

Analysis of the influence of the polymerisation degree on the thermal properties of irradiation-modified poly(tetrafluoroethylene)

G. Pompe, U. Lappan^{*}, L. Häußler

Institut für Polymerforschung Dresden e.V., Hohe Straße 6, D-01069 Dresden, Germany

Received 31 August 2001; accepted 22 October 2001

Dedicated to G.W.H. Höhne and M.J. Richardson on the occasion of their 65th birthday

Abstract

The influence of the polymerisation degree on the thermal properties of poly(tetrafluoroethylene) (PTFE) irradiated with 1.5 MeV electrons under various conditions was investigated. The polymerisation degree of radiation-degraded and radiation-crosslinked PTFE was determined by the analysis of chemical structure such as end groups and branching points using ¹⁹F NMR and IR methods. The melting heat and temperature observed in the as-polymerised and melt-crystallised states deviate from each other for high molecular weight PTFE. The differences vanish at polymerisation degree $X_n < 1600$ produced by irradiation with dose of 100–200 kGy. The representation of melting temperature of the melt-crystallised state as function of X_n permits the estimation of the equilibrium melting temperature T_m° as 605 K, which agrees with values given in the literature for the extended-chain crystals. We conclude that mainly extended-chain crystals were formed for PTFE of $X_n \leq 1600$ at the melt-crystallisation, whereas PTFE of $X_n > 1600$ crystallises as folded-chain crystals. The lamellar thickness l_c of the folded-chain crystals can be estimated as about 100 nm. The irradiation of PTFE in the melt results in crosslinking and branching with a strong influence on the thermal properties.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Poly(tetrafluoroethylene); Irradiation; DSC; Melting behaviour; Polymerisation degree

1. Introduction

Perfluoropolymers exhibit a number of favourable properties such as high-temperature stability, and low surface energy, resulting in unique non-adhesive and anti-friction properties [1]. They are insoluble in all common solvents and highly resistant to chemical attack.

Poly(tetrafluoroethylene) (PTFE) is known to be the most important perfluoropolymer. It is produced by suspension or emulsion polymerisation from the monomer C₂F₄. It is a linear polymer with a very high molecular weight ($M_n \approx 10^7$ g/mol [2,3]).

Since PTFE is insoluble, the determination of the molecular weight is not possible by usual methods. The estimation of the number averaged molecular weight M_n requires the determination of end groups using a radioactive marking [4,5]. Sperati and Starkweather [6] applied the measurement of the density according to ASTM D-1457-62T, because the density

^{*} Corresponding author. Fax: +49-351-4658-284.
E-mail address: lappan@ipfdd.de (U. Lappan).

correlates to the crystallinity, which decreases with increasing molecular weight in the melt-crystallised PTFE [6,7].

The equilibrium melting temperature T_m° of PTFE was given by Lau et al. [3] as 605 K. Starkweather [8] has investigated the melting temperature of the 1st and 2nd heating for commercial, high molecular weight PTFE. He has reported the zero heating rate values as $T_m^\circ = 605$ K for the extended-chain crystals and $T_m^\circ = 596$ K for the folded-chain crystals.

The linear structure without branches results in high crystallinity of PTFE in the as-polymerised state. Crystallinity of 93–98% was calculated from density [6]. The melting enthalpy ΔH_f° of 100% crystalline PTFE varies in the literature from 58 J/g [6,9] up to 102 J/g [10]. Lau et al. [3] using the as-polymerised state of high molecular weight PTFE as 100% crystalline state found $\Delta H_f^\circ = 82$ J/g. This value is accepted and used in this work. We want to note that with this value instead of 102 J/g the determination of crystallinity of high molecular weight PTFE from the DSC data in [10] is 91%, which is the same as obtained by density, infrared, X-ray and NMR measurements [10].

The influence of the molecular weight M_n on the crystallisation enthalpy ΔH_c of high molecular weight PTFE (in the range of 5.2×10^5 up to 4.5×10^7 g/mol) was used by Suwa et al. [11] for the estimation of the molecular weight. They found the empirical relation

$$M_n = 2.1 \times 10^{10} \times \Delta H_c^{-5.16} \quad (1)$$

with ΔH_c in cal/g. This method requires that the heat of crystallisation is almost independent of the cooling rate as experimentally proved in several papers [3,11,12]. However, there are some indications that Eq. (1) is not correct. Apparently, the values of the crystallisation heat come out too small. A comparison of the melting heats for PTFE with comparable molecular weight for both the as-polymerised and the melt-crystallised state published by Suwa et al. [9,11] with the results given by Lau et al. [3] allows the conclusion that the values in [9,11] are too small by a factor of about 1.5. That means the molecular weight determined by Eq. (1) is too low. The relation

$$M_n = 3.5 \times 10^{11} \times \Delta H_c^{-5.16} \quad (1a)$$

found by Weigel and Garske [13] should give more realistic values of M_n .

The molecular weight of PTFE can be drastically reduced predominantly by main chain scission due to ionizing radiation [6]. Several commercial PTFE micropowders are produced by irradiation. The ratio of chain scission to crosslinking reactions depends on the atmosphere and the temperature during irradiation. The presence of oxygen plays a dominant role [14]. Nishioka et al. [15] have shown experimentally that the density of PTFE irradiated in air increases and consequently the apparent molecular weight decreases with increasing dose. Additionally, to the main chain scission, branching and crosslinking are possible if the irradiation is carried out in an oxygen free atmosphere and at temperatures above the melting temperature [16].

First DSC investigations of the influence of irradiation were done by Suwa et al. [11] using γ rays up to doses of 500 kGy (50 Mrad). With increasing dose the melting temperature was decreased and the melting heat was increased in the melt-crystallised state.

In this paper PTFE samples with various polymerisation degree produced by electron beam irradiation of different PTFE types such as as-polymerised powders and sintered films were used. The irradiation was carried out under different irradiation conditions in respect to the temperature and the atmosphere [17,18]. The chemical structure (end groups, branches, crosslinks) used for the calculation of the polymerisation degree was determined by high-resolution fluorine-19 solid-state NMR and IR spectroscopic investigations [16,19,20].

The thermal properties were measured under non-isothermal conditions by means of DSC. An experimental data set for PTFE exists—to our knowledge for the first time in the literature—which permits the analysis of the influence of molecular weight on thermal properties of PTFE in a wide range.

2. Remarks about the influence of the molecular weight on the melting temperature

The influence of the molecular weight M_n on the thermal properties of alkanes/polyethylenes (PEs) was investigated in a very wide range of M_n reviewed in [21,22]. Some estimates of the melting temperature

$T_m = f(M_n)$ exist in the literature [23–26] based on different morphological models, different assumptions for the entropy contribution at the transition and on different kinds of the mathematical approximation.

With an incremental outline for the enthalpy and entropy the relation

$$T_m = \frac{T_m^\circ(c_1 + X)}{c_2 + X} \quad (2)$$

was found by Huggins [23] with T_m° as equilibrium melting temperature and X as polymerisation degree. c_1 and c_2 are adjustable parameters.

Flory and Vrij [24] developed in 1963 a relation including an entropy contribution of the so-called unpairing process $\Delta S_{\text{unpairing}} = R \ln X$ with X as the number of segments in the chain, which is equal to the polymerisation degree in the case of PE. Neglecting terms of higher order, Hay [25] rewrote the Flory/Vrij relation to

$$T_m \approx T_m^\circ \left\{ 1 - RT_m^\circ \left[\frac{\ln X}{\Delta H_{f,u}^\circ X} \right] + \frac{\Delta G_e}{\Delta H_{f,u}^\circ X} \right\} \quad (3)$$

with $\Delta G_e = \Delta H_e - T_m^\circ \Delta S_e$, whereby ΔH_e and ΔS_e as excess contributions included all contributions associated with the end groups.

With the mixing entropy term of the end groups as the most relevant contribution, Hay [25] obtained the following relation

$$T_m \approx T_m^\circ \left\{ 1 - \frac{2RT_m^\circ \ln X}{\Delta H_{f,u}^\circ X} \right\} \quad (4)$$

Hay has used Eq. (4) to fit the experimental data for $X < 500$ with $T_m^\circ = 419$ K.

Wunderlich and Czornyj [21] have analysed data of PE up to $X \leq 6000$ with different models and found that Eq. (2) with $T_m^\circ = 414.6$ K gives the best fit, although Eq. (3) should reflect a more realistic model in the opinion of those authors.

For the explanation of the melting behaviour of cyclic alkanes and other special PE (“nascent” PE–UHMWPE), Höhne [26] developed a model starting from the first principle with an incremental outline analogous to Huggins [23].

Both, PE and PTFE are linear polymers with a similar structure of the repeat unit and a high crystallinity. Therefore, the intention of the presented work is to check the validity of those relations for PTFE.

3. Experimental

3.1. Samples and methods

As PTFE base material for the irradiation experiments the emulsion polymer powder TF 2025 and the suspension polymer powders TF 1750 and TF 1760 (Dynoen GmbH, Gendorf, Germany) as well as 100 μm peel films (Nünchritz GmbH, Glaubitz, Germany) were used.

The irradiation was carried out with 1.5 MeV electrons up to doses of 4000 kGy. The total dose was applied step-by-step for dose ≥ 100 kGy in order to prevent the heating of the samples. As standard the irradiation was carried out at room temperature (RT) in air. Additionally, PTFE powder was irradiated at about -196 °C realised by cooling with liquid nitrogen [17]. In this case the oxygen content in the ambient atmosphere being reduced by nitrogen evaporating (“air”), compared to RT irradiation experiments in air.

The PTFE films were irradiated with doses from 100 kGy up to 3000 kGy at RT in vacuum, and at 365 and 385 °C (above the melting temperature) in vacuum and in N_2 at atmospheric pressure [18].

The DSC investigations were carried out in Perkin Elmer DSC 2 and DSC 7. The special conditions are given in Table 1. The calibration of the temperature and melting heat were done with In and Pb standards. In each case a cycle with 1st heating–cooling–2nd heating was performed. The temperature of the melting peak maximum T_m will be used for the discussion, because the determination of the onset-temperature becomes increasingly difficult with increasing dose because of the broadening of the peak (see Fig. 2). The thermal lag was determined on melt-crystallised, non-irradiated PTFE TF 2025 using the DSC 7 and amounts to 0.5 K for a change in rate by 10 K/min. This value was found for the melting peak temperature of In also.

The temperature limits T_i and the temperature range for the calculation of the melting heats ΔH_f vary with the irradiation dose. Therefore, the values can be only applied for a qualitative discussion. In Table 1 the thermal properties are listed to characterise the initial state of PTFE types.

It should be noted that the suspension polymer has lower crystallinity, both in the 1st and 2nd heating scan. Using the data from the 2nd heating the

Table 1

Thermal data of as-received PTFE determined in the 1st, 2nd heating, and cooling DSC scan

	ΔH_f (1st), J/g	ΔH_f (2nd), J/g	ΔH_f (1st)/ ΔH_f (2nd)	T_m (1st), K	T_m (2nd), K	ΔT_m , K ^a	$T_{c,o}$, K ^a
TF 2025 ^b	77.1	30	2.57	618	597.5	20.5	591
TF 2025 ^c	78	30.7	2.54	616	598	18	588
TF 1760 ^b	60.6	26.8	2.26	616.8	599.6	17.2	591
TF 1750 ^c	66.9	27.7	2.42	610.4	600.4	10	590

^a $\Delta T_m = T_m$ (1st heating) – T_m (2nd heating), $T_{c,o}$ —extrapolated onset-temperature of crystallisation.^b DSC 7, Pyris Software, ± 20 K/min; –60 up to 360 °C.^c DSC 2, without on-line PC, ± 10 K/min; 100 up to 360 °C.

molecular weight of the suspension polymer should be higher than that of the emulsion polymer. The DSC investigations of the peel films were carried out under the same condition as for TF 1760.

3.2. Determination of the polymerisation degree X_n and its dependence on the irradiation conditions

For the irradiated PTFE powders and the PTFE films irradiated at RT the polymerisation degree X_n was determined from the concentration of the end

chain scission is reduced at low irradiation temperature because the macroradical mobility and the oxygen content are lower.

The PTFE film irradiated in the melt is completely in the amorphous, liquid state and in this way the efficiency of the irradiation should be high. The high temperature permits additional reactions of the macroradicals resulting in branching and crosslinking. In this case, the polymerisation degree of network chains $X_{n,cross}$ averaged can be calculated from the NMR results [16,20] (Fig. 1b) using

$$X_{n,cross} = \frac{2}{[\text{CF}_3 \text{ end group}]/[\text{CF}_2] + 2[\text{CF}_3 \text{ side group}]/[\text{CF}_2] + 3[\text{CF}]^*/[\text{CF}_2]} \quad (7)$$

groups determined by ¹⁹F NMR (–CF₃ groups) and IR spectroscopy (–COF, –COOH, –CF=CF₂ groups) [19]

$$X_n = \frac{2}{[\text{end groups}]/[\text{CF}_2]} \quad (5)$$

The end group analysis was done for samples irradiated with doses ≥ 100 kGy. The dependence of the irradiation dose on polymerisation degree is shown in Fig. 1a. For doses ≥ 100 kGy the dependence can be described by

$$X_n = X_n(1 \text{ kGy}) \times (\text{dose})^{-1} \quad (6)$$

with dose in kGy. $X_n(1 \text{ kGy})$ is the polymerisation degree at 1 kGy, a characteristic value mainly determined by the irradiation conditions.

The comparison of the results obtained for film and powder shows that the oxygen content of the atmosphere is the main factor lowering X_n . As expected, the

with $[\text{CF}]^* = [\text{CF}] - [\text{CF}_3 \text{ side group}]$. $X_{n,cross}$ characterises the radiation-crosslinked PTFE and is the averaged number of repeat units (–CF₂–) between two branching points (>CF-) and between branching points and –CF₃ end groups as well as –CF₃ side groups.

4. Results

4.1. Irradiation of PTFE powders at RT and low temperature

For the samples of TF 1760 irradiated at RT in air the DSC scans are shown in Fig. 2. In case of the non-irradiated material the 2nd heating shows a strongly reduced melting peak as a result of a strong hindrance of the crystallisation kinetics due to the high molecular weight.

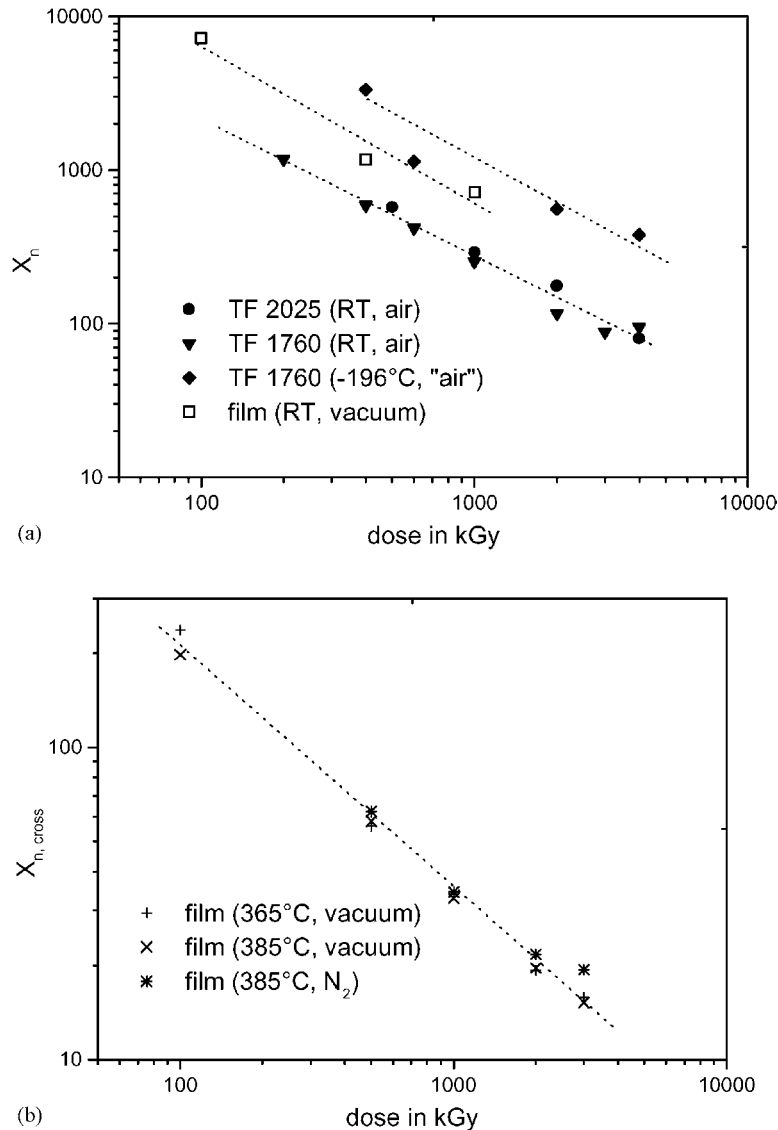


Fig. 1. (a) Polymerisation degree X_n of PTFE irradiated under various conditions versus dose. (b) Polymerisation degree of network chains $X_{n,cross}$ of PTFE film irradiated in the melt versus dose.

At ≥ 1000 kGy the shape of the melting peaks, the melting temperature, and the melting heat of the 2nd heating are similar to that observed in the 1st heating. For doses above 1000 kGy the melting heat is nearly constant, however, the melting peak shifts to lower temperatures and becomes broader. The irradiation results in a statistical chain scission. In this way an increasing M_n distribution by a decrease of the averaged molecular weight with increasing dose is

expected. The broad M_n distribution results in the observed broad melting peak.

4.1.1. The melting temperature

The melting temperature determined for the PTFE powders irradiated at RT and -196 °C are plotted in Fig. 3a versus dose. With increasing dose up to about 100 kGy the melting temperature T_m determined in the 1st heating decreases by 7 K, whereas T_m determined

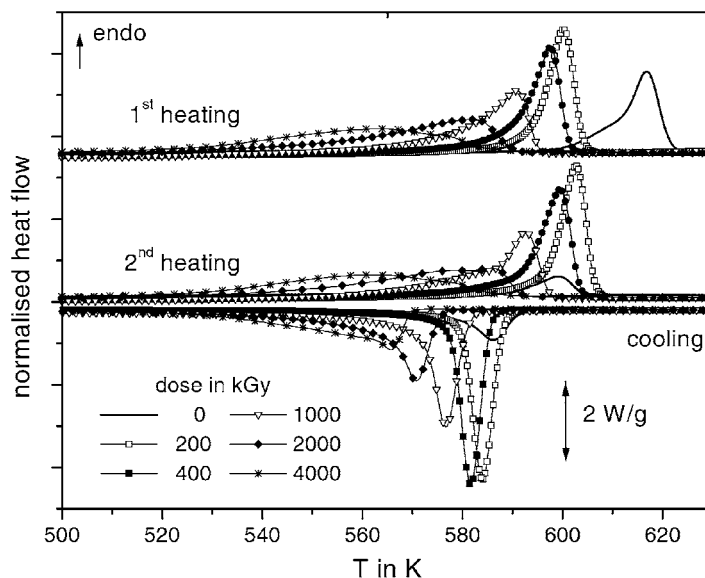


Fig. 2. Heat flow versus temperature of the 1st, 2nd heating and for the cooling scan for TF 1760 with the dose as parameter (scanning rate = ± 20 K/min).

in the 2nd heating slightly increases. The increase observed in the 2nd heating is caused by the crystallinity increasing by a factor 2 with decreasing molecular weight (see Fig. 4). The temperature difference ΔT_m between the melting temperatures of the 1st and 2nd heating is plotted versus dose in Fig. 3b for PTFE powder TF 1750 and TF 2025 irradiated in air at RT from 1 kGy up to 1000 kGy. ΔT_m decreases with increasing dose and becomes about 0 in the range from 50 to 200 kGy. With further increasing dose a stronger decrease of the melting temperatures which are about the same in both heating scans are observed (Fig. 3a) with an almost constant rate of about 1 K/100 kGy.

4.1.2. The melting heat

The melting heats determined in the 1st and 2nd heating scan are shown in Fig. 4 versus dose. Up to dose of about 100 kGy the changes of ΔH_f (1st heating) are small, whereas ΔH_f (2nd heating) increases from about 30 J/g for the initial state to the maximal value of about 70 J/g. For further increasing dose the melting range becomes very broad and the determination of the value will be more and more uncertain. Therefore, in the limit of the uncertainty no tendency of a changed melting heat can be derived from the experimental results.

4.2. Irradiation of PTFE films at RT and in the melt in oxygen free atmosphere

The PTFE film is a sintered PTFE crystallised from the melt. Therefore, no remarkable changes in the behaviour of the 1st and 2nd heating scans are expected. The difference between the melting temperature and melting heat determined in the 1st and 2nd heating are small and become negligible for doses ≥ 100 kGy.

In Figs. 5 and 6 the values of T_m and ΔH_f determined in the 2nd heating are plotted versus dose. For comparison, the results of the powder TF 1760 irradiated at RT in air up to 4000 kGy are shown. The melting temperature and the melting heat of the films irradiated in the melt decrease strongly. As already discussed, the irradiation in the melt state results in branching and crosslinking. In this way, the crystallisation kinetics will be hindered and the crystallinity realised during the cooling scan decreased strongly.

5. Discussion

The analysis of the thermal properties depending on the polymerisation degree X_n was carried out in a

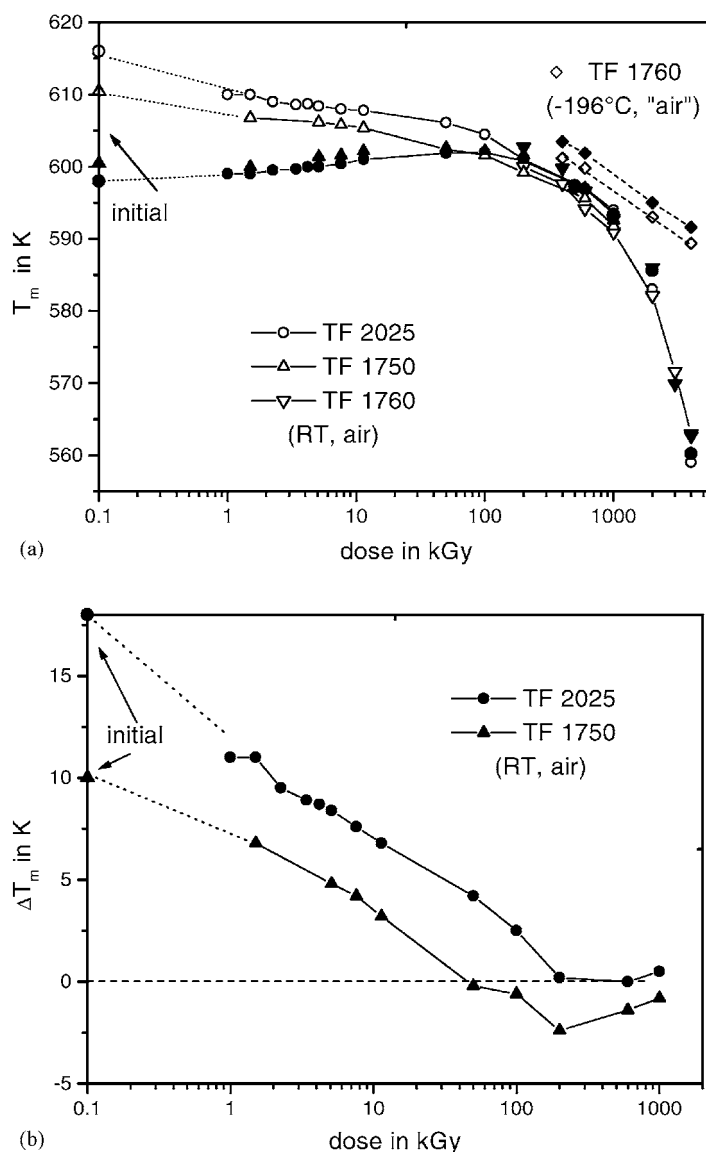


Fig. 3. (a) Melting temperature T_m versus dose of PTFE powder irradiated under various conditions (open symbols—1st heating, closed symbol—2nd heating). (b) Temperature difference $\Delta T_m = T_m$ (1st heating) – T_m (2nd heating) versus dose of PTFE powder irradiated at RT in air (heating rate = 10 K/min).

limited range of X_n because data of the polymerisation degree exist only for samples with dose ≥ 100 kGy. At these doses the thermal properties of the 1st and 2nd heating scans do not show remarkable differences. Therefore, the results of the 2nd heating were used for the analysis. Additionally, the data of the 2nd heating have the advantage that the different thermal prehistory of the synthesis and also by the irradiation was

eliminated by the melt crystallisation in the DSC, and the effect of the superheating on the melting temperature [3,8,27] does not play a role.

Firstly, we used the type of Eq. (2) rewritten in a first approximation as

$$T_m \approx T_m^\circ 1 - A/X_n \quad (2a)$$

with A a adjustable parameter.

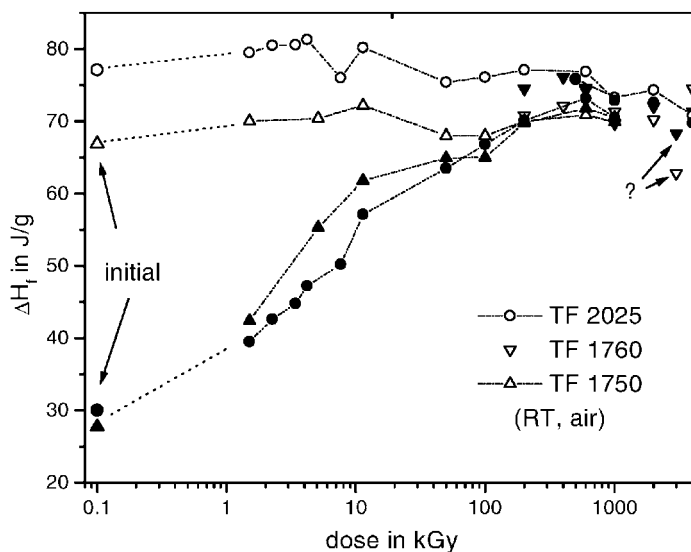


Fig. 4. Melting heat ΔH_f versus dose of PTFE powder irradiated at RT in air (open symbols—1st heating, closed symbols—2nd heating).

T_m (2nd heating) is plotted versus the reciprocal value of the polymerisation degree in Fig. 7 for all samples irradiated at RT and -196°C . Taking into account the higher uncertainty of the polymerisation degree of PTFE in comparison to those of alkanes and PE the quality of the mathematical fit is acceptable. T_m° was obtained as $604 \pm 1\text{ K}$.

Secondly, T_m (2nd heating) is represented versus $\ln(X_n)/X_n$ (Fig. 8) corresponding to Eqs. (3) and (4). T_m° amounts to $606 \pm 1\text{ K}$. The slope obtained is equal to $RT_m^\circ/\Delta H_f^\circ$. That means that the PTFE behaviour is very well described by Eq. (3) if the second term of Eq. (3) is neglected. The conclusion is that the unpairing entropy contribution introduced from Flory and

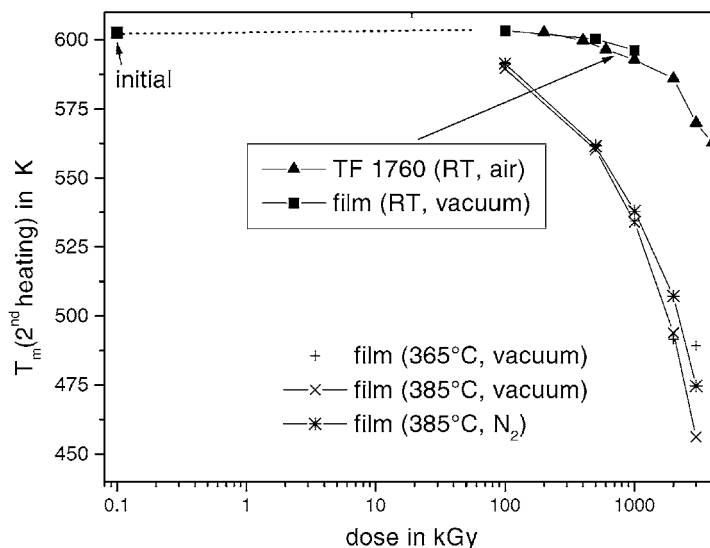


Fig. 5. Melting temperature T_m (2nd heating) versus dose of PTFE film, for the comparison: powder TF 1760 irradiated at RT in air.

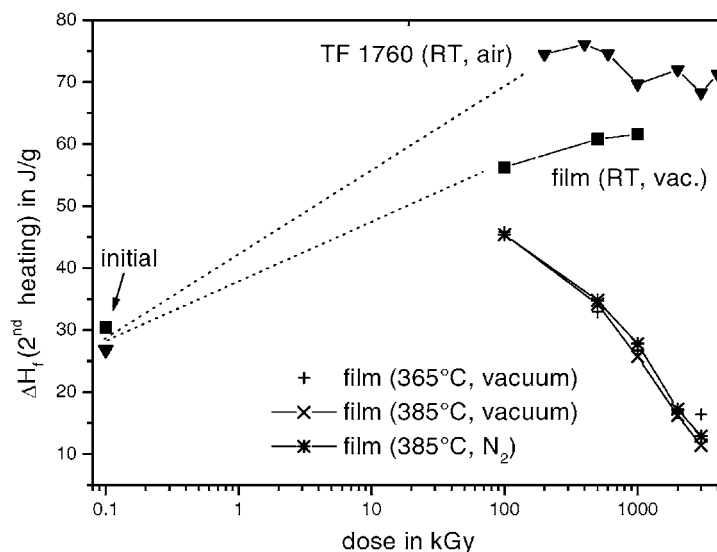


Fig. 6. Melting heat ΔH_f (2nd heating) versus dose of PTFE film irradiated under various conditions, for the comparison: powder TF 1760 irradiated at RT in air.

Vrij [24] is important for the influence of the polymerisation degree on T_m (2nd heating) in a broad range of polymerisation degree from 80 up to 7000 for PTFE.

For the discussion of the result for T_m° the thermal lag (see experimental part) has been corrected. In the literature the following data of T_m° are given: $T_m^\circ = 605$ K [3,8,28] for the as-polymerised state with

extended-chain crystals and $T_m^\circ = 596$ K for the melt-crystallised state with folded-chain crystals [8]. For the non-irradiated PTFE TF 2025 with high molecular weight ($X_n \approx 10^5$) the zero heating rate value of T_m (2nd heating) amounts to 596 K (Table 1) which is in good agreement with the literature value for the folded-chain crystals [8]. The melting temperature

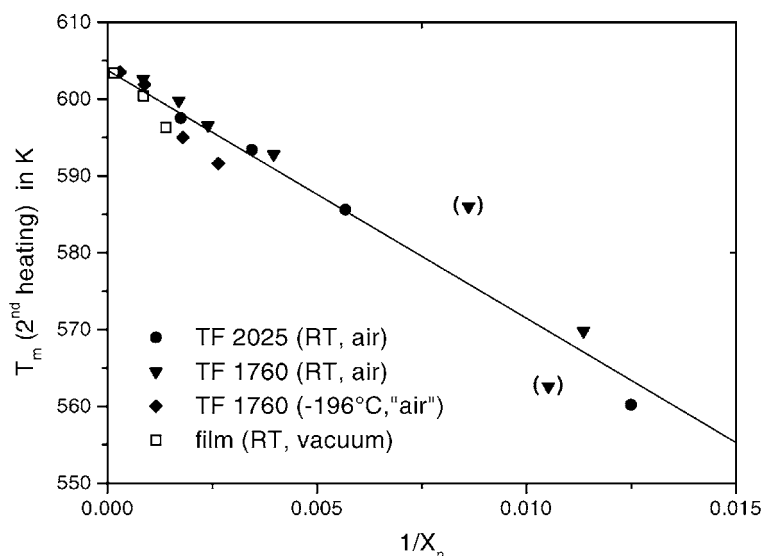


Fig. 7. Melting temperature T_m (2nd heating) versus $1/X_n$ solid line: fit, regression coefficient = 0.988.

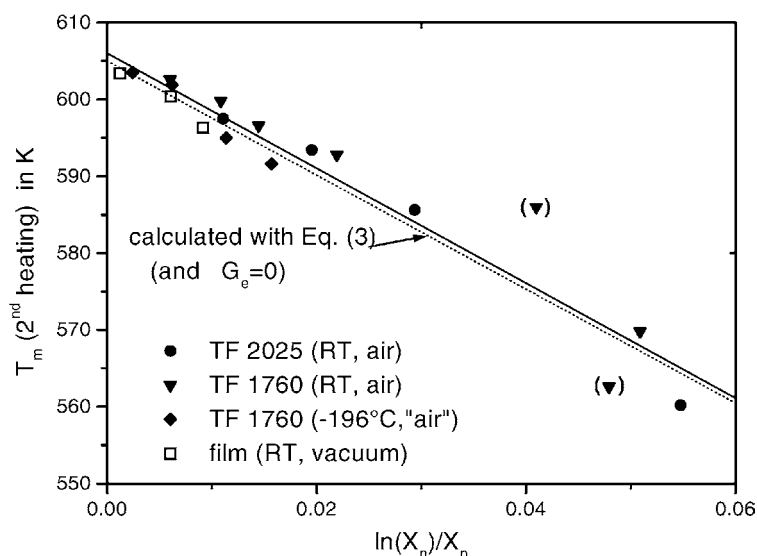


Fig. 8. Melting temperature T_m (2nd heating) in dependence on $\ln(X_n)/X_n$ solid line: fit, regression coefficient = 0.982, dashed line—calculated using Eq. (3).

obtained in the 1st heating scan of the non-irradiated PTFE lies at 616 K, caused by the superheating effect.

It is remarkable that the zero heating rate value T_m° of the fit of the melting temperature in the melt-crystallised state amounts to 605 ± 1 K. That means that extended-chain crystals, the favoured type in the as-polymerised state, exist in the melt-crystallised state.

In Fig. 3a it was shown that the differences between the 1st and 2nd heating vanish for doses above 100 kGy. The averaged polymerisation degree $X_{n,cr}$ of PTFE irradiated at RT in air with doses 100–200 kGy is in the range of 2000 up to 1200 (Fig. 1a). From Fig. 8 we can conclude that PTFE samples with $X_n < X_{n,cr} \approx 1600 \pm 400$ have extended-chain crystals in the melt-crystallised state as in the as-polymerised state.

The most important experimental results are summarised below:

- (i) PTFE with a polymerisation degree $X_n \leq X_{n,cr} \approx 1600$ has about the same thermal behaviour in the 1st and 2nd heating.
- (ii) The fit T_m (2nd heating) = $f(\ln(X_n)/X_n)$ yields $T_m^\circ = 605$ K. This value agrees with the value given in the literature for the extended-chain crystals.

- (iii) PTFE with $X_n \leq X_{n,cr}$ crystallised always as extended-chain crystals independent of the thermal history.

On the other hand we can conclude that PTFE with $X_n > X_{n,cr}$ melt crystallises as folded-chain crystals. This conclusion permits an estimation of the lamellar thickness l_c of the folded-chain crystals. The minimum folded-chain crystal consists of an once folded chain. The lamellar thickness l_c was estimated as

$$l_c = a^* X_{n,cr} / 2 \quad (8)$$

with $a = 0.129$ nm as distance of the CF_2 unit in the helix axis direction [29]. l_c was obtained as about 100 nm for a value of $X_{n,cr} = 1600$. This value is in the same order of magnitude found by Ferry et al. [12] for melt-crystallised, high molecular weight PTFE.

An analogous analysis of the melting temperatures of the alkane/PE using the data from the literature (extended-chain crystals = as-polymerised [21], melt-crystallised = folded-chain crystals [22]) yields a value of $X_{n,cr}$ of about 180 for PE. With Eq. (8) and $a = 0.127$ nm for the distance in the zigzag direction [26] the lamellar thickness l_c was estimated as about 11 nm. Experimental values [26] are similar to the estimated one.

We note that the crystal size of melt-crystallised PTFE characterised by the lamellar thickness is about 10 times higher than in PE. Further differences between PE and PTFE were found fitting of the PE melting temperatures in dependence on $\ln(X)/X$ (analogous to Fig. 8). Hay [25] used experimental data for alkane with $X < 500$ and obtained that the mixing entropy term of the end groups according to Eq. (4) is the most relevant contribution for low molecular weight PE, in contrast to PTFE.

The different results for PE and PTFE in some thermal and morphological properties show that the simple polymer with a similar repeat unit is not adequate to expect a similar behaviour. One reason of the differences between the properties of PTFE and PE could be the various van der Waals radii of hydrogen and fluorine. The van der Waals radius of fluorine is higher than that of hydrogen and does not permit the simple zigzag order of PE. A helical order was observed [29]. This helical order of PTFE is connected with a higher stiffness in comparison to the zigzag order of PE, which could cause the different behaviour.

Note that the PTFE irradiated in the melt was branched and crosslinked. The values $X_{n,\text{cross}}$ characterise the crosslinked state (Fig. 1b). We have checked T_m (2nd heating) of the crosslinked PTFE in the representation as function of $1/X_i$. An increasing

difference between this data and the fit for X_n was found for decreasing $X_{n,\text{cross}}$. The representation in the plot T_m (2nd heating) as function of $\ln(X_i)/X_i$ (Fig. 9) shows a surprising result. The data of crosslinked PTFE agree more or less with the extrapolated fit of the PTFE data obtained by irradiation at RT. That means that the crystals formed in the crosslinked state show a behaviour similar to the extended-chain crystals, although the crosslinking results in a strongly reduced crystallinity (see Figs. 6 and 10).

In Fig. 10 the melting heat ΔH_f (2nd heating) is represented as function of $\ln(X_i)/X_i$. The polymerisation degree X_n of PTFE samples discussed in this paper is low and the crystallisation is hardly hindered. In this way, the polymerisation degree X_n has not remarkable influence on the crystallinity. We note that Suwa et al. [9,11] and Weigel and Garske [13] (Eqs. (1) and (1a)) investigated PTFE with high polymerisation degree, at which the melt-crystallisation is hindered by the long molecular chains.

Remarkable is the influence of the oxygen content on the melting heat, observable by the comparison of the samples irradiated at RT in air (PTFE powder) and in vacuum (PTFE film). The thermal properties are compared for the same polymerisation degree determined by taking into account the different end groups by different oxygen content. The melting temperature is almost the same (Fig. 9), that means that T_m is

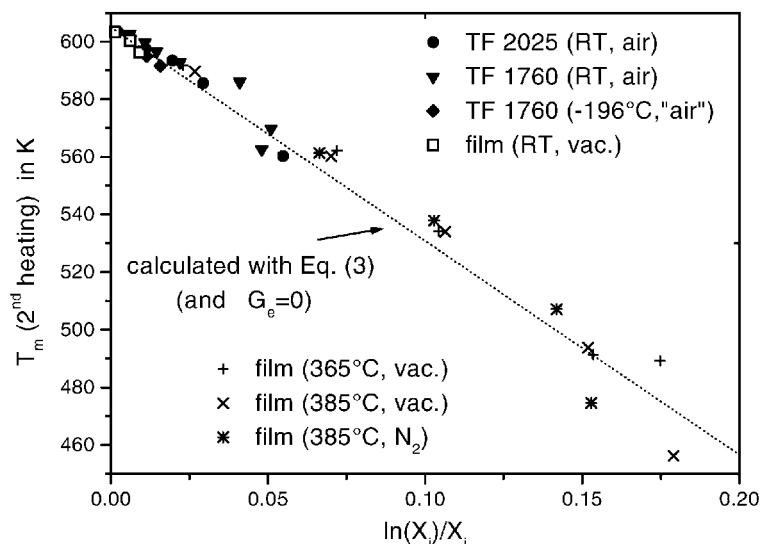


Fig. 9. Melting temperature T_m (2nd heating) versus $\ln(X_i)/X_i$ with $X_i = X_n$ and $X_{n,\text{cross}}$, respectively, dashed line—calculated using Eq. (3).

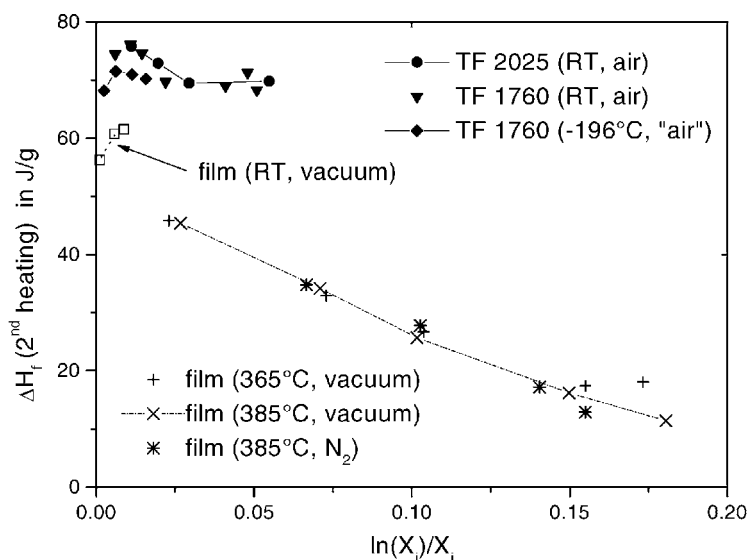


Fig. 10. Melting heat ΔH_f (2nd heating) versus $\ln(X_i)/X_i$ with $X_i = X_n$ and $X_{n,cr}$, respectively.

mainly determined by X_n . On the other hand, the melting heat is lower after irradiation in vacuum than in air. The crystallisation behaviour shows that the width of the crystallisation peak is about the same, and so the crystallisation rate also. However, the crystallisation temperature decreases greatly at irradiation in vacuum than in air. The analysis of the chemical structure shows that only the films irradiated at RT in vacuum show internal double bonds ($-\text{CF}=\text{CF}-$) identified by IR spectroscopy [30] additionally to the end groups used for the calculation of X_n . We assume that these intersegmental structures hinder the crystallisation resulting in lower values of the melting heat.

The melting heat of the crosslinked PTFE shown in Fig. 10 as well is lower in comparison to the non-crosslinked state and the decrease progresses with increasing crosslinking.

6. Conclusion

The analysis of the thermal behaviour of irradiated PTFE depending on the polymerisation degree permits the following conclusions:

- The plot of the experimental values of the melting temperature determined in the 2nd heating shows a

good agreement with the theory of Flory and Vrij [24], introducing the unpairing entropy contribution for the melting process. The equilibrium melting temperature T_m° was found as 605 K, given in the literature [3,8] for the extended-chain crystals.

- The PTFE chains form mainly extended-chain crystals for $X_n \leq X_{n,cr} \approx 1600$, both in the as-polymerised and the melt-crystallised state.
- The lamellar thickness l_c of the folded-chain crystals formed mainly for $X_n > X_{n,cr} \approx 1600$ was estimated as about 100 nm, a value similar to that one found by Ferry et al. [12] for melt-crystallised, high molecular weight PTFE.
- The crystal size of melt-crystallised PTFE characterised by the lamellar thickness is about 10 times higher than in PE. One reason of this difference could be that the van der Waals radius of fluorine is higher than that of hydrogen, and so the crystalline PTFE has a helical order [29] instead the zigzag order of PE.
- The irradiation of PTFE in the melt results in crosslinking and branching. It is surprising that the melting temperature of the crosslinked PTFE more or less agrees with the extrapolated fit of data from the non-crosslinked PTFE. That means that also in crosslinked PTFE extended chain crystals are formed.

Acknowledgements

We thank U. Geißler and K. Schierholz for the preparation of the radiation-degraded and radiation-crosslinked PTFE. The authors express their thanks to B. Fuchs and U. Scheler for the NMR studies, and G.W.H. Höhne for the helpful discussion.

References

- [1] J. Brandrup, E.H. Immergut (Eds.), Polymer Handbook, 3rd Edition, Wiley, New York, 1989.
- [2] C.A. Sperati, H.W. Starkweather, Adv. Polym. 2 (1961) 465.
- [3] S.F. Lau, H. Suzuki, B. Wunderlich, J. Polym. Sci., Polym. Phys. 22 (1984) 379.
- [4] K.L. Berry, J.H. Peterson, J. Am. Chem. Soc. 73 (1951) 5195.
- [5] R.C. Doban, A.C. Knight, J.H. Peterson, C.A. Sperati, The Molecular Weight of Polytetrafluoroethylene, in: Proceedings of the Meeting of the American Chemical Society, Atlantic City, September 1956.
- [6] C.A. Sperati, H.W. Starkweather Jr., Fortschr. Hochpolym.-Forsch. 2 (1961) 465.
- [7] B. Wunderlich, Macromolecular Physics, Vol. 2, Crystal, Nucleation, Growth, Annealing, Academic Press, New York, 1976.
- [8] H.W. Starkweather Jr., J. Polym. Sci., Polym. Phys. 23 (1985) 1177.
- [9] T. Suwa, T. Seguchi, M. Takehisa, S. Machi, J. Polym. Sci., Polym. Phys. 13 (1975) 2183.
- [10] H.W. Starkweather Jr., P. Zoller, G.A. Jones, A.J. Vega, J. Polym. Sci., Polym. Phys. 20 (1982) 751.
- [11] T. Suwa, M. Takehisa, S. Machi, J. Appl. Polym. Sci. 17 (1973) 3253.
- [12] L. Ferry, G. Vigier, R. Vassoille, J.L. Bessede, Acta Polym. 46 (1995) 300.
- [13] P. Weigel, B. Garske, Faserforschung und Textiltechnik 29 (1978) 211.
- [14] L.A. Wall, R.E. Florin, J. Appl. Polym. Sci. 2 (1959) 251.
- [15] A. Nishioka, K. Matsumae, M. Watanabe, M. Tajima, M. Owaki, J. Appl. Polym. Sci. 2 (1959) 114.
- [16] B. Fuchs, U. Scheler, Macromolecules 33 (2000) 120.
- [17] K. Schierholz, U. Lappan, K. Lunkwitz, Nucl. Instrum. Meth. Phys. Res. B 151 (1999) 232.
- [18] U. Lappan, U. Geißler, K. Lunkwitz, Radiat. Phys. Chem. 59 (2000) 317.
- [19] U. Lappan, B. Fuchs, U. Geißler, U. Scheler, K. Lunkwitz, Polymer, accepted.
- [20] B. Fuchs, U. Lappan, K. Lunkwitz, U. Scheler, Macromolecules, submitted for publication.
- [21] B. Wunderlich, G. Czornyj, Macromolecules 10 (1977) 906.
- [22] V.B.F. Mathot, Calorimetry and Thermal Analysis of Polymers, Crystallization and Melting Region, Hanser, Munich, 1994, 234 pp. (Chapter 9).
- [23] M.L. Huggins, J. Phys. Chem. 43 (1939) 1083.
- [24] P.J. Flory, A. Vrij, J. Am. Chem. Soc. 85 (1963) 3548.
- [25] J.N. Hay, J. Polym. Sci., Polym. Chem. 14 (1976) 2845.
- [26] G.W.H. Höhne, Polymer, accepted.
- [27] E. Hellmuth, B. Wunderlich, J.M. Rankin, Appl. Polym. Symp. 2 (1966) 101.
- [28] B. Wunderlich, ATHAS data bank.
- [29] C.W. Bunn, E.R. Howells, Nature 4429 (1954) 549.
- [30] U. Lappan, U. Geißler, K. Lunkwitz, J. Appl. Polym. Sci. 74 (1999) 1571.