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Number-average molecular weight of radiation-degraded poly(tetrafluoroethylene). An end group analysis based on solid-state NMR and IR spectroscopy

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Abstract

Changes in the chemical structure of poly(tetrafluoroethylene) (PTFE) induced by electron beam irradiation at room temperature in air have been studied by ^{19}F solid-state NMR and IR spectroscopy. Chain scission associated with the formation of trifluoromethyl ($-CF_3$), carboxylic acid fluoride (−COF) and carboxylic acid (−COOH) end groups was confirmed to be the predominant process under these conditions. The number-average molecular weight of radiation-degraded PTFE as a function of irradiation dose was calculated based on quantitative end group analysis. It strongly decreases with increasing dose to approximately 4000 g/mol at a irradiation dose of 4 MGy. The molar ratio of CF_3 end groups to oxygen-containing (−COF, −COOH) end groups was found to depend on the irradiation dose and the irradiation conditions. For low dose level, the molar ratio determined experimentally coincides well with the mechanism proposed for radiation-induced degradation of PTFE.

Keywords: Poly(tetrafluoroethylene); Irradiation; End groups

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1. Introduction

High-energy radiation affects the properties of polymers by chain scission and cross-linking reactions. Both types of reaction occur simultaneously. However, one process will usually predominate, depending on the chemical structure of the polymer and the irradiation conditions such as temperature, atmosphere and dose rate [1].

Poly(tetrafluoroethylene) (PTFE) is well known for its excellent chemical resistance. But on the other hand, it is very sensitive to high-energy radiation. PTFE predominantly undergoes chain scission, if the irradiation is performed at room temperature in air or vacuum. The result is a dramatic drop in mechanical properties [2]. However, this shortcoming is exploited converting PTFE into low molecular weight micropowders. These micropowders are compounded into plastics, coatings and lubricants [3]. The use of PTFE micropowders functionalized with COOH groups as additive in polyamides to improve the sliding properties of the materials has been studied in collaboration [4]. During the compounding process in a twin screw extruder the COOH groups of the irradiated PTFE react with the polyamides, subsequently amide bonds are formed. For these studies, it became necessary to investigate the concentration of COOH end groups and the number-average molecular weight of PTFE in dependence of the irradiation dose and the irradiation conditions.

This paper reports on the characterization of PTFE irradiated at room temperature in air using ^{19}F solid-state NMR and IR spectroscopy. Because PTFE is insoluble in common solvents, it was inevitable to perform the analysis on solid samples. In previous solid-state NMR investigations [5,6] it was shown that high-speed MAS ^{19}F NMR provides detailed and quantitative information on structural changes occurring in PTFE as a result of high-energy electron irradiation. The NMR and IR data were used to calculate number-average molecular weight of irradiated PTFE.

2. Experimental

Material. Poly(tetrafluoroethylene) fine powder (Dyneon™ TF 2025) was used as received.

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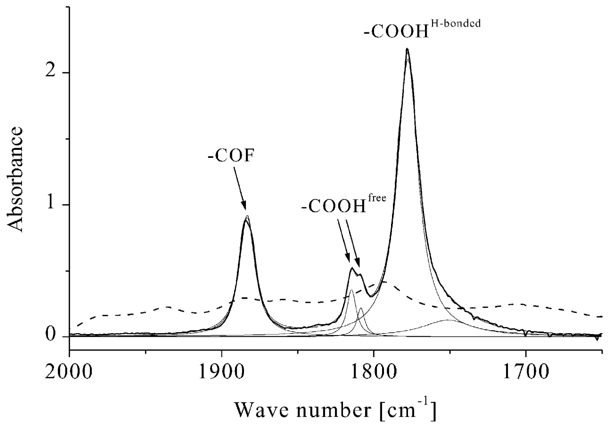

Fig. 1. IR difference spectrum of PTFE irradiated with a dose of 4 MGy (50 kGy/pass) at room temperature in air and non-irradiated PTFE; fitting with five lorentzian peaks in the region of 2000–1650 cm^{-1} (dashed line: spectrum of non-irradiated PTFE).

Irradiation. The PTFE powder was irradiated at room temperature in air at atmospheric pressure with 1.5 MeV electrons using an electron beam accelerator (ELV-2, Budker Institute of Nuclear Physics, Novosibirsk, Russia) described in detail in Ref. [7]. A sample transport system was used, which ensured an irradiation on a step-by-step basis with a dose of 25, 50 and 100 kGy/pass, respectively. The doses of 25 and 50 kGy/pass were applied in a quarter and a half of the time needed for the dose of 100 kGy, respectively. Therefore, the total irradiation time for a dose value was constant in all series.

FTIR. The IR spectra were recorded using Bio-Rad FTS-155 spectrometer (transmission mode, 32 scans, 2 cm^{-1} resolution). Powders were pressed into films at room temperature. The molar ratios of COF, $COOH^{free}$ and $COOH^{H\text{-bonded}}$ end groups to CF_2 units were calculated according to Eq. (1) using the IR absorbance A and calibration factor CF from literature [8]. The thickness d of the PTFE films pressed was measured using a micrometer calliper.

$$[\text{end group}]/[\mathrm{CF_2}] = A \times \mathrm{CF}/d/10^6 \qquad (1)$$

^{19}F NMR. The NMR experiments were performed on a modified Bruker AMX-300 spectrometer operating at a resonance frequency of 282 MHz for fluorine-19. A proton–fluorine CRAMPS probe BL 2.5 accepting MAS 2.5 mm outer diameter rotors permitting sample rotation frequencies up to 35 kHz was used. All NMR experiments were performed at ambient temperature. Frictional heating from the bearing in the MAS system causes the sample temperature to be approximately 30 K above room temperature. Spectra used for quantification were acquired using single pulse excitation at a MAS spinning frequency of 32 kHz with an $\pi/2$ pulse duration of 3 μs, accumulating between 128 and 1024 repetitions for each spectrum depending on the relative content of minor structures. The longitudinal relaxation time (T_1) has been checked for all samples prior to the acquisition of the spectra. T_1 varies between 0.6 and 1.2 s, so the repetition times were adjusted to 10 s. The ^{19}F chemical shifts reported herein are relative to $CFCl_3$, setting the $-CF_2-C\mathit{F}_2-CF_2-$ signal of PTFE to − 122 ppm.

3. Results and discussion

IR and ^{19}F solid-state NMR spectroscopy were used for the study of end groups formed in consequence of radiation-induced main-chain scission in PTFE. IR spectroscopy is known to be very sensitive to formation of carbonyl species in perfluorinated polymers because bands of the C=O stretching vibrations are relatively strong and appear in a region of the spectrum where perfluorinated polymers have only weak overtones and combination bands [9]. Fig. 1 shows the difference spectrum of a PTFE sample irradiated at room temperature in air and non-irradiated PTFE. The difference spectrum was fitted with five lorentzian peaks in the region of 2000–1650 cm^{-1}. The bands are assigned to COF (1883 cm^{-1}), $COOH^{free}$ (1815 and 1809 cm^{-1}) and $COOH^{H\text{-bonded}}$ end groups (1777 cm^{-1}) as it is known from literature [8,10–13] with the exception of the band splitting in the case of the $COOH^{free}$ end group. Usually, the $COOH^{free}$ band is reported to appear at 1812 [8,10] and 1810 cm^{-1} [13], respectively. However, the best fitting resulted in bands at 1815 and 1809 cm^{-1} in all spectra processed. The splitting indicates that $COOH^{free}$ groups in different environments exist. The weak and broad band centred at approximately 1750 cm^{-1} in the difference spectrum cannot be assigned to a chemical structure such as carbonyl groups and double bonds. It is assumed to result from slight differences in the feature of overlapping overtones and combination bands between irradiated and non-irradiated PTFE caused by changes in morphology.

^{19}F solid-state NMR was used to detect further end groups expected to be formed by irradiation. The spectrum of non-irradiated PTFE is dominated by a strong signal at − 122 ppm assigned to the $-CF_2-C\mathit{F}_2-CF_2-$ chain structure. This signal is the only one which could be detected in the spectrum of non-irradiated PTFE. Assuming that signals with intensities in the order of 10^{-4} of the intense $-CF_2-C\mathit{F}_2-CF_2-$ signal are detectable, the PTFE measured is concluded to have an unbranched structure and the number-average molecular weight exceeds 10^6 g/mol, which agrees with data in literature [14]. The ^{19}F solid-state NMR spectrum of a PTFE sample irradiated in air is shown in Fig. 2. In order to show weak signals more clearly, the spectrum is vertically stretched by a factor of 20. As expected, trifluoromethyl end groups identified by signals at − 82 ppm ($-CF_2-C\mathit{F}_3$) and − 126 ppm ($-CF_2-C\mathit{F}_2-CF_3$) were formed by irradiation. In addition, further very weak signals appear in the spectrum. Trifluoromethyl side groups like in poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) were identified by signals at − 68 and − 70 ppm ($>CF-C\mathit{F}_3$), − 112 ppm ($-C\mathit{F}_2-CF(CF_3)-C\mathit{F}_2-$) and

Table 1
Calibration factors CF for COF, $COOH^{free}$ and $COOH^{H\text{-bonded}}$ end groups in perfluorinated polymers

Group	Wave number (cm^{-1})	Calibration factor, CF (mm)			
		Ref. [8]	Ref. [15]	Ref. [16]	Ref. [17]
COF	1883	406	432	440	1118
$COOH^{free}$	1812	335	–	–	1045
$COOH^{H\text{-bonded}}$	1773	320	–	–	141

− 184 ppm (>C*F*−). Furthermore, the signal at 23 ppm arise from CO*F* end groups, which have been identified by IR spectroscopy as well.

Taking into account the fluorine multiplicity for each signal in the NMR spectra, the concentration ratio of CF_3 end groups to CF_2 units can be calculated directly. In the case of IR spectroscopy, the situation is more complicated because of different extinction coefficients. In order to determine the COF and COOH end groups, the method based on IR absorbances was calibrated using so-called calibration factors described in the literature [8]. Slightly different calibration factors for COF groups were mentioned in Refs. [15,16]. However, a set of molar extinction coefficients for COF, $COOH^{free}$ and $COOH^{H\text{-bonded}}$ end groups, which is completely different to those calibration factors in Ref. [8], is proposed in Ref. [17]. For comparison, the molar extinction coefficients ε proposed in Ref. [17] were converted into calibration factors CF using Eq. (2)

$$CF = 10^6 M/\varphi_{film}/\varepsilon \qquad (2)$$

with $M = 50$ g/mol and $\varphi_{film} = 2.08$ g/cm^3 determined experimentally. The calibration factors described and calculated, respectively, are summarized in Table 1.

In spite of the differences, calibration factors have not been determined again. Instead of calibrating with model compounds the fact that the COF group can be detected both by IR and ^{19}F NMR spectroscopy was used. Using the IR calibration factor described in Ref. [8], the molar ratio of COF groups determined by IR to COF groups determined by NMR was found to be 1.1 ± 0.1. However, if the extinction coefficient proposed in Ref. [17] is used, the ratio results in 2.9 ± 0.3 indicating that this coefficient is too high. Regarding the calibration factors for the COOH groups, $-CF_2$–COOH signals have not been identified in the NMR spectra because of superimposition with the intense $-CF_2-CF_2-CF_2-$ signal. Therefore, an indirect method was used in order to study the sets of calibration factors described in Refs. [8,17], respectively. This indirect method based on the fact that COF groups in the irradiated PTFE hydrolyse to COOH groups, which can be accelerated by annealing at 200 °C in moist air. Several irradiated PTFE samples were investigated. The comparison of the IR spectra recorded before and after the annealing indicated that COF groups hydrolysed. The IR data were processed using both sets of calibration factors. Results obtained for two irradiated PTFE samples (**I** and **II**) are shown in Fig. 3 for example. Assuming that the total content of carbonyl groups has not been changed by the annealing step, the set of factors described in Ref. [8] has been found to be correct. On the basis of the results the calibration factors described in Ref. [8] were chosen in this paper.

The results of determination of end groups for PTFE irradiated with different doses and three different doses per pass are shown in Fig. 4. The test series with 50 kGy/pass was used for the compounding into polyamides studied [4]. The other two test series with 25 and 100 kGy/pass were performed in a limited dose range in order to investigate the effect of dose per pass on the content of carbonyl groups in

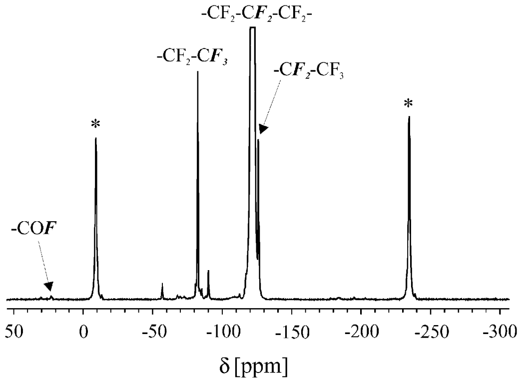

Fig. 2. ^{19}F solid-state NMR spectrum of PTFE irradiated with a dose of 4 MGy (50 kGy/pass) at room temperature in air. Asterisks denote spinning side bands.

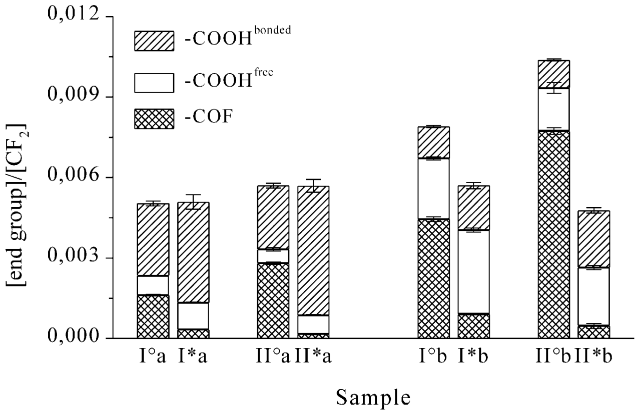

Fig. 3. Molar ratio of carbonyl end groups (COF, $COOH^{free}$ and $COOH^{H\text{-bonded}}$) to CF_2 units in irradiated PTFE samples (**I** and **II**) before (°) and after (*) annealing at 200 °C determined using IR data and calibration factors described in Ref. [8] (a) and in Ref. [17] (b), respectively.

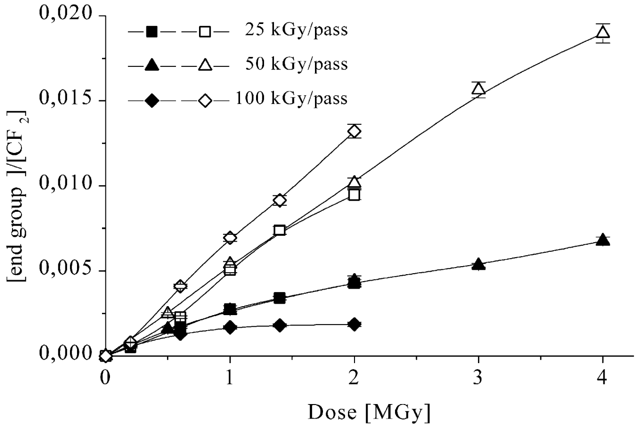

Fig. 4. Molar ratio of CF_3 (open symbols) and carbonyl (closed symbols) end groups to CF_2 units in irradiated PTFE as a function of irradiation dose.

the PTFE micropowder. As expected, the content of both carbonyl and CF_3 end groups increase with increasing dose in all test series. Furthermore, the results of the test series with 25 and 50 kGy/pass are not significantly different. However, in the case of the series with 100 kGy/pass, the content of carbonyl groups is lower and the content of CF_3 end groups is higher compared to others. The lower content of carbonyl end groups is assumed to result from the limited diffusion of oxygen to the radical sites during the higher dose steps.

Based on the content of end groups, the number-averaged molecular weight M_n of irradiated PTFE was calculated. It is plotted as a function of irradiation dose in Fig. 5. Starting with $M_n > 10^6$ g/mol for the non-irradiated PTFE, it strongly decreases with increasing dose to approximately 4×10^3 g/mol at a dose of 4 MGy.

The molar ratio of CF_3 end groups to carbonyl end groups in irradiated PTFE is shown in Fig. 6. The ratio starts at a value of nearly one and increases with increasing dose depending on the irradiation conditions. A difference between the ratio of the test series irradiated with 25 kGy/pass and the ratio of the series irradiated with 50 kGy/pass does not exist as it is expected on the basis of the end group concentrations. However, in the case of the test series irradiated with 100 kGy/pass, the molar ratio increases much stronger than in the case of the other test series. These findings give rise to two questions: which value of molar ratio is expected on the basis of the degradation mechanism point of view? Why does the molar ratio increase with increasing dose?

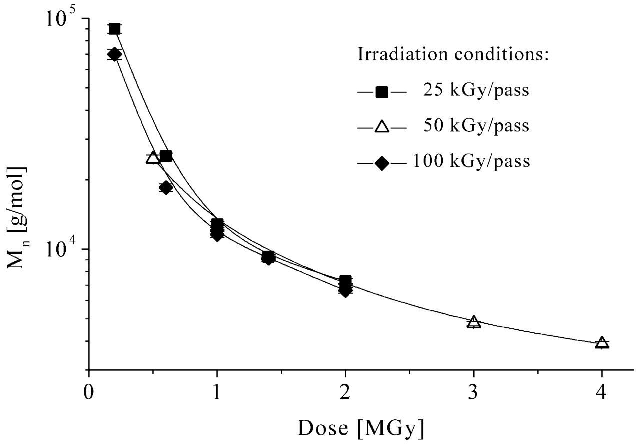

Fig. 5. Number-averaged molecular weight M_n of irradiated PTFE as a function of irradiation dose.

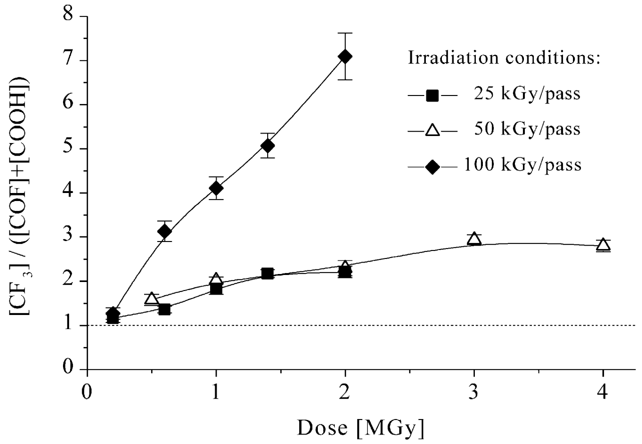

Fig. 6. Molar ratio of CF_3 to carbonyl end groups in irradiated PTFE as a function of irradiation dose.

A mechanism of radiation-induced degradation of PTFE was proposed in Refs. [18,19]. In detail, the degradation of PTFE is characterized by competitive and consecutive reactions. At first mid-chain and end-chain alkyl radicals are formed by C–F and C–C bond scission. These radicals may react with oxygen to peroxy radicals. Mid-chain peroxy radicals are converted into COF end groups and end-chain alkyl radicals by β-scission. The COF end groups partly hydrolyse to COOH end groups by reaction with humidity. End-chain peroxy radicals eliminate COF_2 leaving end-chain alkyl radicals behind, which may react with oxygen again. Assuming this cycle, polymer chains are shortened by COF_2 release. Furthermore, CF_3 end groups are assumed to be formed by reaction of end-chain alkyl radicals and fluorine radicals produced by radiation-induced C–F bond scission. Summarizing the main reactions, apart from COF_2 and peroxy radicals, which partly possess surprising long-term stability at room temperature, COF, COOH and CF_3 end groups are formed inside the irradiated PTFE. Note for the following reflections, that COF groups are formed first. The COOH end groups are result of a consecutive reaction. Looking at the various chemical species and the corresponding fluorine to carbon balance, the F/C ratio is higher (CF_3 group), lower (COF group, mid-chain peroxy radical) and unaltered (COF_2, end-chain radical) compared to the CF_2 repeat unit in PTFE, respectively. The peroxy radicals can be neglected for these reflections because their concentration [20] is considerably lower than the concentration of end groups. Assuming that the main structures formed by irradiation of PTFE were identified, the molar ratio of CF_3 to COF end groups must be equal to one in order to maintain the F/C ratio of two in non-irradiated PTFE after the irradiation in all. This result of the reflections coincides well with the molar ratio determined experimentally for low dose level.

However, the molar ratio of CF_3 groups to carbonyl groups increases with increasing dose. In addition, it depends on the irradiation conditions as described earlier. The following facts are assumed to play an important role. The molar ratio was calculated using NMR and IR data of the solid irradiation product. But, it is well known that volatile compounds are formed by irradiation of PTFE as well [2]. The evolution of volatile irradiation products was experimentally indicated by the mass loss of the PTFE samples during irradiation as it is shown in Fig. 8. The mass loss increases with increasing dose. There is no significant difference between the test series irradiated with 25 and 50 kGy/pass, but in the case of the series irradiated with 100 kGy/pass the mass loss is higher compared to the other ones. This effect is supposed to result from heating up of the PTFE powder during irradiation by absorption of energy. The heating increases with increasing dose per pass. The degradation reactions are assumed to be accelerated by elevated temperature. In this way, large amount of volatile products is formed in the case of 100 kGy/pass. Comparing the results shown in Fig. 6 with the mass loss shown in Fig. 7, the molar ratio of CF_3 groups to carbonyl groups is concluded to be influenced by mass loss among other things.

The experimental set-up used for the irradiation did not allow to investigate the composition of the material evolved during irradiation. Apart from COF_2, low molecular weight homologues containing CF_3, COF and COOH end groups are supposed to escape from the irradiated PTFE [18]. Various perfluorinated homologues such as alkanes, carboxylic acid fluorides, dicarboxylic acid fluorides, carboxylic acids and dicarboxylic acids may be formed because chain scission and end group formation is supposed to be a statistical process. Because that the ratio of CF_3 to COF end groups should be equal to one from the degradation mechanism point of view, the ratio of CF_3 to carbonyl end groups in the volatile compounds averaged must be lower than one in order to compensate for the ratio of CF_3 to carbonyl end groups in the solid material, which is significantly higher than one for high dose level. From this point of view, dicarboxylic acid fluorides and dicarboxylic acids are supposed to evolve predominantly. However, an opposite situation results from the hypothesis that the escape of a compound depends on its boiling point in first approximation. The boiling points of the perfluorinated homologues [21–25] are plotted versus number of C atoms as shown in Fig. 8. Among these compounds, the alkane homologues possess the lowest boiling points. Carbonyl end groups should be enriched in the solid material irradiated. But, this conclusion is inconsistent with the experimental results. Therefore, further low molecular weight compounds, which have not been identified, are assumed to play a key role.

4. Conclusions

The solid-state NMR and IR spectroscopic study has provided quantitative data about the well known fact that chain scission is the predominant process induced by electron beam irradiation of PTFE at room temperature in air. The decrease in number-average molecular weight of PTFE with increasing dose was directly proved using end group analysis. The molar ratio of CF_3 end groups to carbonyl end groups was found to depend on the irradiation dose and the conditions too. For low dose level, the molar ratio determined experimentally coincides well with the mechanism proposed for radiation-induced degradation of PTFE.

With respect to the use of PTFE micropowders as additive in polyamides, the irradiation process carried out with 50 kGy/pass was found the optimal one. It results in a high molar ratio of reactive COOH end groups to inert CF_3 end groups, which is assumed to be favourable for the properties of the PTFE polyamide compounds.

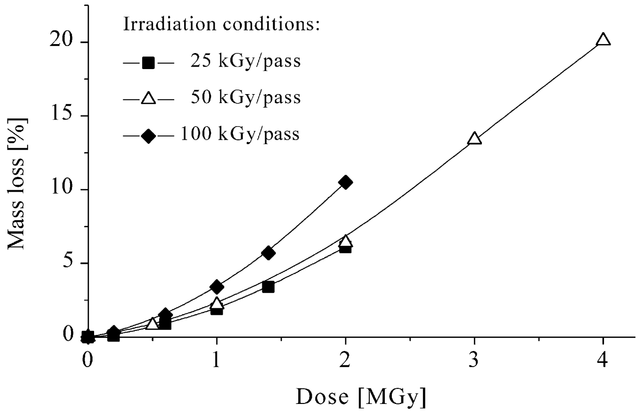

Fig. 7. Mass loss of PTFE induced by irradiation as a function of irradiation dose.

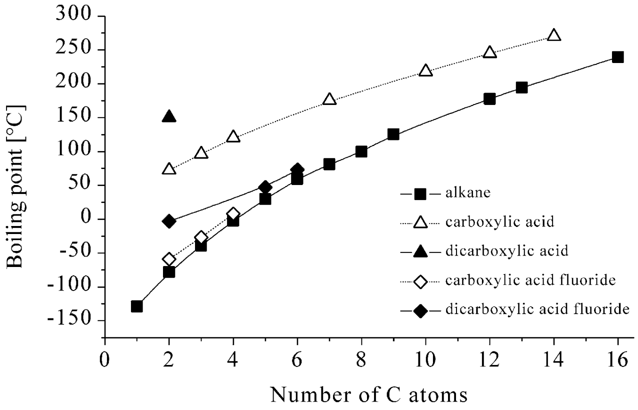

Fig. 8. Boiling point of perfluorinated compounds as a function of number of C atoms.

Acknowledgments

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