Photodegradation of Teflon AF1600 During XPS Analysis

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ABSTRACT: Teflon AF1600, containing perfluorinated dioxole rings, was found to be particularly susceptible to X-ray degradation, such as that occurring during X-ray photoelectron spectroscopy. Because of the presence of O, the degradation mechanism is substantially different from those of fluoropolymers containing only C and F. Each atom of a given element was found to have the same susceptibility to attack, irrespective of its position in the repeat unit, with O at least twice as susceptible as F. At any dose between 60 W* X-ray source power/5 min and 240 W/40 min, O was lost at an amount equal to that of F, which necessitated the breaking of two C—O bonds; O also degraded by breaking only one bond, in which case the oxygen was not lost but formed a free radical. The free radicals produced by the homolytic scission of C—C bonds participated in reactions leading to degradation and crosslinking. *The product of X-ray filament emission current and the potential difference between it and the X-ray anode. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1201–1207, 1998

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INTRODUCTION

Fluoropolymers are known to degrade through homolytic bond scission when exposed to the flux of X-ray photoelectron spectrometers. Such fluoropolymers include Teflon PTFE $[—(CF_2—CF_2)_n]$,[1] Teflon FEP $[—(CF_2—CF_2)_n—(CF_2—CFCF_3)_m$, 85 : 15 w/w],[2] and Teflon PFA $[—(CF_2—CF_2)_n —(CF_2—CFOC_3F_7)$, 97.5 : 2.5 w/w].[2] Because degradation occurs under relatively mild conditions, it is always necessary to assure that the sample does not degrade significantly during data accumulation.[1–3]

These studies showed that degradation proceeded in a similar fashion for all the Teflons so far mentioned, as follows: the scission of C—C and C—F bonds led to graphitization, crosslinking, and the loss of low-molecular weight species, as revealed by mass spectrometry. A decrease was seen in the amount of CF_2, as was a gain in the amount of CF_3; this means that $CF_2\bullet$ must have reacted with $F\bullet$ to produce substantial amounts of CF_3.

Teflon AF (amorphous fluorocarbon) is a newly available Teflon, with the advantage of solubility in certain perfluorinated solvents. It is, in fact, a perfluorinated dioxole[4,5]; the structure of the repeat unit for Teflon AF1600 (1600 indicates a T_g of 160°C[5]) is seen in Figure 1. The presence of the heterocyclic structure makes Teflon AF particularly susceptible to photodegradation by X-rays. It is our experience that degradation becomes noticeable within 5 min, under our XPS normal operating conditions of 240 W. We consider it to be necessary to delineate those conditions necessary for XPS spectral accumulation with minimal
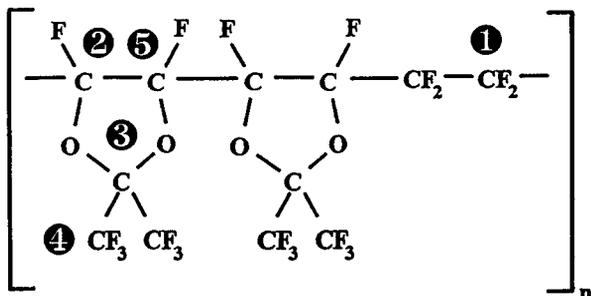
Figure 1 The structure of the Teflon AF1600 repeat unit.

degradation in this polymer in order to properly obtain and interpret such spectra.

EXPERIMENTAL

Teflon AF1600 was purchased from DuPont as a 6% solution in perfluorinated solvent. It was further diluted 50% with Sigma Fluorinert FC-77 and spun at 4000 rpm onto a freshly cleaned Si wafer. After drying for several minutes at room temperature and baking for 10 min at 110°C, the solvent was completely removed by heating for 5 min at 165°C, as recommended by the manufacturer.[6] A film thickness of 3–4 μm was obtained.

X-ray photoelectron spectra were obtained on a VG ESCALAB Mark II instrument, using non-monochromated Mg K_α radiation at 1253.6 eV. Stray electrons were absorbed by a thin aluminum film positioned in front of the X-ray source. Emerging electrons were collected at a take-off angle of 30° from the surface, at a pressure of 2 $\times$ 10^{-9} Torr. High-resolution spectra were obtained at an analyzer pass energy of 25 eV, at an experimentally determined resolution of 0.8 eV, and a measurement error $<$0.1 eV.

No flood gun was used to reduce sample charging; instead, charge compensation was accomplished by fixing the binding energy of the graphitic degradation product at 284.7 eV.[7] In our original study of undegraded AF1600,[8] no such energy calibration markers were available; there, charge compensation was carried out by arbitrarily fixing the binding energy of the highest energy component of the C1s spectrum at 292.0 eV. A comparison of the 2 procedures indicated that the arbitrary procedure originally used gave binding energies 1.0 eV too low. All the peak energies in the present study have been corrected.

Samples were exposed to X-ray source powers varying form the normally used 240 W (12 kV, 20 mA) down to 60 W (6 kV, 10 mA). Spectra were recorded over radiation exposure times from 5 to 40 min, with a minimum dose of 60 W/5 min and a maximum dose of 240 W/40 min. Peak separations of the C1s, O1s, and F1s envelopes were carried out subsequent to background subtraction, using an in-house nonlinear least-mean squares program with full width at half-maximum (FWHM) values experimentally determined on similar polymers. In the case of C1s spectra, where the $K_{\alpha3}$ X-ray satellite, lying 8.4 eV below the main peak, had a propensity to interfere with other peaks, it was subtracted out.

Mass spectroscopy analysis during X-ray exposure was carried out using VG SQ300 mass spectrometer mounted on the analysis chamber. Its mass scale was calibrated using a mixture of He, Ar, and Xe gases, purchased for that purpose. Counts were displayed at 0.5 amu intervals, between 0 and 150 amu.

RESULTS

High-resolution C1s spectra for X-ray doses (power $\times$ time), varying from minimum (60 W/5 min) to maximum (240 W/40 min), are seen in Figure 2. Examples of peak separation for C1s, O1s, and F1s spectra, subsequent to a dose of 200 W/40 min, are seen in Figure 3. The XPS C1s spectrum of undegraded Teflon AF1600 has recently been successfully assigned.[8] While the reader is referred to that study for the complete peak attribution, we review them here so that the present results may be better understood. A listing of the C1s, F1s, and O1s peak binding energies obtained in that study and their attributions are presented in Table I. The reasons for the attributions are to be found in the original study.[8]

Spectral areas were obtained by computer-assisted integration after background subtraction; the experimentally determined error was found previously to be $<$ 3% of the peak area. A comparison of such values as a function of dose revealed the following.

C1s

A typical degradation spectrum, presented in Figure 2, indicates that the peaks may be separated into the original peaks ($>$287 eV) and the degradation products ($<$287 eV). The relative concentration of original peaks is referred to as $C_{undegraded}$ and that of the degradation products, $C_{degraded}$. As seen in Figure 2, the shape of the original peaks during
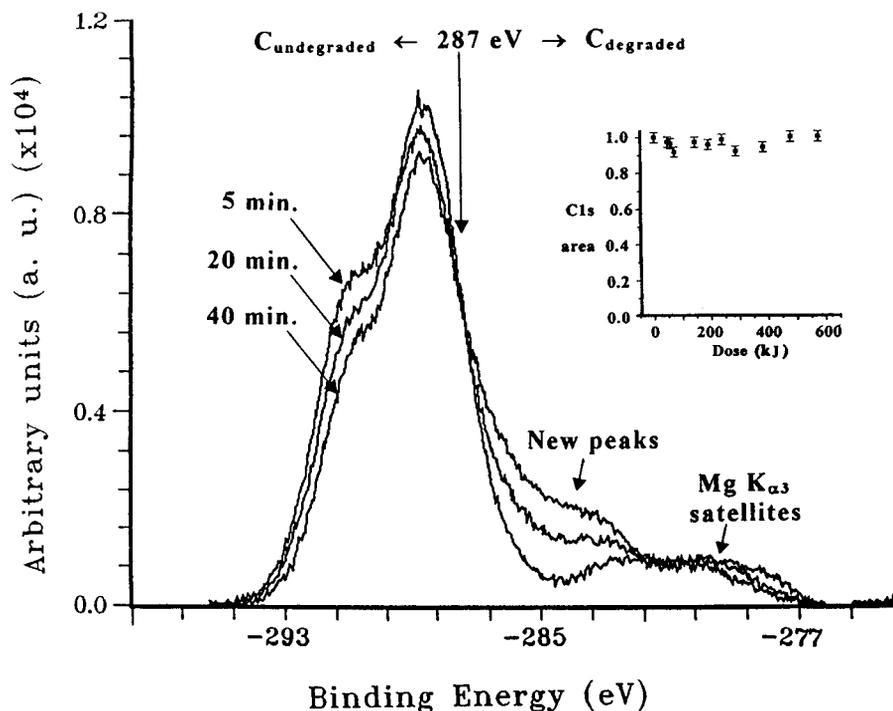
Figure 2   Typical C1s spectra of Teflon AF1600 (power source = 200 W), and C1s total area versus X-ray dose. Inset: C1s peak area as a function of X-ray dose.

degradation appears to be maintained. Further, the area of the entire envelope is maintained, as seen in the inset to Figure 2. This suggests that little or no *C* was lost during X-ray exposure. Another reason for believing so is that the shape of the undegraded C was maintained during degradation, which is highly improbably if C atoms at different sites were lost because their probabilities of bond breaking are expected to be different.

O1s

Oxygen was lost during degradation, as seen in the inset to Figure 3(b); at any X-ray source power, it was lost at a linear rate and at any time, as a linear function of the X-ray source power; a spectral asymmetry, toward the lower binding energy side of the O1s peak, was resolved into new peaks with a slightly larger energy separation than the original 2 peaks, as seen in Figure 3(b); both original peaks decreased at identical rates, which maintained the original peak ratios.

F1s

Fluorine was lost in a fashion similar to that of O, as seen in the inset to Figure 3(c); no evidence was

manifested of new components, and each peak decreased at a rate that maintained the original peak ratios. Here, the loss of F atoms from different sites at the same probabilities is less surprising, given that (1) they are all bonded by 1 simple bond, rather than 2, in the case of C, and (2) the binding energies for the 3 F sites are similar (that is, the chemical shifts for F in different environment are small).

F/O

The F/O ratio was corrected for different sensitivities and inelastic mean free paths by dividing the F1s and O1s peak areas by their sensitivity factors and appropriate attenuation lengths. At any dose, the fractional losses of F and O were identical, with the F/O ratio remaining, within experimental error, equal to 1.

The various XPS spectral changes may be used to evaluate the linearity of X-ray exposure with dose. Degradation may be defined as any of the following ratios: $C_{degraded}/C_{undegraded}$, $O_{lost}/O_{remaining}$, or $F_{lost}/F_{remaining}$. All such plots are well described by a linear relationship: an example is seen in Figure 4 for $C_{degraded}/C_{undegraded}$.

Mass spectroscopic analysis showed that the concentrations of fragments present before X-ray
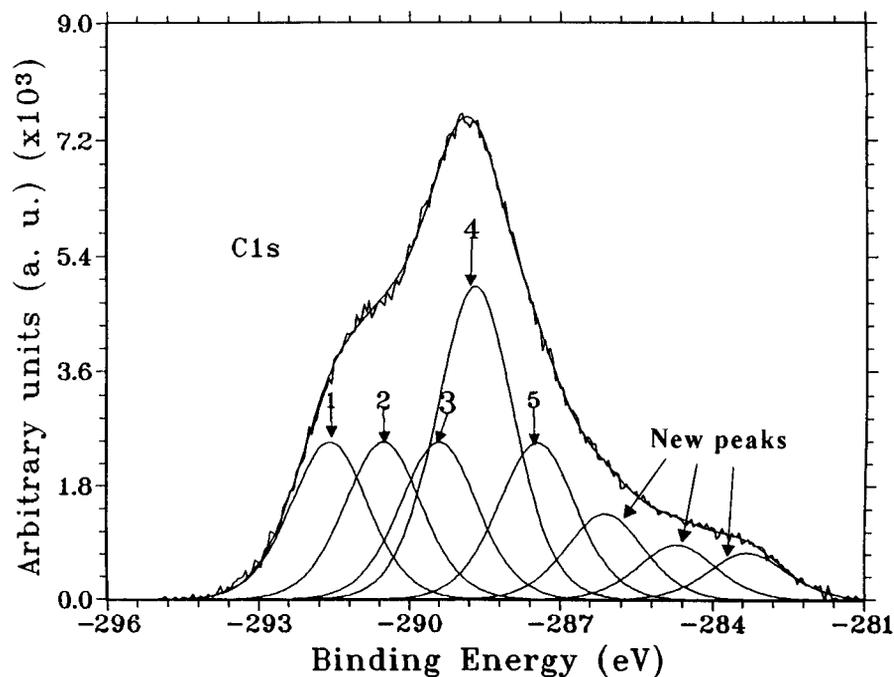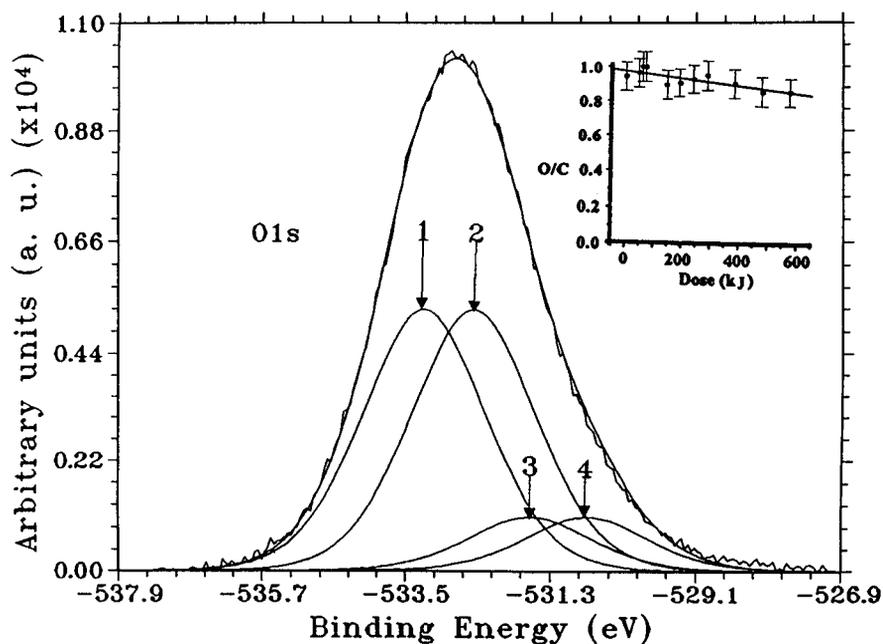
Figure 3 Peak separation of (a) C1s, (b) O1s, and (c), F1s spectra of Teflon AF1600 subsequent to a radiation dose of 200 W/40 min; O/C and F/C versus dose; the ratios are normalized to maximal values. Insets to (b) and (c): O/C and F/C ratios, respectively, as a function of X-ray dose.

exposure began (H_2O^+ at 18.0 amu; CO^+ or N_2^+ at 28.0 amu; CO_2^+ at 44 amu) increased with time as the mass spectrometer quadrupole warmed up and species adsorbed on the walls of the spec-trometer were desorbed. Those fragments pro-duced after X-ray exposure began (CF^+ at 31.0 amu; CF_2^+ at 50.0 amu; CF_3^+ at 69.0 amu, and $C_2F_3O^+$ at 97.0 amu) reached their maximum
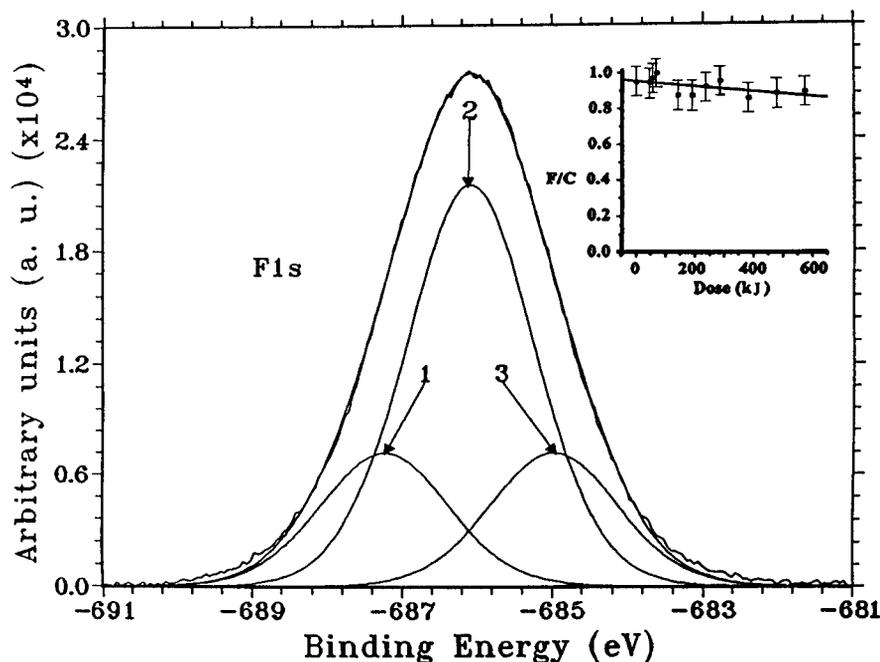
(c)

Figure 3 (*continued from the previous page*)

concentrations during the first scan, followed by steady decreases; an example is seen in Figure 5. These trace amounts would not be evident in an XPS spectrum.

DISCUSSION

The trace amount of C, detected by mass spectrometry is too low to be considered in our XPS

analysis. While new peaks at lower binding energies indicates partial and total defluorination, as well as graphitization and crosslinking, no additional terminal CF_3 is formed, as found for other Teflons.[1,2] The area ratio of the 5 component peaks in the undegraded C1s spectrum, $1 : 1 : 1 : 2 : 1$,[8] is maintained in the undegraded portions

**Table I   Teflon AF1600 XPS Peak Attributions**

XPS Spectrum	Relative Ratio	Binding Energy (eV)	Attribution (Fig. 2)
C1s	1	292.0[a]	Position 1
	1	291.1	Position 2
	1	289.9	Position 3
	2	289.0	Position 4
	1	287.9	Position 5
O1s	1	538.2	$(C—O—C)$[b]
	1	537.15	$(C—O—C)$[c]
F1s	1	687.5	CF_2
	3	686.5	CF_3
	1	685.5	CF

Data from Sacher and Klemburg-Sapieha.[8]
[a] Peak arbitrarly placed at 292.0 eV; see Sacher.[7]
[b] Adjacent oxygens in Figure 2.
[c] Outer oxygens in Figure 2.
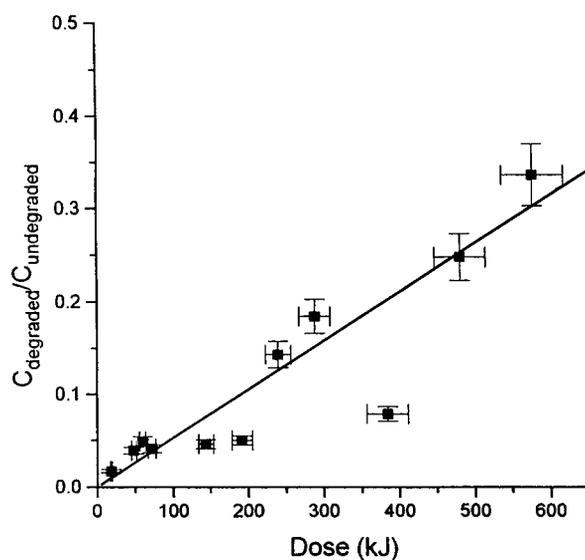
Figure 4 Plot of $C_{degraded}/C_{undegraded}$ versus dose, demonstrating degradation linearity with X-ray exposure.
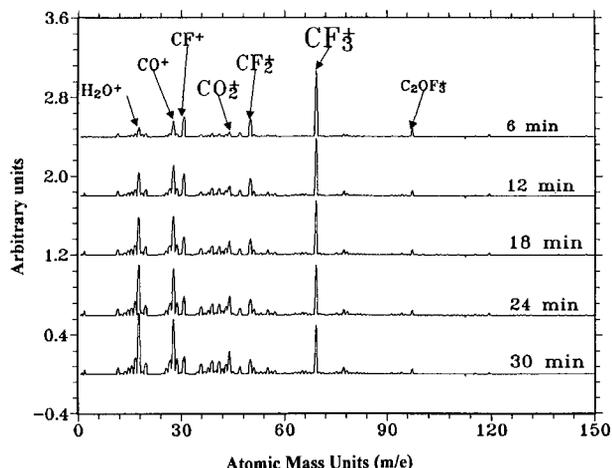
Figure 5 Mass spectra of fragments produced on exposure of Teflon AF1600 to X-rays at a source power of 120 W. The background spectrum, at $t = 0$, has been subtracted.

($C_{undegraded}$) of all the degraded spectra [peaks 1–5 in Figure 3(a)].

The C1s spectrum in Figure 3(a) shows 3 new peaks produced on X-ray degradation; these peaks do not vary in position on degradation but, rather, only increase in intensity. They are attributed to the partial and total (lowest binding energy peak) graphitization of the original structure, as O and F are lost. While the structures contributing to the partially degraded peaks are unknown, and their energy positions cannot be used to confirm their structures with certainty, the C1s energy positions of graphite is well known; it appears at 284.7 eV[7] and is used in this study to compensate for charging.

O1s spectral analysis reveals the formation of new peaks at lower energies. The 2 original peaks [peaks 1 and 2 in Figure 3(b)], due to slightly different ether linkage environments,[8] maintain their 1 : 1 ratio and their original peak separation of 1.1 eV, while the new peaks [peaks 3 and 4 in Figure 3(b)] maintain a 1 : 1 area ratio at a slightly larger separation of 1.6 eV. Since the original peaks represent oxygen at 2 energetically different sites, and the ratio is maintained on degradation, this indicates that each site has an identical propensity for degradation; the 2 new peaks evidently represent energetically different, but structurally similar, degradation products. It is difficult to identify these degradation products because (1) all bonds undergo scission at equal rates, and (2) both O and F are continually lost. It is clear, however, that the degradation products have higher electron densities (that is, lower binding energies) than the original environments; they may involve free radicals.

Because O was lost at a rate identical to that of F, and O loss requires the breaking of 2 bonds, ether linkages appear to be twice as susceptible to X-ray scission as are C—F bonds. Since the newly formed O1s peaks [peaks 3 and 4 in Figure 3(b)] indicate oxygen still retained in the polymer, their presence demonstrates an intermediate stage in the degradation process, where only 1 bond is broken.

F1s spectral analysis reveals neither new peak formation nor any shifts in peak binding energies. The 3 component peaks [peaks 1–3 in Figure 3(c)], due to CF_2, CF_3, and CF in order of decreasing binding energies, retain the 1 : 3 : 1 ratio of the original, undegraded material, again indicating that each F site has an equal propensity to degrade.

The following picture emerges: all bonds of any 1 element have the same susceptibility to X-ray degradation. While O and F are lost in identical amounts at any dose, O must break 2 bonds to do so, while F, only 1. This means that oxygen has a ($\sim 2\times$) greater susceptibility to degrade. O may also degrade without loss, by breaking only 1 of its bonds, as evidenced by the new peaks in the degraded O1s spectrum.

The homolytic scission of bonds under X-irradiation produces free radicals. Electron spin resonance studies[9] show them to be stable for long periods of time; they are capable of abstraction reactions, which give rise to more stable free radicals, as well as of reaction with other free radicals, such reactions having extremely low activation energies. It is thus surprising that new CF_3 groups are not formed, and we can offer no explanation at this time.

The intensities of X-ray induced mass spectral fragments from Teflons PTFE, FEP, and PFA all reached their maxima shortly after X-ray exposure began,[1,2] after which they all steadily decreased; this was taken[1,2] to indicate the formation of a crosslinked surface layer impervious to these fragments. In the present case, however, the intensities of fragments from Teflon AF1600 began to decrease immediately; this is taken to mean that the higher susceptibility of this material to X-ray degradation causes the rapid onset of extensive surface crosslinking.

CONCLUSIONS

The degradation of Teflon AF1600 under X-ray exposure occurs with insignificant C loss; both O and F are lost in equal amounts at any doses between 60 W/5 min to 240 W/40 min, although O must break twice as many bonds as F to do so. Oxygen also

degrades without loss when only 1 bond is broken. The free radicals that remain participate in reactions leading to graphitization and crosslinking. Mass spectral analysis is consistent with the fact that Teflon AF1600 is highly susceptible to X-ray degradation, quickly forming crosslinks.

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