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Positron annihilation spectroscopic studies of fluorinated ethylene propylene copolymer-*g*-polystyrene

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Abstract

Polystyrene was grafted onto FEP by simultaneous irradiation using a ^{60}Co γ-irradiator. Graft copolymers of different degree of grafting were obtained by varying the irradiation dose. Positron lifetime measurements were carried out on FEP and the grafted samples. A systematic decrease in *o*-Ps lifetime and intensity with grafting is seen indicating a decrease in pore size as well as total free volume fraction. Temperature dependent (95–250 K) S-parameter measurements in FEP showed saturation of free volume fraction at temperatures corresponding to the β-relaxation, the onset of which is seen at 150 K. Coincidence Doppler broadening results indicate increase in specific volume in the crystalline region of the polymer. Dynamic mechanical analysis (DMA) showed that tan δ value for β-relaxation of the samples decreased with increasing graft percentage. The results are discussed.

Keywords: Dynamic mechanic analysis; Free volume; Molecular motion

1. Introduction

Radiation induced graft copolymerization of monomers onto fluorine containing polymers has been widely studied to produce membranes for various purposes, such as in separation science and electrochemical applications [1–6]. Grafting of vinyl and acrylic monomers onto poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) films have been studied by several researchers [7–13]. Radiation induced graft copolymerization introduces, structural changes in the starting polymer matrix. This leads to significant changes in the microstructure and morphology of the membranes that affect the overall membrane properties. The incorporation of side chain grafts, represented by the degree of grafting, varies with the reaction parameters, which influences the membrane properties to a large extent. The incorporation of side chain grafts exerts a dilution effect on the grafted film by increasing the amorphous content at the expense of crystallinity of the semi crystalline base fluoropolymers. The structure and the physical properties of the matrix change drastically during the preparative stages. Hence thorough characterization of the membrane in each stage is of paramount importance. The structural changes in the preparative stages of the membrane have been exhaustively studied [14–16]. Gupta et al. [17] have investigated the structural changes on proton exchange membranes, obtained by radiation grafting of styrene onto FEP films and subsequent sulfonation. They have attributed the decrease in the crystallinity of the grafted samples to cumulative effect of the decrease in the crystalline/amorphous ratio due to incorporation of amorphous side chain grafts.

Positron annihilation lifetime spectroscopy (PALS) has found increasing applications in studying molecular arrangement of polymeric materials [18–20]. In polymers a large fraction of positrons form positronium atom (Ps), the bound state of a positron and an electron. The positronium can be either in *para* (spin 0) or *ortho* (spin 1) state. The positron annihilation studies rely on the inherent localization of positron/positronium in defects or free volumes in solids and

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subsequent annihilation with electrons from the surroundings. Both static as well as dynamic free volume holes due to molecular motion can be probed provided the time scale for chain movement is in the order of nanosecond, which is the lifetime of *ortho*-positronium (*o*-Ps). The *o*-Ps lifetime has a strong correlation with the size of the free volume. The annihilation of *o*-Ps in the spherical free volume hole can be described by simple quantum mechanical model of spherical potential well with an electron layer thickness of ΔR. The semi empirical relation between the radius of the free volume hole, R and *o*-Ps lifetime is given by [19]:

$$\frac{1}{\tau_3} = \lambda_3\left(\mathrm{ns}^{-1}\right) = 2\left(1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right) \qquad (1)$$

where $R_0 = R + \Delta R$ and $\Delta R = 1.66$ Å. The product of the hole volume and the *o*-Ps intensity is proportional to the free volume fraction for chemically similar samples.

In the present manuscript PALS is used to characterize FEP and FEP-*g*-PS samples. The results have been correlated with tan δ for β-relaxation of the samples obtained from dynamic mechanical analysis. There seems to be a tangible correlation between the PALS parameters and DMA results. In addition, temperature dependent Doppler broadened annihilation measurements have been carried out from 95–250 K to examine the evolution of free volume across the β-transition in virgin FEP sample.

2. Experimental

Teflon-FEP film (75 μm thickness) was obtained from Du Pont, USA. Styrene (E-Merck) was freshly distilled before use.

2.1. Graft copolymerization

FEP film (5 × 5 cm) with 75 μm thickness was washed with acetone and dried in oven at 50 °C before use. Weighed amount of FEP in varied percentage of monomer (10–35%) in benzene was irradiated for different period at a dose rate of 4.92 kGy/h to obtain grafted films with varied degree of grafting. Irradiation was carried out in a gamma chamber 5000 provided by BRIT, India. The grafted film was freed from homopolymer by Soxhlet extraction with toluene and dried to constant weight. Grafting percent was determined from the weight change between original and grafted films. The virgin sample and representative grafted samples were characterized by XRD technique.

2.2. Dynamic mechanical analysis

Measurement of dynamic mechanical properties for both FEP and FEP-*g*-PS samples was conducted at a frequency of 1 Hz and at a heating rate of 5 °C/min on a Rheometric Scientific DMTA. The temperature range of scanning was from 153 to 423 K.

2.3. Positron annihilation measurements

Positron annihilation lifetime measurements of the membrane samples were performed with a ^{22}Na positron source in sandwich configuration using a fast–fast coincidence spectrometer. A stack of six films was used on either side of the source to ensure complete annihilation of positrons in the sample. The time calibration of MCA was 50 ps/channel. The time resolution of the positron lifetime spectrometer measured for γ-ray of ^{60}Co was 300 ps. The lifetime spectra, typically with 10^6 counts, were analyzed using PATFIT program [21].

For temperature dependent studies on FEP, the sample in sandwich geometry with positron source was mounted on closed cycle helium refrigerator (APD Cryogenics). Simple Doppler broadening spectra were acquired in the range of 70–250 K using 10% HPGe with energy resolution of 2.1 keV at 1333 keV γ-ray of ^{60}Co. The positron lifetime and two-detector coincidence Doppler broadening (CDB) spectra were acquired at few temperatures in the range of 70–250 K. For CDB measurements two HPGe detectors located at an angle of 180° relative to each other were used. The difference in energies of the two annihilation γ-rays i.e., $E_1 - E_2 = \Delta E$, is expressed as cP_L, where P_L is the longitudinal momentum component of the positron–electron and c is the velocity of light. The momentum distribution (ΔE) spectra were obtained by taking the coincidence events between 1022 ± 2.8 keV in the $E_1 + E_2$ axis. The details of the CDB system are described elsewhere [22]. Each CDB spectrum was normalized to unit area and divided by a reference spectrum (silicon) to get the ratio curve.

3. Result and discussion

FEP is a random copolymer of tetrafluorethylene and hexafluoropropylene. It has a structure similar to polytetrafluoroethylene except that a perfluromethyl group replaces an occasional fluorine atom. Fig. 1a shows the effect of total dose on grafting percentage of styrene onto FEP. It is seen that the grafting percentage varies linearly with increasing total dose of exposure. Similar trends in grafting results have been reported earlier [9]. The XRD pattern of virgin and grafted samples are shown in Fig. 1b. The XRD pattern was analyzed by fitting the individual peaks (crystalline and amorphous as the case may be) and the fractional area under the crystalline peak was calculated. The two broad amorphous peaks and the narrow crystalline peak used are indicated in Fig. 1b. The fractional area under the crystalline peak were seen to be 17.6, 17.4 and 18.3% for virgin FEP, 5.2 and 16% grafted samples, respectively. This indicates that there is no significant change in crystallinity upon grafting.

Fig. 2 represents the temperature dependence of tan δ for FEP and FEP-*g*-PS samples. It is seen that FEP has two transitions at 153 and 363 K which may be attributed to β-relaxation and α-relaxation, respectively. Dynamic mechanical analysis of FEP with varying content of hexafluoropropylene has been reported by Sacher [23]. According to Sacher, rise in tan δ at the lowest temperature is an indication of additional peak below

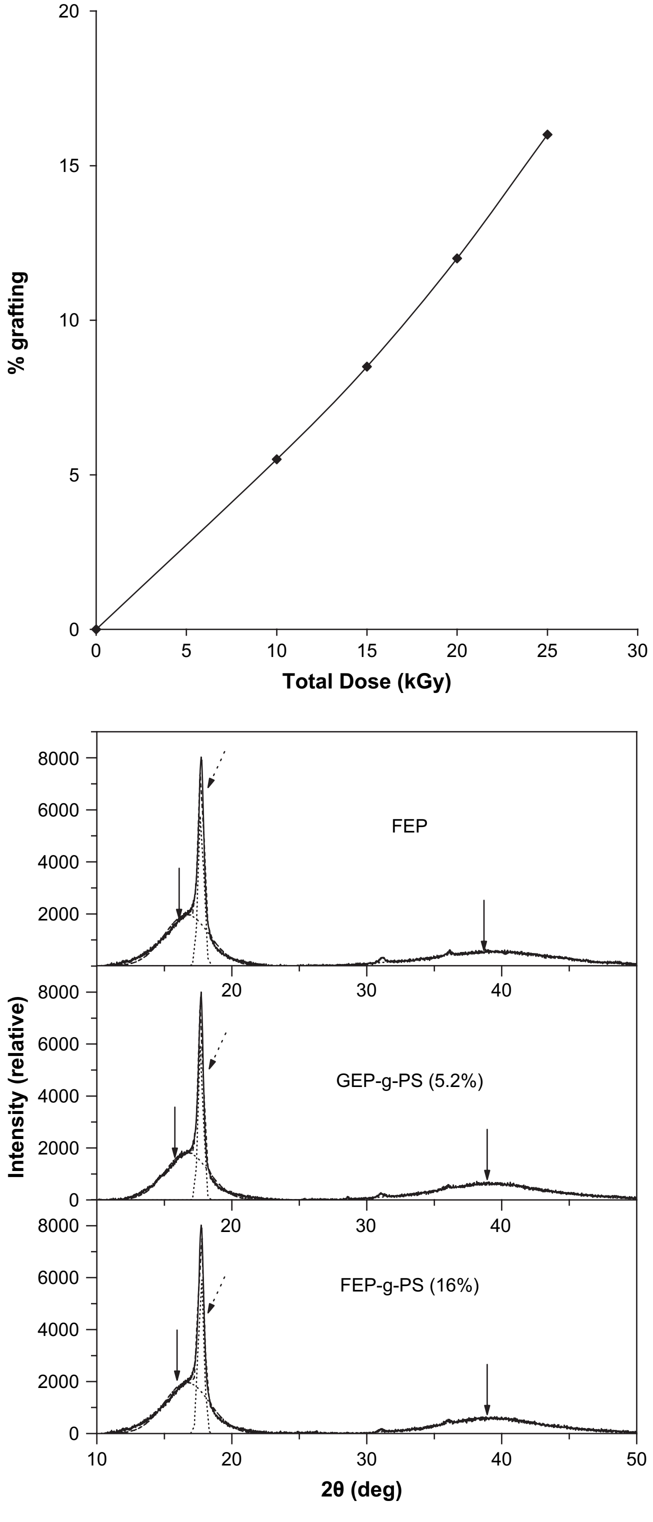

Fig. 1. (a) The dependence of percentage grafting on the irradiation dose. (b) The XRD pattern of FEP and FEP-*g*-PS membranes. The dotted curves are the fit to individual crystalline (dotted arrow) and amorphous (solid arrow) peaks after deconvolution.

the temperature of liquid nitrogen. Eby and Wilson [24] also report such a relaxation in FEP resin, which is attributed to the transition to the motion of side groups.

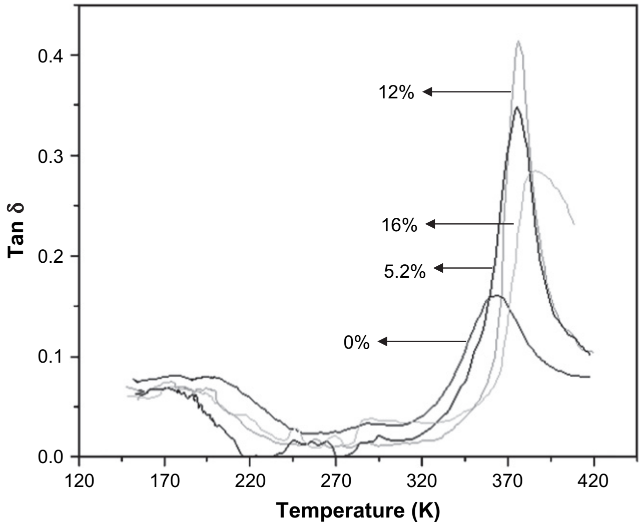

Fig. 2. The dynamic mechanical analysis (DMA) data for FEP and FEP-*g*-PS membranes.

In the present case a hump has been noticed around 170–200 K whose onset might have started from a still lower temperature. In general, a decrease in the plateau of tan δ is seen for grafted polymers as compared to virgin FEP. The tan δ peak due to α-relaxation is seen to undergo a shift towards higher temperature with introduction of polystyrene ($T_g \sim 373$ K) side chain grafts. Single α-relaxation peak indicates that there is no phase separation upon grafting. With increasing percentage of grafting not only the magnitude of tan δ corresponding to α-relaxation increases but the peak is also seen to shift to higher temperature.

The temperature dependent *S*-parameters (shape parameter) were evaluated from the Doppler broadening spectra of FEP are shown in Fig. 3. The temperature dependent lifetimes (τ_3) and intensities (I_3) measured at few select temperatures are shown in Fig. 4. With increase in temperature, *S*-parameter initially increases up to 150 K, attains a constant value till 190 K followed by a monotonous increase. *S*-parameter is

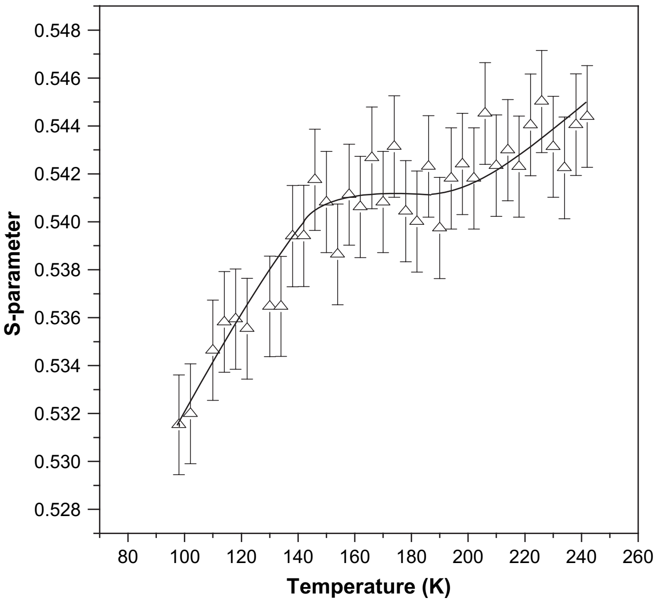

Fig. 3. Temperature dependence of *S*-parameter in virgin FEP.

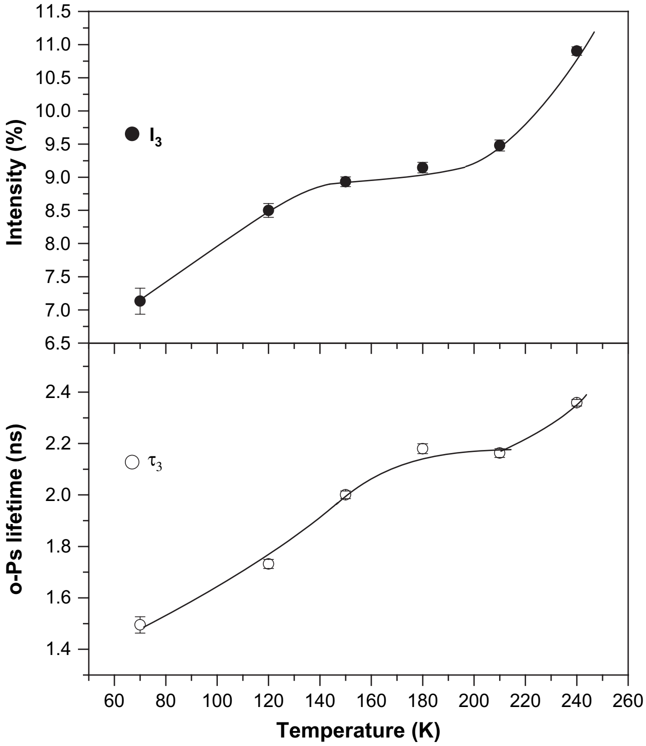

Fig. 4. The temperature dependent lifetimes and intensities in virgin FEP. The lines are eye guide only.

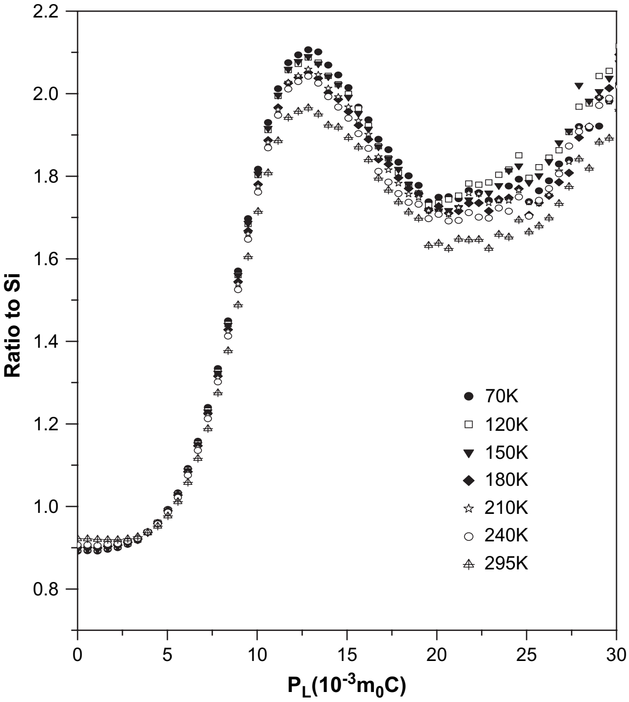

Fig. 5. The ratio curves from the coincidence Doppler broadening (CDB) measurement on FEP at different temperatures.

the measure of *p*-Ps fraction in the matrix, which in turn is proportional to the free volume fraction. In any polymer matrix, free volume increases with temperature thus the *S*-parameter is expected to increase monotonically with temperature. This is consistent with our lifetime data which shows that both τ_3 and I_3 increase with temperature indicating an increase in the number density and size of free volume holes. In the present case, a plateau in the *S*-parameter curve (Fig. 3) was seen corresponding to β-transition which is also reflected in τ_3 and I_3. FEP is a polymer with $-CF_2-$ backbone and CF_3 moieties as the side groups. Generally low temperature transitions are Arrhenius type and it may be suggested that the transition starts around 150 K and it persists up to 190 K. In other words, at 190 K all the concerned segments are in motion corresponding to its activation energy. The start of β-relaxation, which is associated with the motion of small segments in the main chain thus starts at 150 K. DMA studies identify the β-relaxation temperature to be 170 K. It may be noted that *S*-parameter measurements give information about the relaxations in the amorphous region only. To further characterize this polymer, we carried out coincidence Doppler broadening studies, which measures the free positron overlap with fluorine atoms. The ratio of CDB spectra with silicon for a range of temperature from 70 to 240 K is shown in Fig. 5. The peak at 12 m_0c units can be ascribed to the annihilation of positrons with fluorine core electrons. A systematic decrease in the peak with temperature is indicative of the decrease in overlap of positron wave function with the fluorine core electrons. It is tempting to describe this to an increase in the specific volume of the polymer in the crystalline region with increasing temperature that leads to localization of positron wave function and consequently decrease in its overlap with fluorine core electrons. However, it may be mentioned that increase in I_3 and *S*-parameter with temperature might influence the CDB profile as seen in the present case.

The lifetime parameters of *o*-Ps lifetime (τ_3) and intensity of the long-lived component for FEP and FEP-*g*-PS samples at room temperature are shown in Table 1. It is seen that FEP has *o*-Ps lifetime of 3.54 ns. Upon grafting, the *o*-Ps lifetime decreases. The I_3 (intensity) for FEP is 22.84%. The intensity is found to decrease with increasing graft percentage. With 16% grafting the value comes down to 17%. The long-lived component, very sensitive to structural changes in the polymer, is attributed to *o*-Ps pick-off annihilation in free volume. The decrease in *o*-Ps lifetime with grafting indicates that the average free volume hole size decreases upon grafting of polystyrene (see Table 1). In the presence of chemical effect of the polymer on positronium, Eq. (1) may not be valid leading to improper evaluation of free volume hole size and fraction. Bamford et al. [20] have studied the effect of fluorine content on the *o*-Ps lifetime of fluoropolymers. They have observed that the *o*-Ps lifetime decreases with increasing fluorine

Table 1
The positron annihilation lifetime data of FEP and polystyrene grafted membranes

% Grafting in FEP	τ_3 (ns)	I_3 (%)	Free volume radius in Å (from Eq. (1))
Virgin (0)	3.52 ± 0.01	22.84 ± 0.01	3.97
5.2	3.24 ± 0.01	18.33 ± 0.06	3.79
12	3.03 ± 0.01	17.22 ± 0.07	3.65
16	3.01 ± 0.01	17.00 ± 0.10	3.64

content of the copolymers based on butyl methacrylate–heptafluorobutylmethacrylate. This effect has been attributed to the high electronegativity of F atom and the possible formation of (F^-e^+) complexes, which reduces the number of positrons available for *o*-Ps formation. In the present case, as the grafting increases, the F content decreases and I_3 should have increased, contrary to what is observed. This indicates that the chemical effects are negligible and the observed changes are due to change in the free volume structure upon grafting. The grafting by irradiation could change the crystallinity of the polymer leading to changes in the *o*-Ps intensity and lifetime. In the present case, the effect of grafting on crystallinity was found to be insignificant from XRD data. Therefore, the decrease in lifetime and intensity with grafting can be ascribed to reduction in free volume hole concentration and size. Another factor, which could influence the *o*-Ps lifetime and intensity, is the relaxations prevalent in a polymer matrix, which affects the molecular packing in the glassy phase. The reduction of free volume fraction with grafting indicates that the grafting leads to closer packing that might influence the T_g as discussed in the latter section.

There has been an argument whether microcavities probed by *o*-Ps are pre-existing interstitial spaces among the frozen polymer chains or bubbles formed around Ps [25]. Kobayashi et al. [25] have reported that *o*-Ps bubbles are formed in glassy polymers as in liquids. On the other hand judging from the effect of vapour sorption on τ_3 and I_3 for a series of polyimides, Ito et al. [26] have claimed that the microvacancies probed by *o*-Ps are due to pre-existing interstitial spaces among frozen polymer chains. Further, Tanaka et al. [27] have shown from a study based on a series of polyimides that the polyimides with a much higher glass transition temperatures (T_g) show larger τ_3 than glassy polymers with lower T_g, confirming the findings of Ito et al. [26] However, in the present case with increasing degree of grafting, although T_g is increased (as evidenced from DMA results) there has been a decrease in τ_3. According to Stuart–Briegleb model, presence of CF_3 group in FEP causes a localized defect in the molecular conformation [24]. Thus the defects, which perturb adjacent molecular rows, resemble the interstitial defect found in atomic solids. In general, weak molecular interaction, bulky substituents are apt to cause less-efficient packing of the polymer chains and result in large free space holes. Such defects could be reasonably assumed to be the sites for positronium trapping, which in turn would contribute substantially to the free space available in the graft copolymer and FEP [28]. FEP is a flexible random copolymer showing maximum τ_3 and I_3 due to large free volume. On grafting rigid polystyrene moiety onto FEP the free volume is decreased leading to closer packing, which is responsible for increase in T_g with grafting. Further it is seen that β-relaxation mainly due to CF_3 group, manifested by magnitude of tan δ peak at sub-ambient temperature is also decreased on introduction of polystyrene segment. The relaxation intensity decreases due to the inhibited chain movements upon grafting. The same is reflected in the decrease in tan δ for the β-relaxation process. The consequence of hindered chain movement is expected to produce smaller quantity of dynamic free volume holes. It may be mentioned that the molecular motion corresponding to β-transition will persist even at room temperature. This is possibly the reason why the free volume fraction is seen to decrease with grafting as seen from PALS data.

4. Conclusion

Positron lifetime measurements reveal reduction of free volume fraction with grafting indicating closer packing. This is reflected in the increase in T_g with grafting as seen in DMA result. The reduction in free volume fraction with grafting has also been correlated with the hindered β-relaxation seen as reduction of tan δ for grafted polymers. The temperature dependent *S*-parameter data reveals the onset of β-relaxation in FEP at 150 K that persists up to 190 K. Temperature dependent lifetime and intensities are consistent with the measured *S*-parameter with temperature.

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