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Radiochemical Yields for Cross-Links and Branches in Radiation-Modified Poly(tetrafluoroethylene)

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ABSTRACT: For the enhancement of the compatibility of fluoropolymers with other materials radiation modification is applied, for which irradiation with high-energy electrons provides an efficient and flexible possibility. Poly(tetrafluoroethylene) (PTFE) is known to predominantly undergo chain scission under irradiation. To counteract this chain scission and the resulting deterioration of the mechanical properties, PTFE has been irradiated at temperatures above the melting temperature under inert atmospheres. Under these conditions, in addition to chain scission long chain branches and cross-links are formed. The resulting structures have been studied by high-resolution fluorine-19 solid-state NMR applying high-speed magic-angle sample spinning. The structural changes as a function of energy dose and irradiation condition have been investigated upon irradiation under nitrogen atmosphere at 385 °C and under vacuum at 365 and 385 °C. Structures of interest are terminal groups, CF_3 side groups, branches, and cross-links. From quantitative information derived from the ^{19}F NMR spectra, the radiochemical yields, $G(x)$ values, for the formation of CF_3 side groups, branches, and cross-links have been calculated. $G(x)$ values of side groups and branches decrease with radiation dose, while the radiochemical yield of cross-links is nearly constant. These results are interpreted that in the first step in addition to main-chain scission the CF_3 side groups and branches were formed and in the second step after forming a sufficient quantity of side groups and branches the cross-links are formed.

Introduction

Poly(tetrafluoroethylene) (PTFE) has been classified as a polymer that predominantly undergoes main-chain scission upon irradiation.[1] The poor radiation stability of PTFE results in a reduced molecular weight even with small irradiation doses at room temperature and thus deteriorated mechanical properties. A number of recent publications described that in PTFE cross-links are formed upon irradiation in an oxygen-free atmosphere at temperature above the melting temperature.[2−10] The tensile strength and elongation at break were investigated in a wide temperature range and changed drastically by irradiation temperature, especially around the melting point of PTFE.[2,3] Further studies showed a great improvement in the high-temperature properties and radiation stability for PTFE irradiated above the melting point.[4,5] Molecular motion investigated by dynamic viscoelastic measurements was strongly affected by cross-linking.[6] The crystallinity decreased on the irradiation in the molten state but increased on irradiation below the melting point.[7] It was concluded that cross-links are formed in PTFE by irradiation under vacuum above the melting point, and so the formation of crystals is disturbed. Nascent PTFE exhibits a very poor transparency, but the transmission increases much with progress of the cross-linking density.[8]

In previous solid-state NMR investigations[9,10] it has been 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 under vacuum. While chain scission is the dominant process at room temperature, additional branching occurs for high-temperature irradiation under vacuum. Quantitative 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,[10] where a branch terminating in a branching point of another chain is named a cross-link.

In the present study the radiochemical yields, $G(x)$ values, for the irradiation process of PTFE are calculated from the concentration of functional groups such as side groups, branches, and cross-links from ^{19}F solid-state NMR spectra. The $G(x)$ value is a measure for the efficiency of the radiochemical functionalization process and its radiation dose dependence. In addition, it permits a comparison between different radiation modification processes. The initial slope provides information on the efficiency of the radiation modification. Comparison of the dose dependence of $G(x)$ values for different functions may yield information on multistep reactions. Especially the energy dose dependence of the $G(x)$ value describes the development in a multistep functionalization process. Radiochemical yields are compared for different irradiation conditions of PTFE: at 365 °C in a vacuum and at 385 °C in a vacuum or nitrogen at atmospheric pressure. These temperatures were chosen for the irradiation above the melting point of PTFE at 330 °C.

Experimental Section

Materials. Commercial PTFE peel films (500 μm, PTFE Nünchritz GmbH, Glaubitz, Germany) have been used for the irradiation as received.

Irradiation. The PTFE films have been irradiated with 1.5 MeV electrons using an electron beam accelerator (ELV-2, Budker Institute of Nuclear Physics, Novosibirsk, Russia). The irradiation setup is described in detail elsewhere.[11] The irradiation experiments in a vacuum and in nitrogen atmosphere at atmospheric pressure were carried out at 365 and 385 °C, using a vacuum vessel with a window for electron

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penetration, as described in more detail in refs 12 and 13. Before the vessel was filled with nitrogen, it was evacuated to 10^{-2} Pa for 1 h in order to minimize the concentration of oxygen. The polymer film is placed on an electrically heated carrier. The temperature of the carrier is controlled via a resistive thermocouple. To achieve adequate continuous thermal contact between the carrier and the polymer film, the film has been pressed onto the carrier with a glass fiber fabric. The temperatures of the PTFE specimen are understood to be slightly different in a nitrogen atmosphere and in a vacuum, when the same carrier temperature is adjusted at the thermocouple, because of stronger heat dissipation in the gas atmosphere. Thus, the temperature of PTFE in nitrogen at atmospheric pressure is probably lower than in a vacuum because of increased heat dissipation to the surrounding atmosphere. Annealing in a vacuum was performed using a Carbolite 12/38/400 tubular furnace.

The mass loss of the PTFE specimens during the irradiation is discussed in detail in ref 13. It rises approximately linear with increasing dose up to about 50% at a dose of 3 MGy. It is slightly higher during the irradiation in vacuum than under nitrogen, probably due to the lower temperature during irradiation under a nitrogen atmosphere. Furthermore, the removal of low molecular weight compounds is enhanced because of the reduced pressure (10^{-2} Pa) compared to the irradiation under nitrogen at atmospheric pressure. The mass loss of PTFE during irradiation in air at room temperature is significantly lower.[14] In ref 15 it was reported that the radiation-induced mass loss increases rapidly at the melting point of PTFE.

^{19}F NMR. 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 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 in all experiments. The sample volume for the NMR experiments is about 12 μL. All NMR experiments have been performed at ambient temperatures to avoid any additional reactions in modified polymer samples. 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 at ambient temperature 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.[16]

All spectra evaluated here have been 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. For the quantitative analysis of the data, 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 $CFCl_3$, referenced indirectly via the CF_2 signal of PTFE at −122 ppm.

Results and Discussion

Figure 1 depicts spectra of PTFE irradiated with a dose of 3 MGy at 365 and 385 °C under vacuum and at 385 °C under a nitrogen atmosphere. All spectra exhibit the same structures. Most of the structures had been assigned previously.[10] Each main chain is terminated by two CF_3 end groups. CF_3 side groups (trifluoromethyl side groups) and long chain branches are bonded to the main chain by tertiary carbons. A model of the chain structure of PTFE irradiated at temperatures above the melting point is depicted in Figure 2.

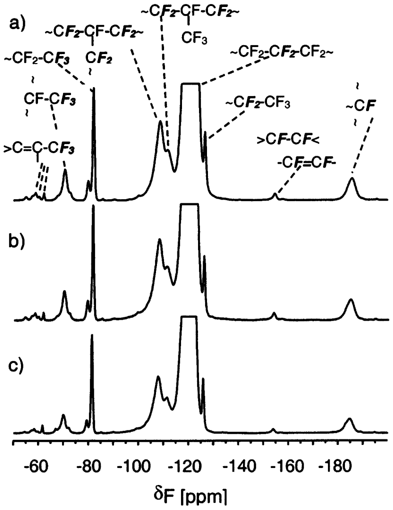

Figure 1. ^{19}F NMR spectra (16 times vertically enlarged) of PTFE sample irradiated with a radiation dose of 3 MGy at 365 °C in a vacuum (a), at 385 °C in a vacuum (b), and in nitrogen (c) with signal assignment on the top spectrum. In each molecular fragment the fluorine atoms assigned to the resonance are indicated in bold italics.

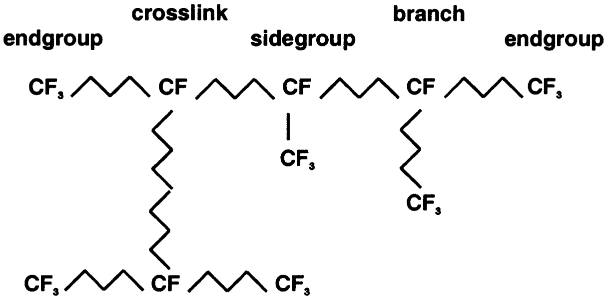

Figure 2. Chain structure model of PTFE irradiated at temperatures above the melting point.

The CF_3 signal of side groups (−72 ppm) can be distinguished from the CF_3 end group (−82 ppm) in the ^{19}F NMR spectrum. The intensities of the signals other than CF_2 increase with the applied radiation dose in all three cases. The signals of the CF groups, CF_2 groups, CF_3 side groups, and CF_3 end groups were analyzed quantitatively by integration of the spectra, taking the multiplicity of the F atoms into account. The quantification of the functional groups requires accurate separation of the different structures. On the basis of this procedure, relative contents of side groups, branches, and cross-links were calculated. The relative content (N_D) refers to the total number of carbons derived from the spectrum as explained in ref 10.

In a first step the number of CF_3 side groups, hexafluoropropylene structures, is determined from the integrated signal at −72 ppm. Equation 1 describes the calculation of relative contents (N_D) of side groups from the relative intensities (I_{rel}) of the integrated signal:

$$N_D(\text{side groups}) = \frac{I_{rel}(\text{side groups})}{I_{rel}(\text{total structures})} = \frac{I_{rel}(\text{CF bonded to side groups})}{I_{rel}(\text{total structures})} \quad (1)$$

The ratio of the CF_3 side group signal and the signal at −112 ppm for the CF_2 groups next to the side group 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 signals at −154 and −183 ppm. The remaining number of CF groups

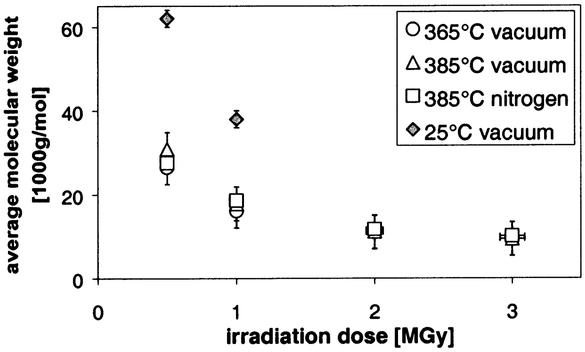

Figure 3. Average molecular weight of irradiated PTFE samples as a function of the radiation dose. The values of the room-temperature-irradiated samples represent an average, and the values of the high-temperature-irradiated PTFE represent a lower limit.

represents the sum of long-chain branches and cross-links as both are linked to the main chain via a tertiary carbon. To separate branches from cross-links, the number of terminal CF_3 groups at −82 and −60 ppm is taken into account. Neglecting the end groups of the main chain, the difference between the remaining number of CF groups and the number of terminal CF_3 groups is the number of cross-linking points. The following eq 2 explains the calculation of the relative contents of branches:

$$N_{\mathrm{D}}(\text{branches}) = \frac{I_{\mathrm{rel}}(\text{end groups})}{I_{\mathrm{rel}}(\text{total structures})} = \frac{I_{\mathrm{rel}}(\text{CF bonded to end groups})}{I_{\mathrm{rel}}(\text{total structures})} \tag{2}$$

Cross-links are regarded as a special type of branch, which are not terminated by CF_3 or any other end group but by a branching point in another chain; eq 3 calculates their relative contents:

$$N_{\mathrm{D}}(\text{cross-links}) = \frac{I_{\mathrm{rel}}(\text{total CF}) - I_{\mathrm{rel}}(\text{side groups}) - I_{\mathrm{rel}}(\text{end groups})}{I_{\mathrm{rel}}(\text{total structures})} \tag{3}$$

For every main chain two additional terminal CF_3 groups are necessary. Thus, the number of cross-links would have to be even higher, when the same number functional groups is distributed on more and thus shorter chains. Because the number of main chains is unknown, the relative content of cross-links represents a lower band.

For the calculation of the molecular weight of the partially cross-linked PTFE all branches and cross-links are neglected in the first step. From the ratio of CF_2 groups to CF_3 groups a chain length is calculated, which defines the minimum molecular weight. 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. This is a lower limit for the molecular weight of high-temperature-irradiated PTFE where calculated and are given in Figure 3. In all cases a drastic loss in average molecular weight is observed. The data of the molecular weight in Figure 3 are very close for all three samples. Because for the cross-linked PTFE only a lower bound for the molecular weight can be determined, this value appears lower than for the PTFE irradiated at room temperature. The molecular weight of the untreated film is in excess of 10^6 g/mol, which is concluded from the fact that there are no signals from terminal groups or CF_2 groups coupled to nonfluorinated terminal groups.

From the relative content of the structural groups (N_{D}), determined as described above the $G(x)$ values were calculated. The $G(x)$ values for the formation of CF_3 side groups, branches, and cross-links were determined from eq 4. Usually $G(x)$ values are quoted in 1/100 eV and describe the number of structures formed per 100 eV of energy absorbed. D is the energy dose, and N_{D} is the content of cross-links, branches, or CF_3 side groups. N_{A} is the Avogadro number, and $M_{\mathrm{CF_2}}$ is the molecular weight of CF_2. The radiochemical yield of cross-links represents a lower bound, while for branches an upper bound is determined.

$$G(x) = \frac{N_{\mathrm{D}} N_{\mathrm{A}}}{M_{\mathrm{CF_2}} D} \tag{4}$$

$$(x) = \text{cross-links, branches, } \mathrm{CF_3} \text{ side groups}$$

$G(x)$ values derived from the NMR data for the formation of side groups, branches, and cross-links are depicted in Figure 4 for three series of samples. The values for PTFE irradiated in a vacuum at 365 °C as a function of irradiation dose are shown in Figure 4a. Radiochemical yields for the formation of branches and CF_3 side groups decrease, while those for the formation of cross-links are nearly constant. A similar behavior is found for PTFE, which has been irradiated in a vacuum at 385 °C as depicted in Figure 4b. Figure 4c shows the $G(x)$ values of PTFE irradiated in nitrogen atmosphere at 385 °C. Again, the $G(x)$ values for the formation of branches and CF_3 side groups decrease with increasing irradiation dose. However, the $G(x)$ values for the formation of cross-links increases initially between 0.5 and 1 MGy; they are nearly constant around 0.4 for higher doses. From the three irradiation series PTFE irradiated at 385 °C in nitrogen has the lowest absolute values of $G(x)$. The unknown small difference in temperature as explained in the Experimental Section may be a reason for the slightly lower $G(x)$ values.

The drastic mass loss during irradiation under vacuum above the melting point (see also Experimental Section) leads to the decreasing total values of $G(x)$. Thus for these three series of samples generally the radiochemical yields of branches and CF_3 side groups decrease with higher irradiation dose. From the three irradiation series PTFE irradiated at 385 °C in a vacuum has the highest $G(x)$ values of cross-links. Already at 0.5 MGy the $G(x)$ value reaches about 0.6/100 eV and does not change remarkably with increasing irradiation dose. Lower $G(x)$ values of cross-links show PTFE irradiated at 365 °C in a vacuum at 0.5 and 1 MGy and PTFE irradiated at 385 °C in nitrogen only at 0.5 MGy. While the $G(x)$ value of about 0.6/100 eV PTFE irradiated at 365 °C in a vacuum reaches it at 2 MGy, PTFE irradiated at 385 °C in nitrogen already reaches it at 1 MGy. The different temperature conditions during the irradiation of PTFE are one reason for different $G(x)$ values of cross-links.

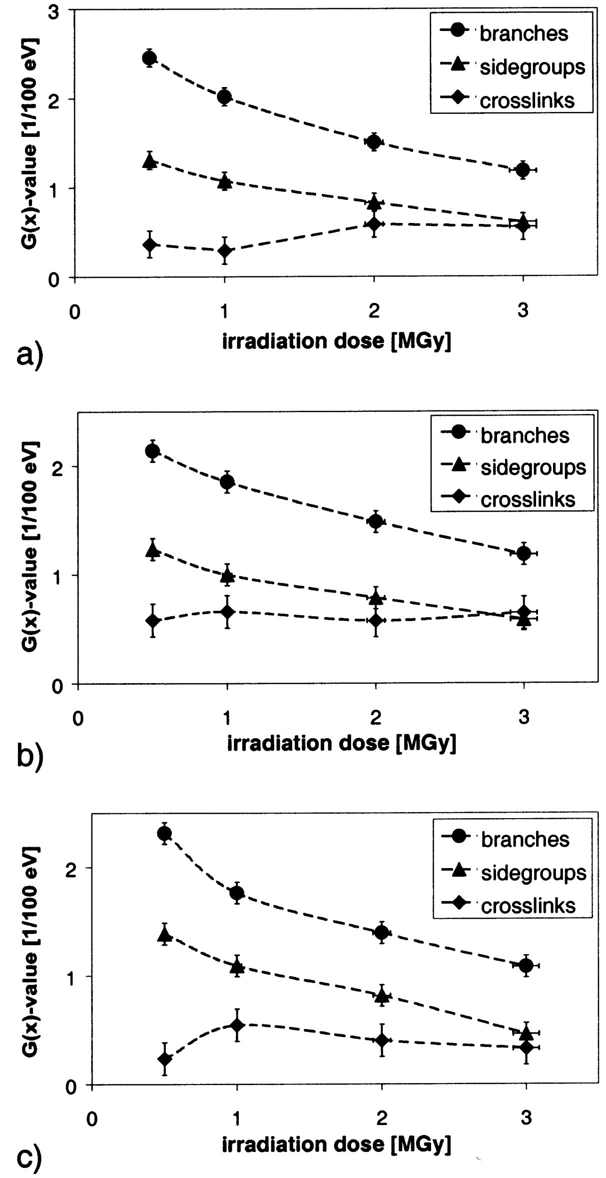

Figure 4. $G(x)$ values of cross-links, branches, and CF_3 side groups for PTFE irradiated in a vacuum at 365 °C (a), in a vacuum at 385 °C (b), and in nitrogen at 385 °C (c) as a function of irradiation dose. The dashed lines are a guide to the eye only.

It is interpreted that in the first step of the irradiation process under an inert atmosphere and temperature above melting point CF_3 side groups and branches are formed and with a certain concentration of this functional groups cross-links start to form. The formation of cross-links appears to be delayed upon the irradiation in a nitrogen vacuum. The data in Figure 4 would be affected by samples with lower molecular weights in this manner that the concentration of cross-links would be increased and the concentration of branches and side groups would be decreased.

Conclusions

From previous studies it was known that PTFE irradiated at high temperatures, above melting temperature, in an oxygen-free atmosphere, shows not only main-chain scission but also branching and cross-linking. Structural data were derived from high-speed MAS ^{19}F solid-state NMR of three series of PTFE samples irradiated under different conditions. From a quantitative analysis of the NMR data radiochemical yields for the irradiation process have been calculated, which provide a measure for the efficiency of the radiochemical process and its radiation dose dependence. The $G(x)$ values for the formation of CF_3 side groups and the formation of long-chain branches decrease with increasing irradiation dose. The $G(x)$ values for the formation of cross-links in a vacuum are independent of the irradiation dose. In a nitrogen atmosphere there appears to be an initial buildup, indicating that the formation of cross-links is delayed.

From the presented data it can be concluded that in a first step of the irradiation process in addition to main-chain scission CF_3 side groups and long-chain branches are formed. Only when a certain concentration of branches has been generated can cross-links be formed in the PTFE. A portion of the long-chain branches can react with a reactive group formed on a neighboring chain to form a cross-link between the two chains.

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