EFFECT OF TEMPERATURE HISTORY UPON STABILITY AND MELTING OF POLY(ETHYLENE OXIDE)

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

The effect of temperature history upon the distribution of molecular weights and melting points has been investigated with high-molecular poly(ethylene oxides). The results obtained by the size exclusion chromatography (SEC) and differential scanning calorimetry (DSC) have shown that a long-term annealing of high-molecular poly(ethylene oxides) results in a distinct degradation of polymeric chains. The change in distribution of molecular weights and the presence of oligomers formed by degradation markedly affect the melting points of poly(ethylene oxide). The diffusion of oligomers from crystalline into amorphous regions is manifested by a time change of melting point and crystallinity degree of poly(ethylene oxide). The degradation is also observed during X-ray measurements.

Considerable attention has been focused on polymeric mixtures in recent years. One of the methods used to study these systems consists in monitoring the melting of a crystalline polymer in its mixtures with other polymers[1]. Poly(ethylene oxide) is one of the most frequently used semicrystalline polymers[2-4] and its properties have been studied in detail from the standpoint of both the crystallization and conformation of polymeric chains in crystals[5-9] and their separation according to molecular weight in the course of crystallization[10-13]. A common feature of all these studies is a relatively long annealing of the samples at temperatures close to the melting point of poly(ethylene oxide). The aim of the present work is to follow the effect of temperature treatment of poly(ethylene oxide) on its crystallization and melting.

EXPERIMENTAL

Materials

The poly(ethylene oxides) with declared molecular weights of 600 and 20 000 (PEO 0.6 and PEO 20, respectively, Fluka). Poly(ethylene oxide) with M.w. 100 000 (PEO 100, Polyscience). The samples investigated had different temperature histories: A dried in vacuum at room temperature; B dissolved in dioxane in a sealed ampoule at 100 °C, then the solvent was evaporated at room temperature;

C the same as B but the solvent was evaporated at 72 °C, and the polymer was dried at the same temperature 3 days; D dried in vacuum at 72 °C 3 days; E sample C redissolved in dioxane and the solvent evaporated at room temperature. All the samples were measured 24 h after preparation, selected ones also after a long-term crystallization at 23 °C.

The codes denoting the samples are composed of PEO denotation (0.6, 20, or 100) and treatment denotation (A, B, C, D, E).

The procedures of preparing a model 1 : 1 mixture of liquid PEO 0.6 and PEO 20 were chosen to minimize the extent of degradation of PEO during preparation. In the first case the two components were mixed without solvent in an ampoule and homogenized at 72 °C for a short time. In the second case the two components were dissolved in dioxane without heating, the solvent was evaporated at room temperature, and the film formed was dried in vacuum at the same temperature. For monitoring the mixing of segregated PEO 0.6 and PEO 20 the film was heated at 360 K 3 min.

Methods

The calorimetric measurements were carried out on a Perkin–Elmer DSC-2 calorimeter. The temperature and power calibrations were carried out with the help of indium and sapphire, respectively. If not otherwise stated, the heating rate of sample was 10 K/min and the initial temperature of measurement was 230 K. The melting temperatures were defined as the temperatures corresponding to the maximum of melting endotherm and were determined with the accuracy of 0.2 K. A correction was introduced for the temperature lag of sample. The degree of crystallinity w^{cryst} characterizing the proportion of crystalline phase in the polymer sample is defined as the ratio of the experimental melting enthalpy to the melting enthalpy of perfectly crystalline polymer. (Δh^{cryst} = 196.6 J/g)[10,14].

The distributions of molecular weights were evaluated by means of SEC using an apparatus consisting of a VCR 40 HPLC pump, a Rheodyne 7125 injection valve (Rheodyne Inc., U.S.A.) with a 100 μl loop, and a differential refractometer R 401 (Waters Assoc., U.S.A.) which was attached to an IBM compatible PC by means of a Black Star 2308 A/D converter (Black Star Ltd., U.K.). Two stainless steel columns (250 × 8 mm I.D.; Tessek Ltd., Prague) in a series were packed with a modified packing[15] Lichrospher 300 and 1 000 by the slurry technique at 30 MPa using methanol–dioxane (1 : 1 v/v) as the slurry liquid. The mobile phase was a 1 : 1 (v/v) mixture of methanol and 0.01 M aqueous NaCl. The columns were calibrated with poly(ethylene oxide) standards (Polymer Laboratories Ltd., U.K.) in the M.w. range from 10 300 to 1 390 000. The samples were dosed as 0.1 wt.% solutions in the mobile phase.

RESULTS AND DISCUSSION

The melting of PEO is affected distinctly by temperature treatment. Figure 1 shows the DSC curves of PEO 100 after various kinds of treatment. The curves for PEO 20 were of the same character. Table I summarizes the melting temperatures corresponding to the temperature maxima of the individual melting endotherms, the overall degree of crystallinity, and the crystallinity degree corresponding to the main fraction with the highest melting temperature. In some cases the main melting endotherm exhibited two maxima.

Thermally treated samples show a characteristic splitting of melting endotherm into a number of maxima. According to Buckley and Kovacs[5,6] the multiplicity of melting endotherm can be due to a transition of crystals with a higher number of folds of

TABLE I
Melting temperatures $T_{m,i}$ (K) and degrees of crystallinity w_i^{cryst} (%) of PEO with various thermal histories

No.	PEO	$T_{m,1}$	$T_{m,2}$	$T_{m,3}$	$T_{m,4}$	w_{1-4}^{cryst}	w_4^{cryst}
1	0.6A	–	–	–	294.2	67.0	67.0
2	20A	–	–	–	342.1	98.6	98.6
3	20B	–	–	–	332.8	80.5	80.5
4	20C	–	–	296.5	323.9	70.7	52.8
5	20C[a]	–	281.4	297.9	327.3	70.2	59.5
6	20D	–	–	292.5	326.2	72.2	65.7
7	20D[b]	–	276.9	296.3	329.3	72.0	67.5
8	100A	–	–	–	341.5	94.2	94.2
9	100B	–	–	–	337.4	84.2	84.2
10	100C	–	266.4	291.7	312.3	28.6	6.2
11	100E	–	297.7	304.8	319.5	42.0	25.2
12	100E[c]	262.2	274.2	287.9	317.6	34.3	25.3
13	100E[c,e]	–	–	–	318.0	–	23.0
14	100D	277.2	292.2	318.3	320.9	41.7	36.0
15	100D[a]	–	275.6	291.9	328.2	53.7	51.4
16	100C[f]	–	266.4	291.7	312.3	28.6	6.2
17	100C[g]	–	297.9	303.9	320.8	53.8	0.5
18	100C[g,h]	280.2	298.8	305.2	320.5	43.4	18.8
19	100C[d,g,h]	–	271.3	289.4	323.9	49.5	41.1

Crystallized at 23 °C for: [a] 5 months; [b] 6 months; [c] 4 months; [d] 3 months; [e] measured from 300 K; [f] dried in air; [g] dried in vacuum; [h] irradiated by X-rays.

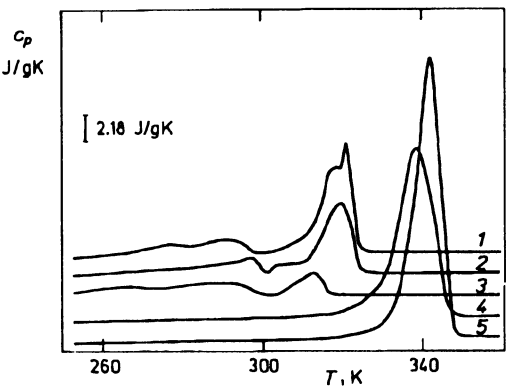

FIG. 1
DSC melting traces of PEO 100 with various thermal histories *1* D; *2* E; *3* C; *4* B; *5* A

polymeric chain in a crystal lamella to more perfect crystals with a lower number of folds. In this case the areas of individual peaks (the melting enthalpies of individual fractions) depend upon the heating rate of sample during the DSC measurements[5]. Wunderlich[14] explains this multiplicity by the irreversible melting of metastable crystals and suggests the monitoring of melting at various heating rates (time depending melting) as one of possible methods of detection of this process. A characteristic feature of irreversible melting is an increase of melting temperature with decreasing heating rate of sample[14]. The third possible reason given for the multiplicity of endotherm is the segregation of polymeric chains by their length during crystallization[10 - 12].

Table II gives – as an example – the enthalpies and temperatures of melting of two differently pre-treated PEO samples obtained at various heating rates of sample. From the table it is obvious that the melting enthalpy of the fraction with the highest melting point (Δh_4) as well as the overall melting enthalpy of the fractions with lower melting temperatures (Δh_{1-3}) are practically independent of the heating rate of sample for the individual samples. The melting temperatures ($T_{m,i}$) of fractions in all the samples slightly increase with increasing rate of heating. This increase is due to the overheating of crystals at high rates of heating[14]. These results show that the multiplicity of melting endotherms of thermally treated PEO is caused neither by a change in number of folds of polymeric chain in crystal lamella nor by an irreversible melting of metastable crystals.

For an evaluation of segregation of polymeric chains in the course of crystallization one must know the distribution of molecular weights in the samples investigated. Figures 2 and 3 give the M.w. distributions of various pre-treated PEO 20 and PEO 100 samples obtained by SEC. To be more clear, the individual curves are shifted along the

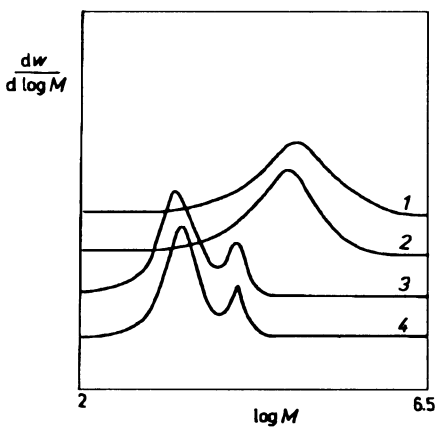

FIG. 2
Distribution function of molecular weights of PEO 100 with various thermal histories *1* A; *2* B; *3* C; *4* D

y axis. At first sight it is obvious that annealing of PEO as low as the temperatures near its melting temperature results in a very distinct change in M.w. distribution (Fig. 2). With regard to the high value of the temperature of half decomposition, $T_{d,1/2}$ = 618 K, determined by the method of differential thermal analysis[16], the decomposition of PEO does not go down to volatile portions but probably involves scission of polymeric chains. At the temperatures of 370 – 420 K the thermograms of PEO exhibit a distinct exotherm which can be due to oxidative degradation. The tendency of long PEO chains to degradation is also indicated by the decrease of viscosity of PEO solutions with time[17].

TABLE II
Melting temperatures $T_{m,i}$ (K) and enthalpies Δh_i (J/g) of two PEO samples at various heating rates (K/min)

PEO	Heating rate	$T_{m,1}$	$T_{m,2}$	$T_{m,3}$	$T_{m,4}$	Δh_4	Δh_{1-3}
20A	5	–	–	–	338.8	191.0	–
	10	–	–	–	342.1	193.0	–
	20	–	–	–	340.2	189.6	–
	40	–	–	–	345.1	176.9	–
20C[a]	5	280.4	296.3	304.1	325.1	116.7	15.9
	10	281.9	298.5	306.6	327.3	117.3	11.8
	20	281.9	298.5	306.5	328.7	114.4	11.0
	40	285.1	301.4	–	330.3	119.1	15.6

[a] Crystallized at 23 °C for 5 months.

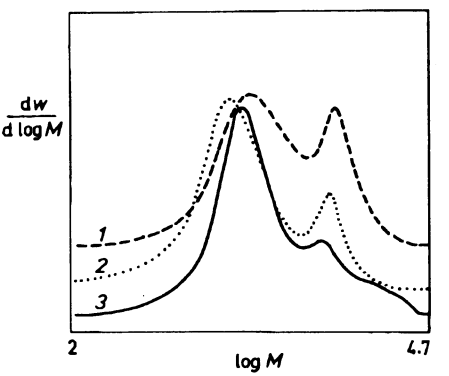

FIG. 3
Distribution function of molecular weights of PEO 100C and PEO 20C. Sample Nos (see Table I): *1* 17; *2* 10; *3* 4

Figure 2 represents the M.w. distribution of various treated PEO 100 samples. As little a treatment as mere dissolution of PEO in dioxane at enhanced temperature and subsequent evaporation of the solvent at room temperature will cause a change in M.w. distribution (curve *2*). Annealing at 72 °C leads to a very distinct degradation (curves *3* and *4*), the presence of solvent (curve *3*) or air (curve *2*, Fig. 3) making the degradation deeper. The relative M.w. decrease is much more marked with longer polymeric chains (curves *1* and *2*, Fig. 3). The comparison of melting temperatures and crystallinity degrees of various thermally treated samples of PEO 20 and PEO 100 (Table I) with the relative decrease in molecular weights (Figs 2 and 3) shows an obvious correlation between them.

The PEO chains are degraded not only by a long-term annealing at enhanced temperatures but also by action of the X-rays during X-ray measurements (samples Nos 17 and 19, Table I).

Further discussion needs an explanation of the effect of measuring technique upon the character of the melting endotherm of thermally treated PEO samples. The samples crystallized at room temperature. At this temperature crystallized the fractions corresponding to the peaks with the highest melting temperature. Other fractions are either amorphous or liquid (the case of oligomers) at this temperature. After cooling to the starting temperature of measurement, 230 K, these portions crystallize. The comparison of melting temperature and degree of crystallinity corresponding to the peak with the highest melting temperature of the sample No. 12, Table I, which was measured from 230 K, with those of sample No. 13 measured from 300 K shows that the crystallization of the highest-melting fraction took place at room temperature and is not substantially affected by additional undercooling to 230 K. On this undercooling, only the fractions with lower melting points are transformed into crystalline state. The share of these fractions in the overall melting enthalpy is 10 – 20%. Both samples were measured at the heating rate of 5 K/min.

With the model mixture both ways of preparation give samples whose melting endotherm exhibits two separate peaks corresponding to the melting of PEO 0.6 and PEO 20 (Table III), which indicates a very distinct separation by molecular weight during the crystallization of PEO. The respective melting temperatures are lower than those of pure components (samples 1, 2 in Table III and 1, 3 in Table I). This agrees with the results by Prud'homme[18] and Mandelkern et al.[13]. Mandelkern gives a relation between the melting temperature of crystalline component and composition of the mixture of chemically identical components[13]

$$1/T_m - 1/T_m^0 = -(R/\Delta H_{cryst})\,[(\ln \varphi_x)/x + 1/x - 1/\bar{x}_N]\,, \qquad (1)$$

where T_m and φ_x are the equilibrium melting temperature and volume fraction of crystalline component in the mixture, respectively, the molecule of this component contain-

ing x segments; T_m^0 is the melting temperature of pure crystalline component, ΔH_{cryst} is the melting enthalpy referred to a mol of repeating units, and $\bar{x}_N$ is number average degree of polymerization in the mixture.

Using Eq. (*1*) we calculated a model phase diagram of the mixture PEO 0.6/PEO 20 (Fig. 4). The calculation adopted the experimental melting points of pure components (Table I) and Δh^{cryst} = 196.6 J/g according to Cheng et al.[10]. For the segment we chose the repeating unit $-CH_2CH_2O-$. The sbranchof dependence of melting temperature of PEO 20 upon the composition of mixture is given by curve *1* in Fig. 4. This branch begins to decrease steeply to the eutectic point only at very low concentrations of PEO 20. The eutectic point is practically at infinite dilution of PEO 20 and its temperature is

TABLE III
Melting temperatures $T_{m,i}$ (K) and degrees of crystallinity w^{cryst} (%) of PEO 0.6/PEO 20 (1 : 1) mixtures prepared in various ways

Sample	T_m (PEO 0.6)	T_m (mix)	T_m (PEO 20)	w^{cryst} (PEO 0.6)	w^{cryst} (mix)
1[a]	292.3	–	332.2	29.9	77.4
2[b]	290.4	–	330.1	30.8	75.9
3[b,c]	292.1	–	332.2	29.4	77.2
4[b,d]	292.6	–	332.8	30.6	78.6
5[b,g]	285.5	308.5	326.0	17.3	63.8
6[b,e,g]	287.5	316.0	327.5	25.1	72.2
7[b,f,g]	287.8	320.6	328.4	26.5	74.3

[a] Mixed in the melt; [b] mixed in solution; crystallized at 23 °C for: [c] 1 month; [d] 2 months; [e] 1 day; [f] 6 days; [g] heated at 360 K for 3 min.

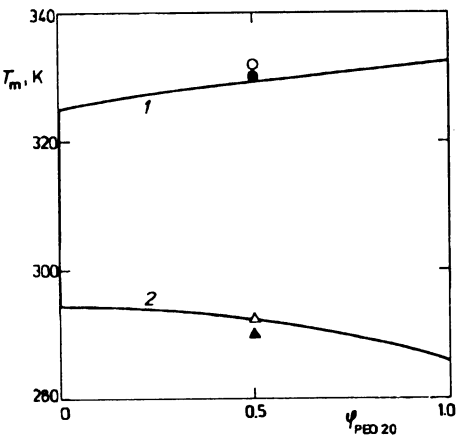

FIG. 4
Model phase diagram of 1 : 1 mixture PEO 0.6/PEO 20. *1* Melting of PEO 20, *2* melting of PEO 0.6. Sample Nos (see Table III): ○, △ 2; ●, ▲ 4

close to that of melting of pure PEO 0.6. The branch *2* of theoretic diagram corresponds to the crystallization of PEO 0.6 in the mixture with hypothetical amorphous PEO 20.

In the case of equilibrium course of crystallization during cooling of the mixture the resulting mixture should contain crystals of PEO 20 with the melting temperature corresponding to the nominal composition of the mixture and crystals of pure PEO 0.6. However, experimental melting temperatures are different. The melting temperature corresponding to the melting of PEO 20 in a freshly prepared mixture from a solution (sample No. 2, Table III) is 330.1 K. This value is higher than that corresponding to the nominal composition $w_2 = 0.5$. (Presuming the densities of both components to be approximately the same in amorphous state, it is $\varphi_2 \approx w_2$.) The experimental value of melting temperature of PEO 20 corresponds to the theoretical composition $w_2 = 0.65$. This shift in composition is caused[9 - 14] by the segregation of PEO 0.6 during the crystallization of PEO. The melting temperature of PEO 0.6 in the mixture is lower than that of pure PEO 0.6. This cannot be interpreted with the help of equilibrium crystallization and it contradicts also the mass balance. The explanation can be found in the nonequilibrium crystallization of PEO 0.6. The melting temperature of polymeric crystals depends – inter alia – also on their magnitude and perfection[14]. Prud'homme[18] showed that the segregated fractions which crystallize at lower temperatures remain trapped in the already crystallized portion and there they can later crystallize. The magnitude of inclusions of fractions thus segregated, and hence the magnitude of potential crystals, depend on the concentration and degree of mixing of the components in the mixture. In the case of sample No. 2 (Table III) prepared from a solution it can be presumed that the distribution of PEO 0.6 in the sample volume will be relatively uniform. In the course of crystallization at room temperature, PEO 0.6 is separated as small inclusions, and after cooling to 230 K it crystallizes in the form of fine crystallites with decreased melting temperature. This hypothesis is supported by the higher melting temperature of PEO 0.6 in the sample No. 1 (Table III) prepared by direct mixing of both components in a melt. In this case the degree of mixing of the two components is lower than that of sample No. 2, which is manifested by higher values of melting temperatures of both components in sample No. 1 as compared with 2.

The sample No. 2 (Table III) heated at 360 K for 3 min shows a third peak the melting temperature of which corresponds to very low concentrations of PEO 20 in the vicinity of eutectic point (Fig. 5, curve *4*, Table III, sample 5). The temperature of maximum of the middle peak increases with the time of crystallization at room temperature. At the same time the proportion of PEO 0.6 crystallizing on undercooling to 230 K increases too (samples 5 – 7, Table III, curves *2* – *4*, Fig. 5) and both values approach those of the starting sample No. 2, Table III. This can be interpreted in the following way. A short heating of sample No. 2, Table III, to 360 K leads to mixing of PEO 0.6 and PEO 20 components at the interface of separated regions. The higher

viscosity of melt and low values of diffusion coefficient of polymeric component prevent an extensive homogenization during short heating. The change in temperature of the maximum of the central peak and the growth of the amount of segregated PEO 0.6 with the time of tempering at room temperature is due to diffusion of liquid PEO 0.6 from the crystalline portion to the already separated liquid PEO 0.6. In the same way it is possible to interpret the change in melting temperature and degree of crystallinity of thermally treated samples of PEO 0.6 and PEO 20 with the time of crystallization at room temperature. The presence of newly developed maxima in the region of low temperatures with the samples from long-term crystallizations at room temperature represents another confirming of separation of oligomeric fractions. A very distinct effect of separation of oligomers upon the melting of PEO can also be observed with the sample exposed to a dose of X-radiation corresponding to the frequent SAXS measurement (samples Nos 18 and 19, Table I).

The different melting of the samples 10 and 11 (Table I) indicates a significant influence of distribution of oligomeric components in the sample volume. The M.w. distribution is the same in both the samples, because the sample PEO 100E was prepared by dissolving the sample PEO 100C in dioxane and evaporation of the solvent at room temperature. Both samples, however, differ in the distribution of oligomeric portions in the volume of sample. With PEO 100C there took place the degradation and subsequent crystallization in the melt. This leads to a relatively uniform distribution of oligomers in the volume of sample. On the other hand, the crystallization from solution accompanied by evaporation of solvent has the consequence of much more extensive separation of low- and high-molecular fractions, which will make itself felt by both increasing melting point and increasing degree of crystallinity of the highest-melting fraction.

The experimental results given show that the high-molecular PEO undergoes easy degradation during long-term tempering at enhanced temperature. This degradation is

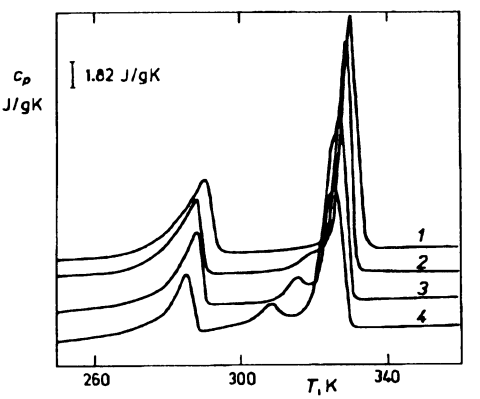

FIG. 5
DSC melting traces of 1 : 1 mixture PEO 0.6/PEO 20 (sample 2, Table III) *1* original sample. Heated at 360 K 3 min and crystallization at 296 K for: *2* 6 days; *3* 1 day; *4* 0 days

accelerated by the presence of air and it also proceeds on action of X-rays. The oligomers formed in this degradation influence the melting and degree of crystallinity of PEO, and the gradual separation of these oligomers in the sample leads to time changes in melting temperature and degree of crystallinity of thermally treated PEO.

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