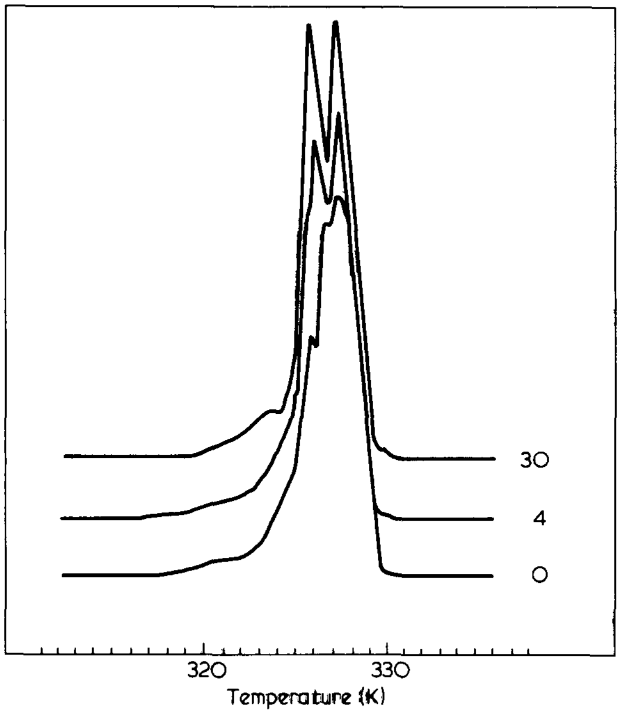

Figure 4 Melting curves of No. 6000. Sample weight = 0.0122 g. range = 2 mcal s^{-1}, scan speed = 1K min^{-1}, T_c = 309K. Times (min)

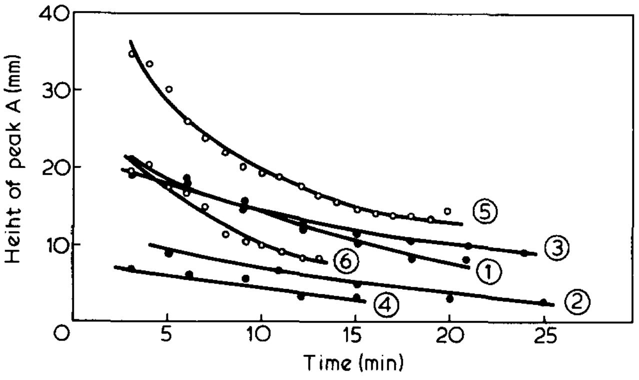

Figure 5 Decrease of the peak A for No. 4000

Experiment no.	Range (mcal s^{-1})	Scan speed (K min^{-1})	Sample weight (g)
①	16	8	0.0051
②	16	8	0.0124
③	32	16	0.0124
④	8	4	0.0124
⑤	8	8	0.0124
⑥	4	4	0.0124

Table 1 Number-average molecular weight $\bar{M}_n$, melting temperature T_m and crystallization temperature T_c of poly(ethylene oxide)

Sample	$\bar{M}_n$ in C_2H_5OH	$\bar{M}_n$ in C_6H_6	T_m^* (K)	T_c^* (K)
No. 20 000†	17 900	–	329	315
No. 6000	8430	7880	327	309
No. 4000	3500	4080	323	303
No. 2000	1950	1990	317	–
No. 1540	1500	1650	309	–

* D.s.c. conditions: scan speed = 8 K min^{-1}; range = 16 mcal s^{-1}, sample weight = 0.0024 ~ 0.0027 g

† Experimental sample

cular crystals and exhibits chain folding after heat treatment[7]. When the sample was heated at a scan speed suited to the thermal motion of the chain, less stable folded-chain crystallites melt at lower temperature than T_m of extended crystals, i.e. peak A, and the molten molecules immediately recrystallize to form extended monomolecular crystals at the crystallization peak C. When the sample was kept at T_c longer than one hour, the transition of the chain-folded crystallites to the extended chain crystals has been completed and melting peak B was observed by d.s.c.

The rate of decrease of peak A is a measure of transition velocity from the chain folded crystallites to the extended chain crystals. Peak A decreases with the period at T_c = 303K. The rate of decrease in peak A was observed with 6 different combinations of range and scan speed for the same sample, No. 4000 (0.0124 g). Examples are shown in *Figure 3*. It was difficult to obtain the precise area of peak A; thus, the height of peak A is plotted against the period at T_c in *Figure 4*. The slope of the curve depends on the ratio of the range and the scan speed. The slopes for experiments 5 and 6 are apparently twice those for experiments 1–4, because the thermal energy supplied per unit time for experiments 5 and 6 is one half for the others. Discussion of kinetics of the results will be presented elsewhere.

The samples No. 6000 and No. 20 000 demonstrated changes in melting curves after thermal treatments. Under experimental conditions of range = 2 mcal s^{-1} and scan speed = 1K min^{-1}, two or three peaks appeared for No. 6000 and No. 20 000. At scanning speeds higher than 1K min^{-1}, the sample showed only one melting peak. Dependence of the melting curve on the period at T_c are different for No. 4000 and for No. 6000 or No. 20 000 as follows: (i) the sample No. 4000 indicated the crystallization peak C, but the crystallization exothermic peak was not found for No. 6000 or No. 20 000; (ii) the typical time dependency for No. 4000 is shown in *Figure 3*, where peak A decreases with the period kept at T_c = 303K. However, for No. 6000 and No. 20 000 the new peak appeared after thermal treatments. It increased with the period at T_c = 309K for No. 6000 (*Figure 5*). The samples No. 6000 and No. 20 000 have relatively large molecular weights $\bar{M}_n$ of about 8000 and 20 000, respectively. PEO molecules of a molecular weight of this range exhibit only folded-chain crystals[12]. The melting characteristics of these polymers[7] would be determined by crystallite thickness rather than molecular dimensions. In once melted materials, a mixture of the crystallite lamellae with different folding periods was formed after cooling down, depending on the temperature and annealing time. The annealing effect on the size of lamellae has been investigated by dilatometry and X-ray diffraction[2,3]. The d.s.c. analysis of melting makes it possible to separate the melting points for these lamellae with different thicknesses but with the same molecular weight[9]. For example, PEO No. 6000 shows only one melting peak on a heating curve with range = 8 mcal s^{-1} and scan speed = 8K min^{-1}. But separation of the melting peaks is obtained by measuring with a range = 2 mcal s^{-1} and scan speed = 1K min^{-1}, as shown in *Figure 5*. The peak area, namely the crystallinity of the sample, increases very slowly with the period at T_c.

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Linear representation of viscosity data as a function of molecular weight: 2. Extension into the domain of high expansion coefficients

George Staikos and Anastasios Dondos

University of Patras, Faculty of Engineering, Laboratory of Organic Chemical Technology, Patras, Greece

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In previous papers two new relations were proposed for a linear representation of the intrinsic viscosity of a polymer as a function of its molecular weight[1,2]. These relations were obtained by taking into account the difference in the segment density of the macromolecular coil at the Θ conditions and in the good solvent considered[3].

In this report we will try to extend the linear relation between the intrinsic viscosity and the molecular weight of a polymer in the domain of high molecular weights and high expansion coefficients. This is achieved by a modified Stockmayer–Fixman–Burchard equation containing two additional parameters. Such a relation, covering the entire domain of molecular weights, is necessary because for high expansion coefficients not only the Stockmayer–Fixman–Burchard (SFB) equation is inadequate[4,5], but even the proposed modified SFB relation[2], containing only one additional parameter, does not give an acceptable linear representation.

From reference 2 we take the equation:

$$\left(\frac{1}{[\eta]_\Theta} - \frac{1}{[\eta]}\right) M^{1/2} = A_2(M^{1/2} - DM) + A'$$

and substitute $D - CM$ for D, where C is a new constant. Thus,

$$\left(\frac{1}{[\eta]_\Theta} - \frac{1}{[\eta]}\right) M^{1/2} = A_2(M^{1/2} - DM + CM^2) + A'$$

and instead of the corrected SFB equation:

$$\frac{[\eta]}{M^{1/2}} = \frac{1}{A_1} + \frac{A_2}{A_1^2} M^{1/2}(1 - DM^{1/2}) + \ldots \qquad (1)$$

from reference 2 we obtain finally:

$$\frac{[\eta]}{M^{1/2}} = \frac{1}{A_2} + \frac{A_2}{A_1^2} M^{1/2}(1 - DM^{1/2} + CM^{3/2}) + \ldots \qquad (2)$$

As described in reference 2 the parameter D is given by:

$$D = 12 \times 10^{-4}(a - 0.5) \qquad (3)$$

where a is the exponent of the Mark–Houwink–Sakurada (MHS) equation. Using a large number of experimental results taken mainly from the literature we have attempted to find a value for the constant C, maintaining the same value for D. The best value of C, giving a linear relation over the entire domain of molecular weights when $[\eta]/M^{1/2}$ and $M^{1/2} - DM + CM^2$ are plotted according to the new equation (2), is given by:

$$C = 6 \times 10^{-8} D \qquad (4)$$

as seen from the following examples.

Poly(vinyl acetate)/CHCl$_3$ and poly(vinyl acetate)/acetone

The experimental results for these systems were taken from Ueda and Kajitani[6]. In *Figure 1* we represent these

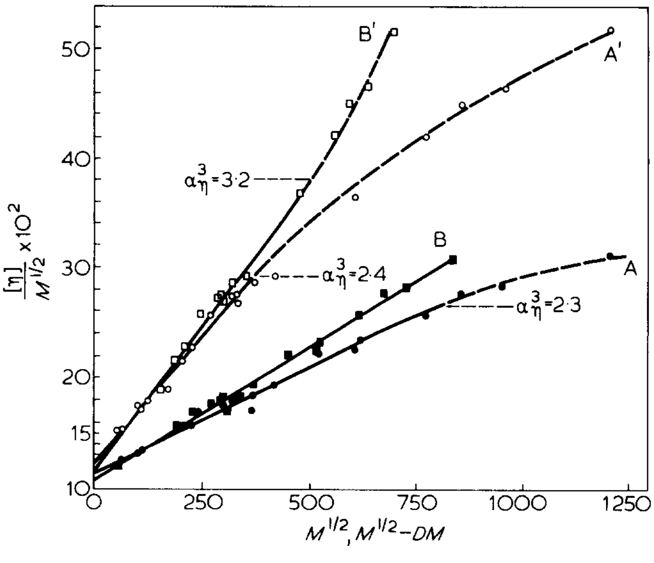

Figure 1 A (●), Plot of $[\eta]/M^{1/2}$, and B (■), *versus* $M^{1/2} - 2.52 \times 10^{-4} M$ for poly(vinyl acetate) samples, in acetone at 6°C. A' (○), plot of $[\eta]/M^{1/2}$ and B' (□) *versus* $M^{1/2} - 3.48 \times 10^{-4} M$ for poly(vinyl acetate) samples in CHCl$_3$ at 6°C. Results from ref 6

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