Branching and Cross-Linking in Radiation-Modified Poly(tetrafluoroethylene): A Solid-State NMR Investigation

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ABSTRACT: Fluoropolymers exhibit a number of favorable properties such as high-temperature stability, chemical resistivity, and a low surface energy. However, the possibility to incorporate fluoropolymers into other materials is limited because of the low surface energy. Modification procedures such as radiation modification can be applied to overcome these difficulties. High-resolution fluorine-19 solid-state NMR using high-speed magic-angle sample spinning has been applied to investigate the structural changes resulting from irradiation of poly(tetrafluoroethylene) (PTFE) with high-energy electrons under vacuum. PTFE irradiated at room temperature mainly shows chain scission. PTFE irradiated at high temperatures, above the melting point, under vacuum, however, contains branches as well as cross-links. Evidence for cross-links in this material is derived from structural information. A quantitative analysis of the data is used to establish the density of side groups and branches. The excess of branches to end groups is interpreted as cross-links.

Introduction

Fluoropolymers exhibit a number of favorable and unique properties such as high-temperature stability, chemical resistivity, and a low surface energy, resulting in unique surface properties.[1] The low surface energy, however, restricts the possibility to incorporate fluoropolymers into other materials, and the chemical resistivity prohibits bonding of the fluoropolymers onto substrates. In addition to attempts at synthesizing copolymers, various modification procedures are being carried out to increase the compatibility of fluoropolymers with other materials without degrading their favorable properties. Examples are plasma treatment and radiation modification using high-energy electrons.

Radiation treatment on a variety of polymers can induce cross-linking. NMR studies of this radiation-induced cross-linking up to now have been focused on changes in molecular mobility which are manifested in proton relaxation data or wide-line spectra.[2,3] No evidence for cross-links has been found in structural investigations of irradiated poly(ethylene) using ^{13}C CPMAS spectra.[4] In the present work, evidence for the formation of cross-links is derived from structural information obtained from high-resolution solid-state fluorine-19 NMR spectra. Fluorine-19 provides unique possibilities as a probe nucleus for NMR due to its high receptivity and large chemical shift range. A large chemical shift range implies that the Larmor frequency depends strongly on the chemical environment of the nucleus under study and therefore allows a detailed assignment of different molecular structures. To observe high-resolution solid-state ^{19}F NMR spectra, the dipolar coupling between the fluorine nuclei and the anisotropy of the chemical shift have to be averaged out. This is conveniently achieved by high-speed magic-angle sample spinning (MAS). In previous works high-resolution solid-state fluorine-19 NMR has been applied to the characterization of radiation-modified fluoropolymers.[5,6]

Upon irradiation by high-energy electrons, poly(tetrafluoroethylene) (PTFE) is known to exhibit mainly chain scission.[7,8] From indirect methods based on mechanical and thermal properties, a lowered molecular weight has been concluded. Depending on the reaction conditions and atmosphere, additional reactive groups may be formed, which could be utilized for generating bonds between the fluoropolymers and other materials. However, mechanical properties are usually deteriorated as a result of the drastically lowered molecular weight. A way to counteract the degradation of mechanical properties is to introduce cross-links during the modification process. Cross-links would improve the mechanical stability of the polymer. On the other hand, the formation of branches and cross-links counteracts the decrease in molecular weight, as fragments are linked together. This means that the average molecular weight is usually higher in the branched polymer. As demonstrated previously, radiation modification carried out at temperatures above the melting point of PTFE facilitates the formation of branches and cross-links in favor of chain scission.[9] In the present study from a quantitative analysis of high-resolution solid-state fluorine-19 NMR spectra, the molecular weight and the density of branches and cross-links in high-temperature-irradiated PTFE are derived.

Experimental Section

PTFE (500 μm peel film, PTFE Nünchritz GmbH, Glaubitz, Germany) was radiation modified using a linear electron accelerator.[10] To avoid any interaction with gases present during the modification, the irradiation was performed under vacuum. Details about the radiation procedures and the experimental setup including the vacuum device are described elsewhere.[11] For comparison, three types of poly(tetrafluoroethylene-*co*-hexafluoropropylene) (*f*luoro*e*thylene-*p*ropylene, FEP) obtained from Dyneon GmbH, Gendorf, Germany, were used.

The NMR experiments have been performed on a modified Bruker AMX-300 spectrometer operating at a resonance frequency of 282 MHz for fluorine-19. A linear amplifier was used for fluorine excitation. A proton-fluorine CRAMPS probe BL 2.5 accepting MAS 2.5 mm outer diameter rotors permit-

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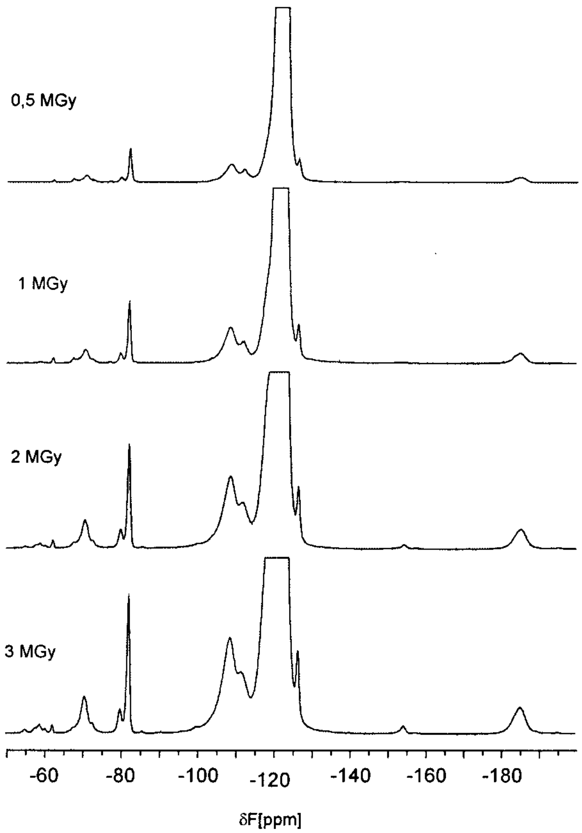

Figure 1. Series of ^{19}F high-speed MAS spectra of high-temperature radiation-modified PTFE using electrons of 1.5 MeV. Irradiation doses as indicated at the traces. All spectra have been vertically amplified by 12.5.

ting sample rotation frequencies up to 35 kHz was used in all experiments. The sample volume is about 12 μL. Other studies have demonstrated that additional sample heating could provide further line narrowing and better resolution.[12,13] To avoid any additional reactions, especially in the samples containing residual radicals as a result of the radiation modification, all experiments have been performed at ambient temperatures. However, frictional heating from the bearing in the MAS system causes the sample temperature to be approximately 30 K above room temperature. As has been shown previously, high-speed MAS with spinning rates in excess of 30 kHz is sufficient to acquire high-resolution ^{19}F solid-state NMR spectra of fluoropolymers and radiation-modified fluoropolymers.[6,14]

All spectra shown here were acquired using single pulse excitation at a MAS spinning frequency of 32 kHz with an $\pi/2$ pulse duration of 3 μs, accumulating 2048 repetitions for each spectrum. For quantitative analysis of the data, the longitudinal relaxation time (T_1) for all samples has been checked prior to the acquisition of the spectra. Depending on the residual concentration of radicals in the samples, T_1 varies between 0.6 and 1.7 s. The repetition times were adjusted respectively to be between 6 and 10 s. The chemical shifts reported herein are relative to $CFCl_3$ referenced externally to the CF_2 signal of PTFE at −122 ppm.

Results

Figure 1 depicts a series of spectra of PTFE irradiated at 365 °C at different radiation doses. All spectra exhibit the same structures. The intensity of the signals other than CF_2 increases with the applied radiation dose. For comparison, room-temperature-irradiated PTFE and various types of nonirradiated FEP have been investigated. Two spectra of these samples are shown in Figure 2. The FEP samples were used as standards to establish a measure for the precision of the quantitative analysis. Concentrations determined spectroscopically are accurate within 5% of their values. The comonomer contents in the FEP samples have been determined to be 25, 11, and 8 mol %.

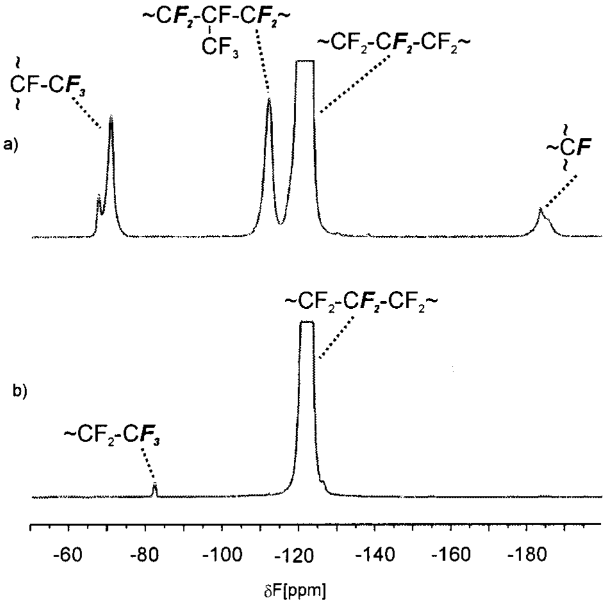

Figure 2. ^{19}F NMR spectra (a) of the FEP sample with a comomomer content of 8% and (b) of PTFE irradiated at room temperature at a radiation dose of 1 MGy. The spectra were acquired under the same experimental conditions as the spectra in Figure 1. In each molecular fragment the fluorine atoms assigned to the resonance are indicated in bold italics.

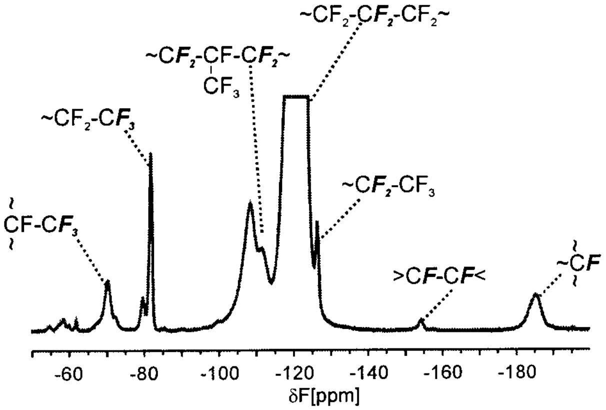

Figure 3. ^{19}F NMR spectrum of the PTFE sample irradiated at 365 °C with a radiation dose of 3 MGy for the illustration of peak assignment. In each molecular fragment the fluorine atoms assigned to the resonance are indicated in bold italics.

Figure 3 shows the ^{19}F spectrum of the PTFE sample irradiated at 365 °C at a radiation dose of 3 MGy with peak assignment. Assignment of signals from the CF_3 side groups and the neighboring CF and CF_2 groups was made comparing with the FEP spectrum shown in Figure 2. Further assignments are made with the help of model compounds and reported ^{19}F chemical shifts.[15,16] The signal at −108 ppm most likely is the signal from the CF_2 groups next to the CF groups at long-chain branches. The relative intensity of this signal for all samples is agreement with this assumption.

While in the FEP only short branches of CF_3 side groups are expected, in the high-temperature radiation-modified fluoropolymers CF_3 side groups and long-chain branches are expected. The spectra reveal signals originating from both types of structures. The side groups can be clearly identified by the chemical shift of the CF$_3$ fluorine appearing at about -72 ppm. The end groups of longer branches cannot be distinguished from the end groups of the polymer main chain. The signal of CF$_3$ groups bonded to CF$_2$ results in a chemical shift of -82 ppm. The high-temperature-irradiated samples contain both CF$_3$ side groups and side chains terminated by CF$_3$ groups.

If the recycle time in a single-pulse NMR experiment is long compared to the longitudinal relaxation time T_1, the peak areas give a measure of the number of spins contributing to each signal and therefore provide a quantification of the functional groups in the sample. During the radiation modification of fluoropolymers radicals are formed in the first step. Depending on the reaction conditions, these radicals can have a long lifetime, which has been confirmed by ESR.[17] Under heat treatment radicals can recombine which is manifested in a longer fluorine T_1. However, structural changes occur in the samples upon heat treatment, because the radicals recombine and small fragments may escape. Because the coupling to the unpaired electron provides a very effective nuclear relaxation mechanism, the radicals have a strong influence on the nuclear longitudinal relaxation time T_1. The untreated FEP has a T_1 of 0.9 s, while untreated PTFE has a T_1 of 1.7 s at room temperature. T_1 of PTFE irradiated at high temperature at 3 MGy has a T_1 of 0.9 s and room-temperature-irradiated PTFE, 0.6 s. The difference in the T_1 of the samples shown here is mainly attributed to different radical concentrations. Variations in the molecular mobility manifest themselves in T_1 and especially in its temperature dependence as well.[18] It is expected that the relaxation rate depends linearly on the concentration of unpaired electrons.[19] No signals from spins in the vicinity of the radicals could be detected due to the strong coupling. For the purpose of quantitative analysis, it is assumed that the radicals are uniformly distributed in the sample and all functional groups are similarly effected. Fast spin diffusion between the fluorine nuclei leads to a uniform single-exponential T_1 for all signals assigned to different structures throughout each sample.[18]

The further quantitative analysis is based on the assumption that all kinds of end groups other than CF$_3$ groups can be neglected. This assumption was confirmed by IR investigations and other NMR studies.[18] A concentration of COF groups, leading to a signal at 25 ppm, on the order of 0.1% of the total fluorine content was found for samples irradiated in a vacuum followed by postirradiation treatment in air at high temperatures. In all other experimental conditions the concentration of COF groups is well below that. In the present investigation all irradiations were performed in a vacuum which further lowered the possibility of reactions with oxygen. Another possible type of end group would be COOH groups, which cannot directly be detected in the NMR spectra but in infrared spectra. Infrared spectroscopic studies showed that the concentration of COOH groups is very close to that of COF groups, assuming similar extinction coefficients for these two types of groups.[20] From these data it is concluded that the number of COOH and COF groups is by at least a factor of 30 lower than the number of CF$_3$ groups and can thus be neglected for the present analysis.

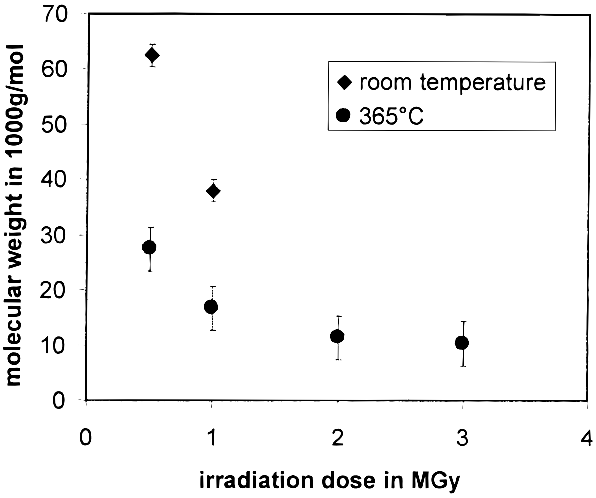

Figure 4. Average molecular weight of the radiation-modified PTFE samples as a function of the radiation dose. The triangle represent the room-temperature-irradiated samples, and the circles represent samples irradiated at 365 °C. For the samples irradiated at 365 °C, the molecular weight determined represents a lower limit.

The spectrum of the nonirradiated PTFE shows no other signal than the signal from CF$_2$ groups in a CF$_2$ environment. Signals from any other groups, especially CF and CF$_3$, would clearly be resolved in the ^{19}F NMR spectra. Assuming that it is possible to detect signals on the order of 10^{-4} of the most intense signal in the spectrum suggests that the PTFE is linear, and the molecular weight exceeds 10^6 g/mol, which is the expected result.

PTFE irradiated at room temperature exhibits predominantly chain scission. The spectrum in Figure 2b shows one dominant CF$_2$ peak from the PTFE and an additional peak assigned to CF$_3$ end groups at -82 ppm. Since no additional signals indicating branches or cross-links are present, this is consistent with the common interpretation that chain scission is the dominant process during the irradiation of PTFE at room temperature. From these data an average molecular weight can be easily established. The numbers of CF$_2$ and CF$_3$ groups are obtained from the integrals of the respective peaks. Assuming two terminal CF$_3$ groups per chain, an average chain length and thus an average molecular weight can be established. For the sample irradiated at a radiation dose of 1 MGy, an average molecular weight of about 40 000 g/mol was determined, which is depicted for comparison together with other values in Figure 4.

The quantitative analysis is more complicated for the samples irradiated above the melting point. As seen in Figure 3, these samples contain a variety of different structures, which makes it more difficult to establish a picture of the average chain. The most important result from the spectra reported herein is that the number of branches, CF groups, is significantly higher than the number of end CF$_3$ groups. As opposed to ref 9, cross-links are seen as a special type of branch, which are not terminated by CF$_3$ or any other end group, but by a branch in another chain. The conclusion drawn is that cross-links exist in the high-temperature-irradiated samples.

The quantification requires careful separation of the different structures. In a first step the number of CF$_3$

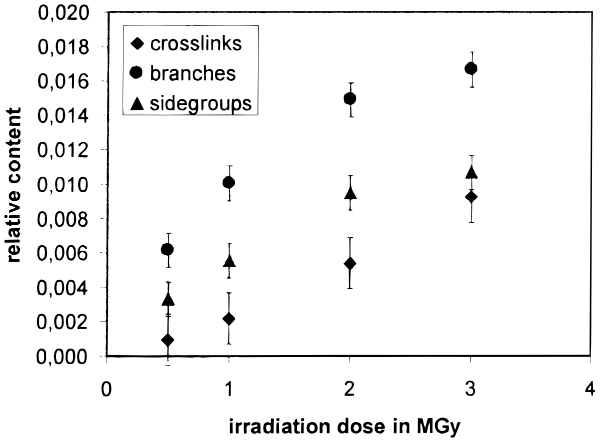

Figure 5. Density of side groups, branches, and cross-links in the high-temperature-irradiated PTFE as a function of radiation dose.

side groups, hexafluoropropylene structures, is determined from the integrated signal at −72 ppm, the CF_3 side groups, and the signal at −112 ppm for the CF_2 groups next to the side groups. The ratio of the respective integrals is in good agreement with the expected ratio of 3:4. Because each hexafluoropropylene structure contains one CF group, the number of CF_3 side groups is subtracted from the integral of the CF signal. The remaining number of CF groups represents the sum of long-chain branches and cross-links. To separate branches from cross-links, the number of terminal CF_3 groups is taken into account. Neglecting the end groups of the main chains, the difference between the remaining number of CF groups and the number of terminal CF_3 groups is the number of cross-linking points. For every main chain two additional terminal CF_3 groups are necessary. Thus, the number of cross-links would have to be even higher, to get the same ratio of CF to CF_3 groups, when the same number of functional groups is distributed on more and thus shorter chains. Because the number of main chains is unknown, the cross-link density, determined here, represents a lower limit. On the basis of this procedure, a density of side groups, branches, and cross-links were calculated, and the results are plotted in Figure 5. The number of cross-links represents a lower bound, while the number of branches appears as an upper bound.

The molecular weight in the branched and partially cross-linked polymer is more complex, because the average chain length cannot be as easily calculated as in the case of nonbranched samples. It is possible to distribute the same number of functional groups to a higher number of polymer chains, which means the number of cross-links would be increased, because for each additional chain two additional terminal CF_3 groups are necessary. To establish a molecular weight, an iterative procedure has been used. All branches and cross-links are neglected in the first step. From the ratio of CF_2 groups to CF_3 end groups a chain length can be calculated. This defines the absolute minimum molecular weight, because each additional branch introduces a side chain which increases the molecular weight. The density of branches is high enough to incorporate at least one branch to this hypothetical chain. In a second step from the ratio of CF_2 groups to CF groups, the CF groups next to the CF_3 side groups have been subtracted; the number of branches in this hypothetical chain is calculated. The number of CF_2 groups in the chain is increased. As stated above, there is no information to derive a termination condition from; therefore, this iteration procedure could go on until the entire sample would be represented by one polymer chain. As no additional data are available, the iteration has been terminated at this point. The molecular weights established for the high-temperature-irradiated samples depicted in Figure 4 are lower limits for the true molecular weight. The molecular weight determined for the sample irradiated at 1 MGy at 365 °C is 17 000 g/mol. This value, a lower bound, is lower than the value for the sample irradiated at room temperature with the same radiation dose.

Conclusions

We have demonstrated 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 under vacuum. While chain scission is the dominant process at room temperature, additional branching occurs for high-temperature irradiation under vacuum. Quantitative spectral analysis shows that the number of branching groups exceeds the number of terminal groups, which can only be explained by the presence of cross-linked polymer chains. Evidence for the existence of cross-links is derived from structural infomation rather than from changes in the molecular mobility.

For the room-temperature-irradiated samples an average molecular weight can be calculated on the basis of the concentration of end groups. For the samples containing branches and cross-links only lower limits for the average molecular weight and the cross-link density can be derived. The concentration of functional groups such as side groups, branches, and cross-links increases approximately linearly with the irradiation dose in the dosage range and irradiation conditions investigated here.

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