

Molecular Dynamics in Semifluorinated-Side-Chain Polysulfone Studied by Broadband Dielectric Spectroscopy

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ABSTRACT: The molecular dynamics of a set of polysulfone polymers have been studied with broadband dielectric spectroscopy. The materials comprise main-chain polysulfones attached to semifluorinated (SF) oxydecylperfluorodecyl side chains. Through the analysis of the dielectric data together with information from differential scanning calorimetry and small-angle X-ray scattering, it can be shown that the oxydecylperfluorodecyl side chains are microphase-separated and form nanodomains with an independent dynamic glass-transition (δ_{SF}) relaxation. In addition to the α process (which is the glass transition of the main chain), other relaxation processes can be detected with Arrhenius-type activation

energies of $38\text{--}90 \pm 2$ kJ/mol. A γ_{SF} process, observed only in polysulfone with SF side chains, can be assigned to librational fluctuations of the perpendicular component of the fluoroalkyl group. A γ_B relaxation reflects fluctuations of the dipole moments (O=S=O and C=O) of the polymer, whereas a β process, with high activation energies ($>70 \pm 2$ kJ/mol), is assigned to packaging defects in the material. A detailed description of the processes is provided together with a proposed relaxation scheme. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 201–207, 2007

Key words: dielectric properties; molecular dynamics

INTRODUCTION

Polymers with semifluorinated (SF) side chains have been investigated for many years. The term *SF* here stands for chemical segments consisting of alkyl and perfluorinated alkyl parts, which are connected by a covalent C—C linkage, having the general structure $X_1\text{--}(\text{CH}_2)_n\text{--}(\text{CF}_2)_m\text{--}X_2$. Alkyl and perfluoroalkyl chains are thermodynamically not miscible with each other. Such compounds are characterized by strong microphase separation resulting in the formation of typically layerlike, well-organized, solid-state structures.^{1,2} If the fluorinated segments are attached to polymeric backbones, the microphase separation of the fluorinated segments can often be maintained if we assume that the number of C atoms in the SF segments (in both the alkyl and perfluoroalkyl parts) is above a critical value. This has been demonstrated for a set of polymers with various polymer backbones and different fluorinated

side chains, such as fluorinated polystyrene,³ polystyrene–polyisoprene diblock copolymers,⁴ poly(methyl methacrylate),⁵ polyesters,^{6–9} polysulfones (PSUs),¹⁰ and segmented polyester–PSU block copolymers.^{11,12} In special cases in which the SF side chains are long enough, the ordered solid state results in the formation of a well-organized surface structure, resulting in polymeric materials with extremely low surface free energy.^{13–16}

Materials consisting of perfluoroalkyl groups offer a wide range of interesting properties, such as wettability, durability, chemical resistance, and thermal stability.¹⁷ The hydrophobic nature (i.e., very low solid surface tension) of fluoropolymers is used to develop coatings with low wetting behavior. Such modified surfaces can be used, for example, as soil release agents on different substrates and also to prevent the attachment of microorganisms such as algae and other marine life. Although wettability (water/oil repellency) is confined to the surface, the need to have mechanically stable materials in the bulk coupled with excellent surface properties is vital.

In the past few years, perfluorinated side chains have been investigated in acrylic,^{18,19} methacrylic,¹⁸ styrenic,²⁰ polyester,^{8,21} maleimide,²² and block copolymer backbones.^{12,23} The focus has been mainly on understanding the surface properties (dewetting, surface free energy, surface tension, etc.) of the SF side chains. More recent work has been devoted to obtaining additional understanding of the underlying

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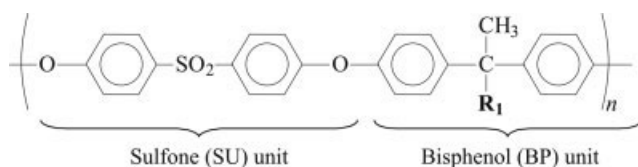


Figure 1 Chemical structure of the PSU polymer. Side chain R_1 is terminated with either $-\text{CH}_3$ (the PSU backbone) or $-(\text{CH}_2)_2-\text{COO}-m$, m being $\text{H}(\text{COOH-PSU})$ or $-(\text{CH}_2)_{10}-(\text{CF}_2)_9-\text{CF}_3$ (SF-PSU).

dynamics of the materials, especially the backbone. A few investigations have been conducted with dendrimers,^{24–26} polyesters,²⁷ and poly(styrene-*b*-butadiene)²⁸ as backbones with SF side chains. It is the intention of this work to extend the studies to other backbone systems. The choice of PSU as a backbone lies in the fact that the polymer has good mechanical properties (high toughness, high stiffness, and excellent oxidative and thermal stability)²⁹ with a high glass-transition temperature ($T_g > 180^\circ\text{C}$). When PSU is combined with SF side chains, T_g drops significantly (by more than 60°C),¹¹ and the surface properties of PSU are simultaneously modified for possible use in medical implants and membranes. The principal chemical structure of the investigated polymers is outlined in Figure 1.

Three different materials have been investigated: a PSU main chain with no side chains (PSU backbone), a PSU main chain with COOH-terminated side chains (COOH-PSU), and another PSF with SF side chains (SF-PSU).

EXPERIMENTAL

The synthesis and characterization of the PSUs have been published elsewhere.^{10,30} To prepare the samples for broadband dielectric spectroscopy measurements, the materials were heated *in vacuo* until they melted and were kept between two brass electrodes (diameter = 10 mm) with 50- μm glass-fiber spacers. Isothermal dielectric measurements were performed in the frequency range from 0.1 Hz to 10 MHz with a high-resolution dielectric alpha analyzer (Novocontrol GmbH, Hundsangen, Germany). Dielectric spectra were obtained, starting from the highest temperature in the range of 500–120 K in steps of 2 K. In this temperature range, the polymers were found to be thermally stable. The sample temperature was controlled by a gas heating system based on the evaporation of liquid nitrogen (Quatro, Novocontrol) with a precision of ± 0.02 K. The details of the setup can be found in Ref. 31.

To analyze the dielectric results, the dielectric loss (ϵ'') was fitted to the superposition of a conductivity contribution with one or two relaxation functions according to Havriliak and Negami.³²

$$\epsilon''(\omega) = \frac{\sigma_0 a}{\epsilon_0 \omega^s} + \text{Im} \left[\frac{\Delta\epsilon}{[1 + (i\omega\tau)^\beta]^\gamma} \right] \quad (1)$$

The first part on the right-hand side of the equation describes the conductivity, whereas the second part (that is added) is the dipole contribution to the ϵ'' function. In this notation, one relaxation process is assumed. β and γ are dimensionless parameters describing the symmetric and asymmetric broadening of the distribution of the relaxation times, respectively, with $0 < (\beta, \beta\gamma) \leq 1$. For $\beta = \gamma = 1$, eq. (1) coincides with the ideal Debye relaxation. ϵ_0 is the permeability in free space (8.854×10^{-12} F/m), and σ_0 is the direct-current conductivity. Exponent s equals 1 for ohmic behavior, whereas deviations ($s < 1$) are caused by electrode polarization or Maxwell–Wagner polarization effects (ω is the angular frequency and a is a factor defined in units of Hz^{s-1} for $s \neq 1$). From the fits according to eq. (1), relaxation rate $1/\tau_{\text{max}}$ (where τ_{max} is the maximum relaxation time) can be deduced, which is determined at the frequency of the maximum ϵ'' value for a given temperature. Within the experimental uncertainty, eq. (1) describes our data well. The term $\Delta\epsilon$ is the relaxation strength, which can be used to estimate the value of the net dipole moment (μ) taking part in the relaxation process. This can be done through the Kirkwood–Fröhlich theory^{33–36} as follows:

$$\Delta\epsilon \approx n \frac{\mu^2}{3k_B T \epsilon_0} g_{\text{FK}} \quad (2)$$

where g_{FK} represents the Kirkwood–Fröhlich dipole correlation factor, n is the dipole density, k_B is the Boltzmann constant, and T is the absolute temperature.

RESULTS AND DISCUSSION

Figure 2 shows ϵ'' as a function of frequency for SF-PSU at temperatures between 130 and 340 K.

The dielectric data for SF-PSU are characterized by one ϵ'' peak (γ_{SF}) at temperatures below 200 K [Fig. 2(a)]. Above 200 K, two more processes, β and δ_{SF} [Fig. 2(b)], can be observed in addition to the dynamic glass-transition (α) relaxation (Fig. 3). The PSU backbone and COOH-PSU exhibit an additional γ_B process at temperatures below 250 K (Fig. 4). Figure 5 shows ϵ'' for COOH-PSU fitted with eq. (1). The fitting parameters are given in Table I.

In Figure 6, the relaxation times [obtained from the Havriliak–Negami (HN) fitting procedure] are plotted against the inverse temperature for all the PSU polymers investigated. All the investigated materials exhibit α and β relaxations. Additional processes, that is, γ_{SF} , γ_B , and δ_{SF} , can be detected in the different polymers, depending on the chemical composition of the main chain and side group R_1 (Fig. 1). A detailed analysis of each relaxation process is given next.

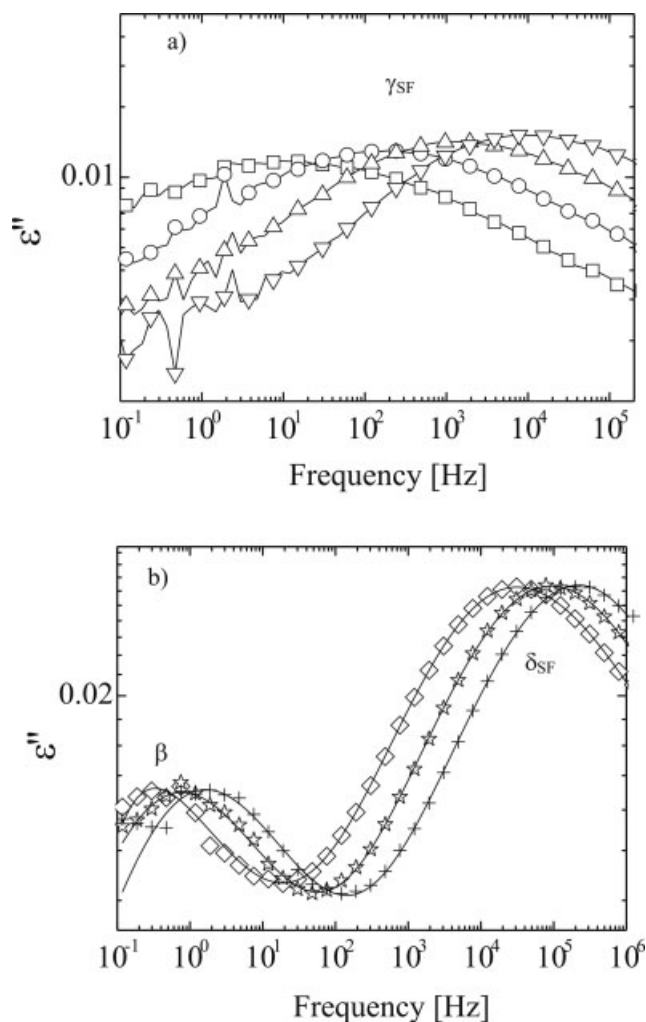


Figure 2 Frequency dependence of ϵ'' of SF-PSU at different temperatures: (\square) 130, (\circ) 140, (\triangle) 150, (∇) 160, (\diamond) 316, ($*$) 326, and ($+$) 336 K. The continuous line in part b is fit to the data according to the HN function [eq. (1)].

α Relaxation

This is the dynamic glass-transition process of the polymer. The temperature dependence of the relaxation time (Fig. 6) can well be described by the empirical Vogel–Fulcher–Tammann (VFT)³⁷ function:

$$\tau = \tau_0 \exp \left[\frac{DT_0}{T - T_0} \right] \quad (3)$$

where D is the fragility parameter³⁸ and T_0 is the Vogel temperature or ideal glass-transition temperature. The calorimetric glass-transition temperature (T_g) is conventionally defined as the temperature at which the relaxation time is 100 s.³⁹ By the extrapolation of the VFT dependence to $\log(1/\tau_{\max}) = -2$, the T_g 's of the compounds can be estimated. The PSU backbone has a T_g of 185°C, which increases to 190°C when COOH side chains are introduced and decreases to 120°C when the backbone is attached to

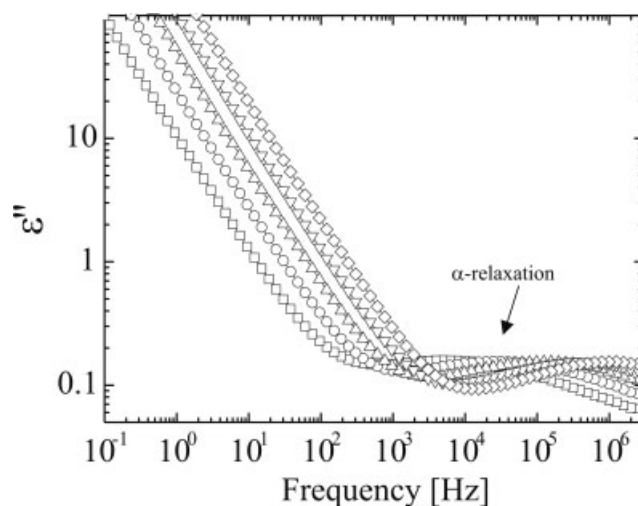


Figure 3 Frequency dependence of ϵ'' of SF-PSU, showing α -relaxation peaks at (\square) 450, (\circ) 460, (\triangle) 470, (∇) 480, and (\diamond) 490 K.

SF side chains.¹¹ The values obtained from the estimates according to eq. (3) are in good agreement. The fact that the T_g 's of the PSU backbone and COOH-PSU correspond to those estimated proves that the α relaxation reflects the dynamic glass transition of the main chain.

δ_{SF} Relaxation

This process is observed in SF-PSU only. Similarly to the α relaxation, the temperature dependence of the relaxation times can be described by the VFT law, indicating that the δ_{SF} process is also a glass-transition relaxation. From X-ray scattering characteriza-

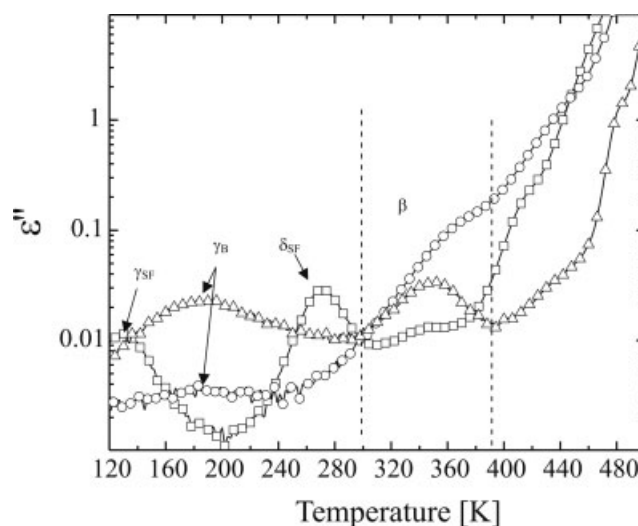


Figure 4 Temperature dependence of ϵ'' of (\square) SF-PSU, (\triangle) COOH-PSU, and (\circ) the PSU backbone at 6 Hz. For clarity, only the γ_{SF} , γ_B , δ_{SF} , and β -relaxation peaks are indicated.

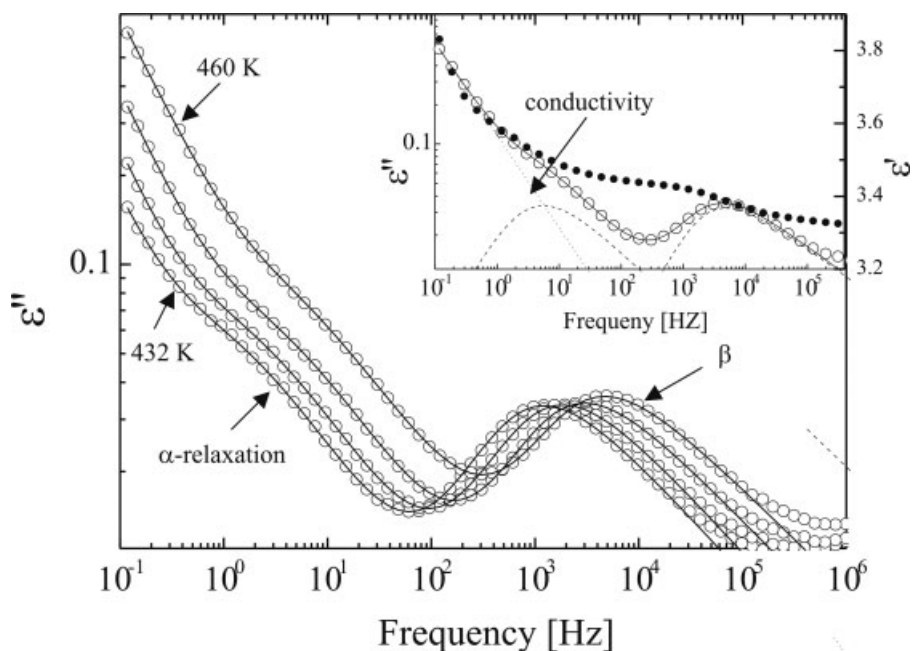


Figure 5 Frequency dependence of ϵ'' of COOH-PSU, showing the β - and α -relaxation peaks at 432, 440, 450, and 460 K. The inset shows the deconvolution of the two processes with eq. (1) (see the fitting parameters in Table I). The fitting technique enables the separation of the conductivity contributions from the relaxation processes. The filled symbols show the real part of the dielectric function, ϵ' .

tion,^{10–12,27,40} the SF side chains are found to microphase-separate, forming nanodomains separated from the main chain. The δ_{SF} relaxation can therefore be considered an independent glass transition of the SF domain. This assignment is in accordance with similar relaxations in other SF polymers.^{27,28,41}

β Relaxation

This process can be observed in all the PSUs investigated and therefore can be traced to backbone fluctuations. Its temperature dependence on the relaxation time can be defined according to the Arrhenius law:

$$\tau = \tau_0 \exp \left[\frac{-E_A}{RT} \right] \quad (4)$$

where E_A denotes the activation energy, τ is the relaxation time, τ_0 ($= 1/2\pi\nu_0$) is a pre-exponential factor, and R is the universal gas constant. From the fits

according to eq. (4), the E_A values are 73 ± 2 , 75 ± 2 , and 90 ± 2 kJ/mol for SF-PSU, COOH-PSU, and the PSU backbone, respectively. The high E_A values are uncharacteristic of local dipole fluctuations⁴² and therefore indicate that possible nonlocal fluctuations are involved. The β relaxation can be correlated with a process usually observed at about 80°C at a frequency of 100 Hz in PSUs. The β peak is associated with packaging defects that are known to disappear after extended annealing.^{43,44}

γ_B Relaxation

Similarly to the β process, the activation plot of the γ_B relaxation can be described by the Arrhenius function with E_A values of 43 ± 2 and 46 ± 2 kJ/mol for COOH-PSU and the PSU backbone, respectively. The Arrhenius law dependence on low E_A values is characteristic of local fluctuating units.⁴² The assignments of this process, usually termed the relaxation peak

TABLE I
HN Fitting Parameters for Compound COOH-PSU (Shown in Fig. 5)

Temperature (K)	σ_0 ($\times 10^{-13}$)	a	HN fitting parameters							
			α				β			
			$\Delta\epsilon$	τ ($\times 10^{-2}$)	β	γ	$\Delta\epsilon$	τ ($\times 10^{-4}$)	β	γ
432	9.5 ± 1.0	0.8 ± 0.1	0.1 ± 0.1	19.1 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	0.1 ± 0.1	2.7 ± 0.2	0.9 ± 0.1	0.4 ± 0.1
440	13.9 ± 1.0	0.8 ± 0.1	0.1 ± 0.1	13.7 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	0.1 ± 0.1	1.7 ± 0.2	0.9 ± 0.1	0.4 ± 0.1
450	23.7 ± 1.0	0.8 ± 0.1	0.1 ± 0.1	7.3 ± 0.1	0.8 ± 0.1	0.7 ± 0.1	0.1 ± 0.1	1.1 ± 0.2	0.9 ± 0.1	0.4 ± 0.1
460	43.6 ± 1.0	0.7 ± 0.1	0.1 ± 0.1	5.0 ± 0.1	0.8 ± 0.1	0.6 ± 0.1	0.1 ± 0.1	0.7 ± 0.2	0.9 ± 0.1	0.4 ± 0.1

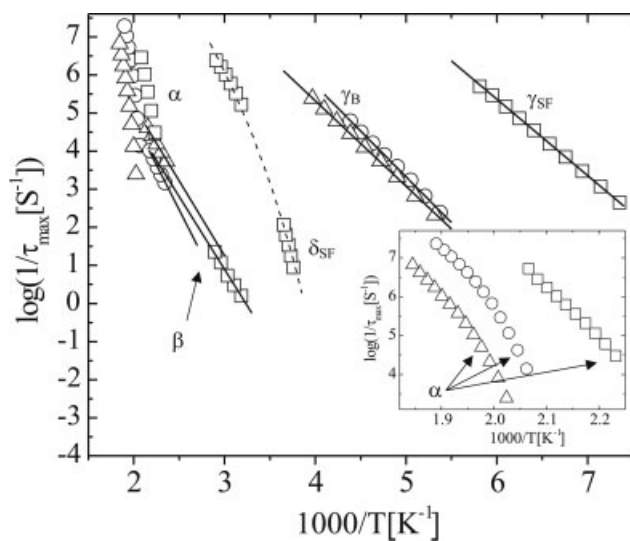


Figure 6 Temperature dependence of the relaxation times of all the PSU materials studied. (○) The PSU backbone and (△) COOH-PSU show a dynamic glass-transition (α) relaxation alongside two other processes (γ_B and β). (□) SF-PSU shows two new processes (γ_{SF} and δ_{SF}) while suppressing the γ_B process. The straight lines are Arrhenius fits [eq. (3)], and the dotted line is a guide to the eye to show the VFT time-temperature dependence of the relaxation time [eq. (4)]. The inset shows an enlargement of the α relaxation to show the VFT temperature dependence.

detected at -100°C at a frequency of 1 Hz in PSUs and polycarbonates, has been a subject of debate in the past, probably because of the different techniques applied. It has been assigned to fluctuations of the rings associated with the bisphenol (BP) side⁴⁵ or the ones on the sulfone (SU) side⁴⁶ and sometimes even a superposition of phenyl ring fluctuations.⁴⁷ The PSU backbone has two nonequivalent types of phenyl rings, namely, the BP unit and the SU unit (Fig. 1). It has been argued⁴⁸ with single-chain conformation analyses⁴³ that the SU unit is quite rigid and therefore the rings associated with the BP unit fluctuate faster than their SU counterparts. Dielectric spectroscopy probes the relaxation of a dipole moment, and the SU unit is the only polar unit in the PSU backbone. Hence, it can be deduced that the γ_B process is a relaxation of the SU (O=S=O) group in the PSU backbone (i.e., with $R_1 = \text{CH}_3$).

The addition of the COOH group to the backbone (sample COOH-PSU) seems to slow down the process. If the γ_B assignment is correct, then the introduction of the COOH unit should not affect the relaxation (COOH is attached on the BP side). This indicates that the assignment of the γ_B process for the two polymers is different. Figure 4 shows that the ϵ'' intensity of the γ_B peak at 184 K increases from 0.003 to 0.02 when the $-\text{CH}_3$ unit is replaced by the COOH termination at R_1 . This amounts to an approximately 10-fold increase in the ϵ'' intensity. The dielectric

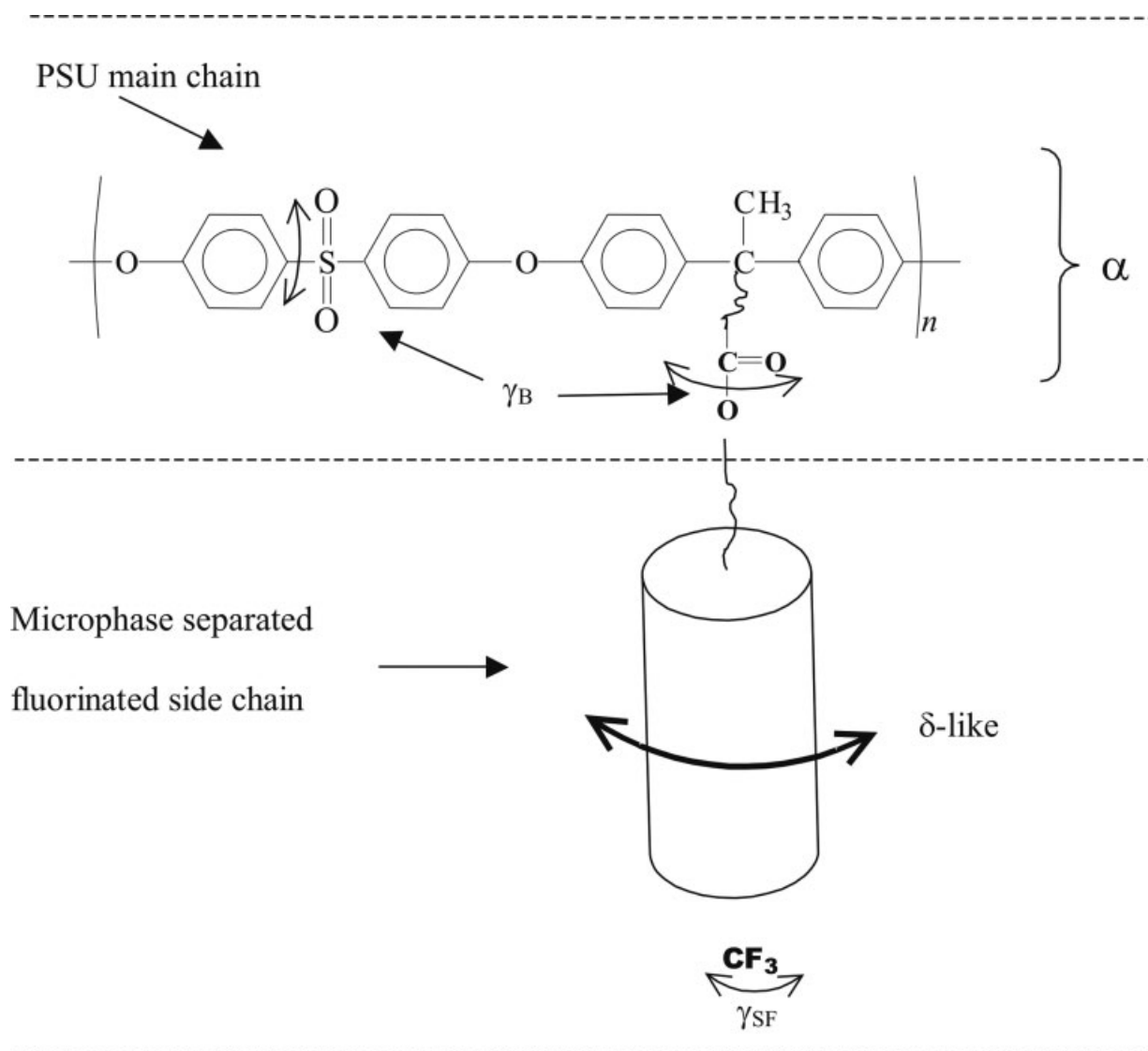
strength of the PSU backbone ($\Delta\epsilon_{\text{PSU}}$) is 0.075, whereas the dielectric strength of COOH-PSU ($\Delta\epsilon_{\text{COOH}}$) is 0.267, implying $\mu_{\text{COOH}} \approx 4\mu_{\text{PSU}}$ with eq. (2). From the literature,^{37,49} the effective dipole moments of the ester group range between 1.79 and 2.2 D, and that of SU (O=S=O) is 1.63 D. With these values, it can be seen that the ester group (formed by the C=O and the oxygen) is a stronger dipole and hence results in increased ϵ'' intensity. Multiplying the magnitude of the SU dipole by 4 gives a higher value than that of the ester group dipole. This suggests that the experimental $\Delta\epsilon_{\text{COOH}}$ value comes not only from the ester group relaxation but also from the fluctuation of the BP unit as a whole. On the basis of the analysis of the ϵ'' intensity, $\Delta\epsilon$, and μ , the γ_B process in COOH-PSU can be assigned to fluctuations of the BP unit. Because of the COOH side chain, the BP unit is bulky; therefore, the γ_B relaxation is slowed. It is also known from surface characterization¹⁰ that COOH-PSU is hydrophilic with high intermolecular interactions. Thus, its relaxations are shifted to higher temperatures in comparison with the PSU backbone.

γ_{SF} Relaxation

This process is observed only in the SF-PSU polymer. It occurs at temperatures below -100°C with a temperature dependence of the relaxation times described by the Arrhenius equation. Fluoroalkane units are generally described as stiff, rodlike segments with dipole moments parallel and perpendicular to the side chain axis.²⁶⁻²⁸ The parallel component (μ_{\parallel}) originates from the uncompensated end fluorine atom in the stiff alkyl parts of the perfluoroalkyl chain. The perpendicular component (μ_{\perp}) is a result of contributions from the ester group^{50,51} and a small fraction of the CF bonds (which amounts to ca. 16% of μ_{CF} due to the helical structure of the molecule²⁵). The dipole moment of the CF_3 end group is given as 2.3 D.^{52,53} From the Arrhenius fit, E_A is found to be 38 ± 2 kJ/mol, which is within the range of local dipole fluctuations (i.e., $E_A < 50$ kJ/mol).⁴² The fact that the γ_{SF} relaxation is observed in the polymer with the SF side chain and not in the others proves that the process originates from dipole fluctuations in the SF side chain. With previous the dipole and E_A analyses, the γ_{SF} relaxation is assigned to librational fluctuations of μ_{\perp} of the perfluoroalkyl side chain. The assignment is in accordance with our previous work.^{27,41} An illustration of the relaxation processes is shown in Scheme 1.

CONCLUSIONS

The molecular dynamics in SF-PSUs have been investigated with broadband dielectric spectroscopy. The polymers have been studied in the frequency range of



Scheme 1 Illustration of the relaxation processes observed in the studied PSUs.

0.1 Hz to 10 MHz and in the temperature range of 120–500 K. In general, five relaxation processes have been detected and analyzed. The γ_{SF} , γ_B , and β processes exhibit a temperature dependence of the relaxation times according to the Arrhenius law, with E_A in the range of $38\text{--}90 \pm 2$ kJ/mol. The γ_{SF} process is observed only in SF-PSU and is assigned to librational fluctuations of the perpendicular component of the dipole in the fluoroalkyl side group. The γ_B relaxation reflects fluctuations of the active dipole moments (O=S=O and C=O) of the polymer, whereas the β process, with high E_A values ($>70 \pm 2$ kJ/mol), is designated to packaging defects in the material. In all the polymers investigated, the dynamic glass transition (α relaxation) has been observed, and it corresponds to fluctuations of the polymer main chain. Additionally, because of microphase separation in the SF-PSU polymer, a δ_{SF} relaxation has been

detected that reflects the glass-transition dynamics of the fluoroalkyl nanodomains.

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