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Reorientational Dynamics of Polyethylene Glycol/PAMAM Dendrimer Blends

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Summary: The reorientational dynamics of dipoles in a series of blends of Polyethylene Glycol (PEG) and poly(amidoamine) (PAMAM) dendrimers were investigated by broadband dielectric relaxation spectroscopy (DRS). Measurements were performed over a wide range of frequency and temperature. Neat PEG exhibits three relaxation processes: the segmental process in the amorphous phase and two faster processes due to the localized motions in the amorphous regions and the rotation of hydroxyl end groups. Addition of dendrimers to the PEG matrix slows down the segmental process in the amorphous phase, but has no effect on the relaxation time of local processes in PEG. However, H-bonding which forms between the PEG oxygen and the amino groups on dendrimer surface is responsible for a shift of local processes in dendrimers to lower frequency. A detail analysis of the effect of temperature, concentration of dendrimers and molecular weight of PEG on the relaxation dynamics is offered.

Keywords: blends; dendrimers; dynamics; polyethylene glycol

Introduction

Polyethylene Glycol (PEG) is a water soluble, non-toxic and non-immunogenic polymer.[1,2] Due to these characteristics, PEG is of considerable interest for drug delivery applications. PEGylation, the process of covalent attachment of PEG chains to another molecule, reduces immunogenicity, increases the hydrodynamic size of the agent and provides water solubility to hydrophobic drugs. PEGylation of drugs, proteins, liposomes, and nanoparticles was shown to be an efficient approach for extending their circulation in the blood stream.[3] PEGylated dendrimers are of particular interest because of dendrimers' unique properties such as well defined and highly branched compartmentalized structure in the nanometer size range. The globular morphology of these polymers lends itself favorably to encapsulation of drugs within the interstitial space of their branches for subsequent targeted delivery.[4–8] In order to optimize PEGylated dendrimers for highly specialized tasks in complex environments, such as *in vivo* targeting, it is essential to acquire detailed knowledge of the molecular motions that underlie the physical response of these materials to applied external fields. As a precursor to the study of dynamics of PEGylated dendrimers, we have conducted an investigation of the dynamics of PEG/dendrimer blends.

The published reports on molecular dynamics of polymer/dendrimer blends are scarce.[9,10] Viscoelastic properties and phase behavior of 12-tert-Butyl Ester Dendrimer/Poly(methyl metacrylate) blends were investigated.[9] It was suggested that with increasing dendrimer content, the molecular mobility of PMMA chains increases as a result of an increase of the free volume of the system.

In this work we use Dielectric Relaxation Spectroscopy (DRS) to probe dynamics of PEG/dendrimer blends. DRS is a powerful

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tool for the study of dynamics and was used in our recent investigation on blends of PAMAM dendrimers with three linear polymers: poly(propylene oxide) and two poly(propylene oxide)/poly(ethylene oxide) block copolymers with different mol ratio (29/6 and 10/31).[10] In that work we discovered that dendrimers act as hard sphere diluents in the PPO matrix by decreasing the self association of PPO chains and promoting their mobility. In the 29PPO/6PEO copolymer no effect of dendrimer concentration on the relaxation time was observed, while in the 10PPO/31PEO copolymer dendrimers restrict chain mobility in the amorphous phase.

The principal objective of this study is to conduct a systematic investigation of the dynamics of PEG/dendrimer blends. Specifically, we wish to evaluate the effect of molecular weight of PEG on various relaxation processes and quantify the effect of concentration and temperature on blend dynamics. To the best of our knowledge this study marks the first published report on the dynamics of PEG/dendrimer blends as studied by DRS.

Experimental Part

Materials

Three samples of poly(ethylene glycol), PEG, with different molecular weight (2000, 10000 and 20000 Da) were obtained from Polysciences, Inc. Their melting temperature and degree of crystallinity are shown in Table 1.

Generation 3 poly(amidoamine) PAMAM dendrimer with ethylenediamine core and amino surface groups in methanol solution (20 wt.%) was obtained from Aldrich. Blends were prepared by mixing the desired amounts of PEG and dendrimer in methanol using a high speed stirrer. Samples were then placed in a vacuum oven for 7 days in order to remove the solvent completely. In the sample code for blends, symbol D stands for dendrimer and the number that follows describes the weight percent of dendrimer in the blend. The number after PEG is its molecular weight in kDa (kg/mol). For example, D18%-PEG10 represents a blend of dendrimer at 18% weight fraction and PEG with molecular weight of 10 kDa. All investigated blends and their codes are summarized in Table 2.

Table 1.
Melting temperature, degree of crystallinity and molecular weight of PEG samples.

Code	Tm (K)	Xc (%)	MW (Da)
PEG2	328	83	2000
PEG10	340	92	10000
PEG20	342	84	20000

Technique

Dielectric measurements were performed in the frequency range from 10^{-1} to 10^{6} Hz using Novocontrol α Analyzer, which was interfaced to computers and connected to a heating/cooling unit (modified Novocontrol Novocool System), that can control temperature from 173 K to 523 K with a precision of ±0.5 K. Samples were placed between two aluminum electrodes, 12 mm in diameter and with 50 μm spacing between them. Further details about our experimental facility for dielectric measurements are given elsewhere.[11]

Results and Discussion

The fundamental aspects of DRS are well established and hence will not be discussed here. However, the interested reader is referred to several excellent books and key

Table 2.
Investigated blends.

Description	wt % of dendrimers in blend	Code
D + PEG 2K	5	D5%-PEG2
D + PEG 2K	10	D10%-PEG2
D + PEG 2K	18	D18%-PEG2
D + PEG 10K	5	D5%-PEG10
D + PEG 10K	18	D18%-PEG10
D + PEG 20K	5	D5%-PEG20
D + PEG20K	10	D10%-PEG20
D + PEG 20K	18	D18%-PEG20

reviews.[12–16] The presentation of our results will be divided in two sections: (1) dynamics of neat PEG and (2) dynamics of PEG/dendrimer blends. Dielectric properties of dendrimers have been described in great details in our recent publication and will not be reviewed here.[17]

Dynamics of PEG

Dielectric loss of PEG10 in the frequency domain with temperature as a variable is shown in Figure 1. The solid lines in the figure are the combined fits of the sum of ionic conductivity and the Havriliak-Negami (HN) functional form:[18]

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = -i\left(\frac{\sigma_c}{\varepsilon_0\omega}\right)^N + \sum_{k=1}^{n}\left[\frac{\Delta\varepsilon_k}{\left(1+(i\omega\tau_k)^{a_k}\right)^{b_k}} + \varepsilon_{\infty k}\right] \tag{1}$$

where ε_0 is the vacuum permittivity, σ_c is the conductivity, a and b are the shape parameters that define the breadth and the symmetry of the spectrum, respectively, and τ is the average relaxation time.

The two processes observed in the temperature range between 193 and 273 K are defined as β and γ in the order of increasing frequency at constant temperature; their locations are marked with arrows in Figure 1. The β process is due to the localized motions in the amorphous regions of PEG.[19] This process shifts to higher frequency and decreases in intensity with increasing temperature. We acknowledge that local processes typically increase in intensity with increasing temperature, but our result for the β process show opposite trend possibly due to the presence of lamellar crystals. The γ process shifts to higher frequency too, but it increases in intensity with increasing temperature. This process is attributed to the rotation of hydroxyl end groups. These findings are in good agreement with the previously published results for PEG.[20–22]

The effect of molecular weight of PEG on the relaxation spectra was examined next. PEG20 is also characterized by two relaxation processes, β and γ, with similar characteristics to PEG10. Dielectric behavior of PEG2 is dominated by conductivity even at very low temperature and for that reason only the fastest (γ) process can be described with certainty. The γ and the β process do not depend on the molecular weight of PEG.

Next we consider the dynamics of the segmental process. In the temperature range where the segmental process appears (T > Tg), dielectric loss in PEG is masked

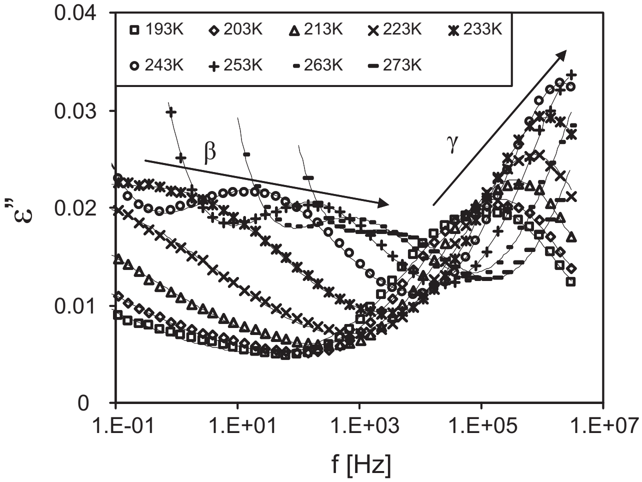

Figure 1.
Dielectric loss of PEG10 in the frequency domain with temperature as a parameter.

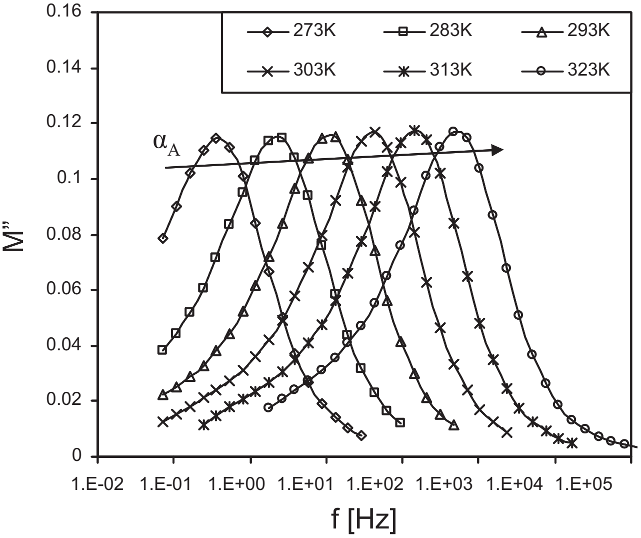

Figure 2.
Dielectric loss modulus of PEG10 in the frequency domain with temperature as a parameter.

by strong conductivity and in such cases dielectric modulus is the preferred form of data representation.[23] Dielectric modulus is defined as the reciprocal of complex permittivity:

$$M^*(\omega) = \frac{1}{\varepsilon^*} = M'(\omega) + iM''(\omega) \qquad (2)$$

We acknowledge that the relaxation times obtained from these two formalisms (τ_M from dielectric modulus and τ_ε from dielectric loss) are close but not identical.[24] Nonetheless in the reminder of the text we shall refer to τ_M obtained from the frequency at maximum loss modulus as the average relaxation time.

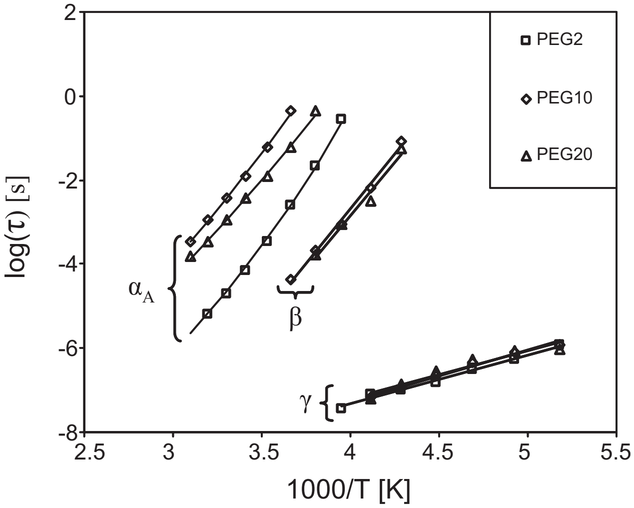

Figure 3.
Average relaxation time as a function of reciprocal temperature for various relaxation processes in a series of PEGs.

Table 3.
VFT Parameters for the segmental process.

Code	τ_0 (s)	B (K)	Tv (K)	T_g^{Diel} (K)
PEG2	1.0×10^{-14}	3598	136	234
PEG10	1.0×10^{-14}	5365	101	247
PEG20	1.0×10^{-14}	5484	87	236

Dielectric loss modulus of PEG10 in the frequency domain between 273 and 323 K is shown in Figure 2. The observed process, termed α_A, is believed to originate in the segmental motions within the amorphous phase. The α_A process shifts to higher frequency and increases in intensity with increasing temperature, which is in agreement with the previously reported characteristics of segmental motions within the amorphous phase of crystalline polymers.[25–27]

The temperature dependence of the average relaxation time for all processes is plotted in Figure 3. The average relaxation time for the local processes was obtained from the HN fits and τ_M was calculated from the frequency at maximum loss modulus. The β and the γ process show Arrhenius behavior, while the data for the segmental process are well described with the Vogel-Fulcher-Tammann (VFT) equation.

The effect of PEG molecular weight on the average relaxation time for local and segmental processes is interesting. The calculated value of the activation energy for the β process is 98.9 kJ/mol for PEG10 and 95.6 kJ/mol for PEG20. For the γ process we obtain: 22.5 kJ/mol for PEG2, 23.2 kJ/mol for PEG10 and 21.8 kJ/mol for PEG20. From these results it is safe to conclude that the molecular weight does not affect the relaxation time of local processes. This is not surprising because secondary relaxations are by definition attributed to localized and not to large scale motions. For the segmental process, the VFT parameters are summarized in Table 3. The dielectric glass transition temperature in Table 3 is an operational value defined as the temperature where τ_{max} equals 100 s. It is well known that the relaxation time for the segmental process in amorphous glass formers is not a function of molecular weight.[15] However, the presence of crystalline phase adds a new dimension to segmental relaxation in PEG. For PEG2, PEG10 and PEG20 the degree of crystallinity, estimated from the heat of fusion, is 83%[28], 92%[29,30] and 84%[30], respectively. The results shown in Figure 3. suggest that the segmental process in the amorphous phase slows down with increasing degree of crystallinity. This is not surprising because a study of the segmental relaxation during isothermal crystallization shows that the relaxation time increases with increasing crystallization time and a reduction of overall chain mobility in the amorphous phase.[31]

Dynamics of PEG/Dendrimer Blends

We proceed with the discussion of the results for PEG/dendrimer blends. In the text that follows we focus on the key parameters that define dynamics, namely (A) dielectric loss and dielectric loss modulus, (B) shape of the relaxation spectra, (C) relaxation strength, and (D) average relaxation time and its dependence on concentration, temperature and molecular weight of PEG.

Dielectric Loss and Dielectric Loss Modulus

We start by examining the dynamics of D-PEG2 blends. In Figure 4A, we show dielectric loss in the frequency domain at 233 K for D (neat dendrimer), PEG2 and DX–PEG2 at three different dendrimer concentrations (X = 5, 10 and 18 wt%). The three processes similar to those observed in the neat dendrimer are seen in the blends and they are marked with arrows in the figure. The β process in dendrimers originates from local fluctuations of branch ends which include amino groups, while the δ process is attributed to the motions of terminal amino groups.[17] Both processes shift to lower frequency and decrease in intensity with decreasing dendrimer concentration. The γ process is present in the blends but is ‘‘hidden’’ in the frequency range between the β and the δ process. The molecular origin of the γ process lies in the

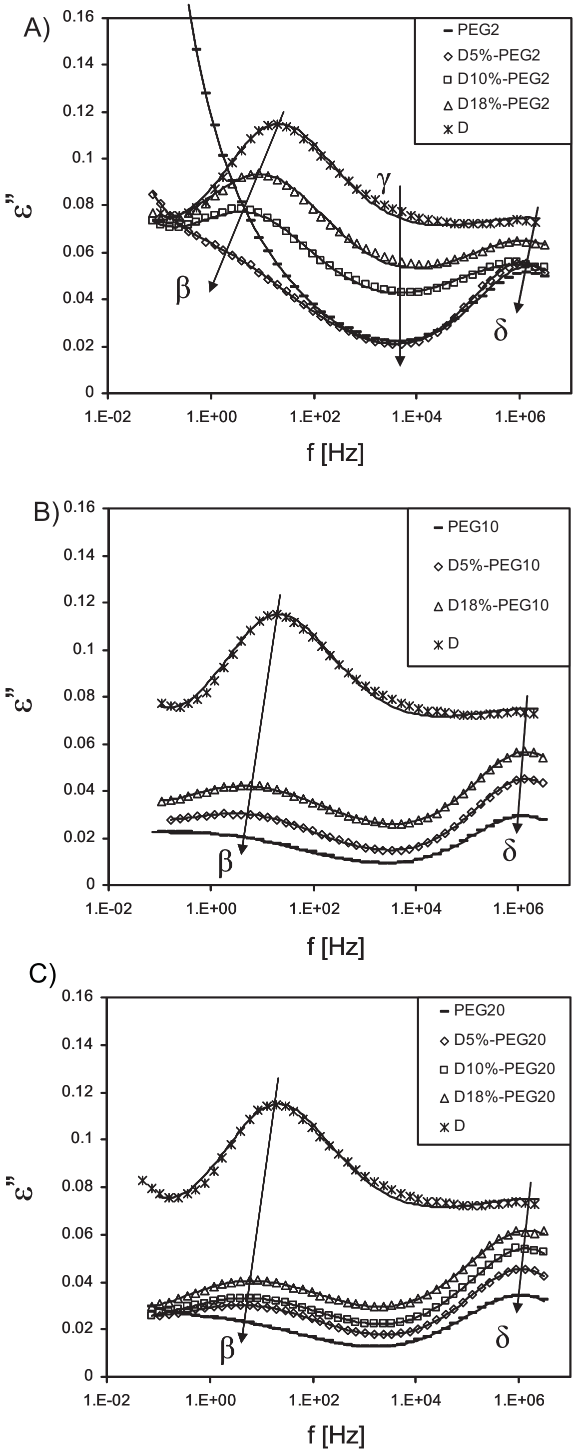

Figure 4.
Dielectric loss in the frequency domain with dendrimer concentration as a parameter at 233 K for: (A) D-PEG2, (B) D-PEG10 and (C) D-PEG20.

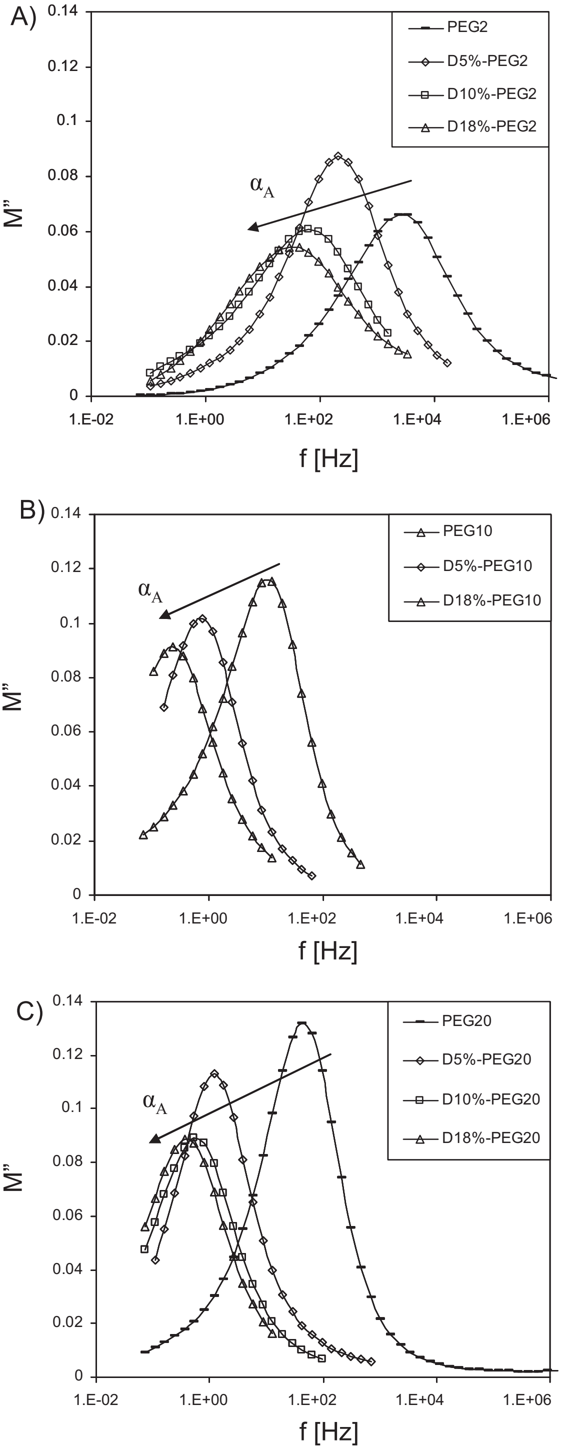

Figure 5.
Dielectric loss modulus in the frequency domain with dendrimer concentration as a parameter at 293 K for: (A) D-PEG2, (B) D-PEG10 and (C) D-PEG 20.

motions of amide groups that are not involved in hydrogen bonding.[17]

Results for D-PEG10 blends are shown in Figure 4B. Interestingly, in these blends, only the β and the δ process are observed. Both processes decrease in intensity and shift to lower frequency with decreasing dendrimer concentration.

The dielectric loss in the frequency domain for D-PEG20 blends with dendrimer concentration as a parameter is shown in Figure 4C. For these blends, too, we detect the β and the δ process. With decreasing dendrimer concentration both processes decrease in intensity and shift to lower frequency. A comparison of Figure 4A, 4B and 4C reveals that molecular weight does not affect the dynamics of local processes in neat PEG but does in blends.

Dielectric modulus formalism was employed to describe the segmental process in the blends. Figure 5 shows dielectric loss modulus in the frequency domain at 293 K for the following blends: DX-PEG2 (Figure 5A), DX-PEG10 (Figure 5B) and DX-PEG20 (Figure 5C) where X = 5, 10 and 18%. The segmental process in the amorphous phase (α_A) observed in the neat PEGs is also found in the blends. With increasing dendrimer concentration the α_A process shifts to lower frequency. This is an interesting observation and we shall revert to its origin in the text below.

Shape of the Relaxation Spectra

The shape of the relaxation spectra is described by the HN parameters a and b which define the spectral breadth and symmetry, respectively. For all local processes in all samples the HN parameter b is constant at 1 and hence the data are well described with the Cole-Cole equation.[32] The effect of dendrimer concentration, PEG molecular weight, and temperature on the HN parameter a is as follows. The spectra for the β and the δ process become narrower with increasing dendrimer concentration. The HN parameter a for the γ process in the PEG2 matrix is independent of dendrimer concentration and equal to 0.2. This is the same value observed in the neat dendrimer. With increasing molecular weight of PEG parameter a decreases for the β process and increases for the δ process. With increasing temperature the δ process (in all blends) becomes narrower.

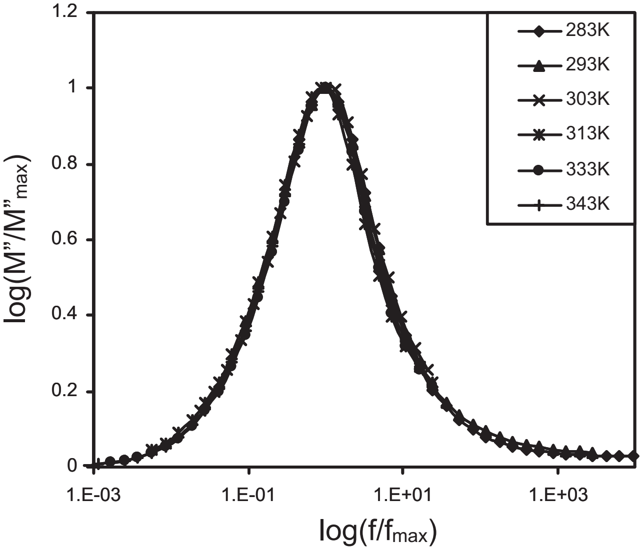

Figure 6.
Normalized dielectric loss modulus spectrum for D5%-PEG20. Note: the segmental process is thermodielectrically simple.

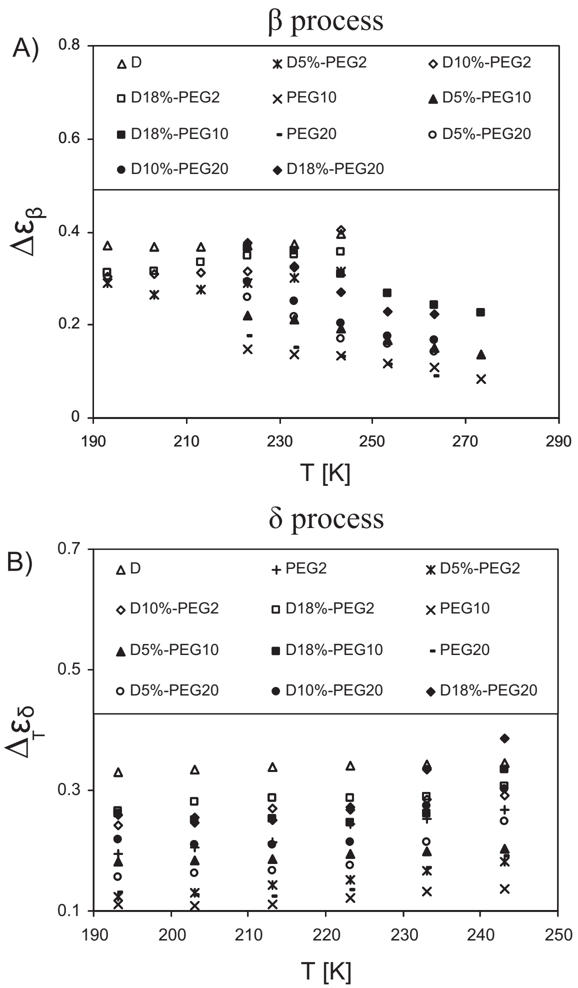

Figure 7.

Dielectric relaxation strength as a function of temperature with dendrimer concentration as a parameter for D-PEG blends for (A) the β process ($\Delta\varepsilon_\beta$) and (B) δ process ($\Delta\varepsilon_\delta$).

The β process becomes narrower in D-PEG10 and D-PEG20, and broader in D-PEG2. The broadening of the β process was observed in the neat dendrimer. Apparently, lower molecular weight PEG has less influence on the β process.

The effect of temperature on segmental relaxation is exemplified in Figure 6 which shows a normalized loss modulus spectrum for D5%-PEG20. The segmental process is thermodielectrically simple in the temperature range from 283 to 343 K for this and all other blends. However, with increasing molecular weight of PEG the segmental process becomes narrower. It is also observed that the α_A process becomes broader with increasing dendrimer concentration. The reason is that the individual segmental reorientations occur with different rates in variety of environments that are rendered more complex with the addition of dendrimers.

The Dielectric Relaxation Strength

The effect of temperature, dendrimer concentration and PEG molecular weight on

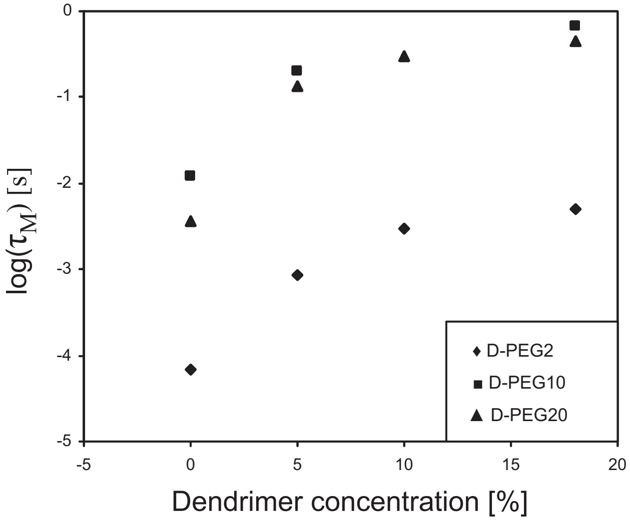

Figure 8.
Average relaxation time for the segmental process in the amorphous phase as a function of dendrimer concentration at 293 K.

the dielectric relaxation strength ($\Delta\varepsilon$) in blends is described next. Dielectric relaxation strength ($\Delta\varepsilon_i$ where $i = \alpha, \beta, \gamma\ldots$) of a given process is defined by the relationship $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ where ε_0 and ε_∞ represent the limiting low and high frequency dielectric permittivity, respectively. $\Delta\varepsilon$ is proportional to the concentration of dipoles and the mean squared dipole moment per molecule. $\Delta\varepsilon$, obtained from the HN fits of dielectric permittivity in the frequency domain is plotted as a function of tempera-

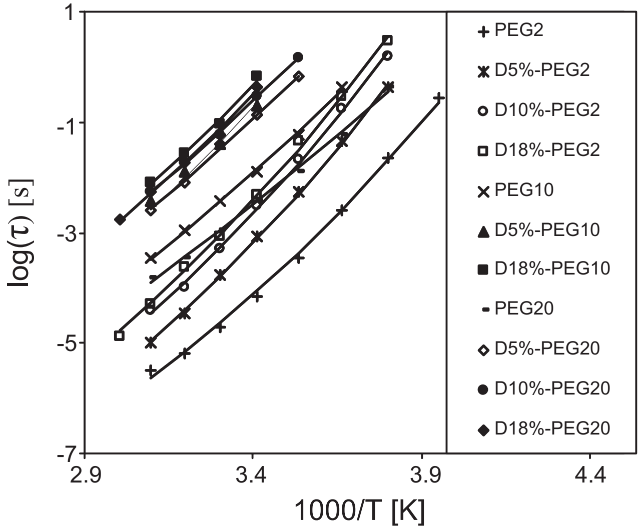

Figure 9.
Average relaxation time as a function of reciprocal temperature for D-PEG blends for segmental process in the amorphous phase.

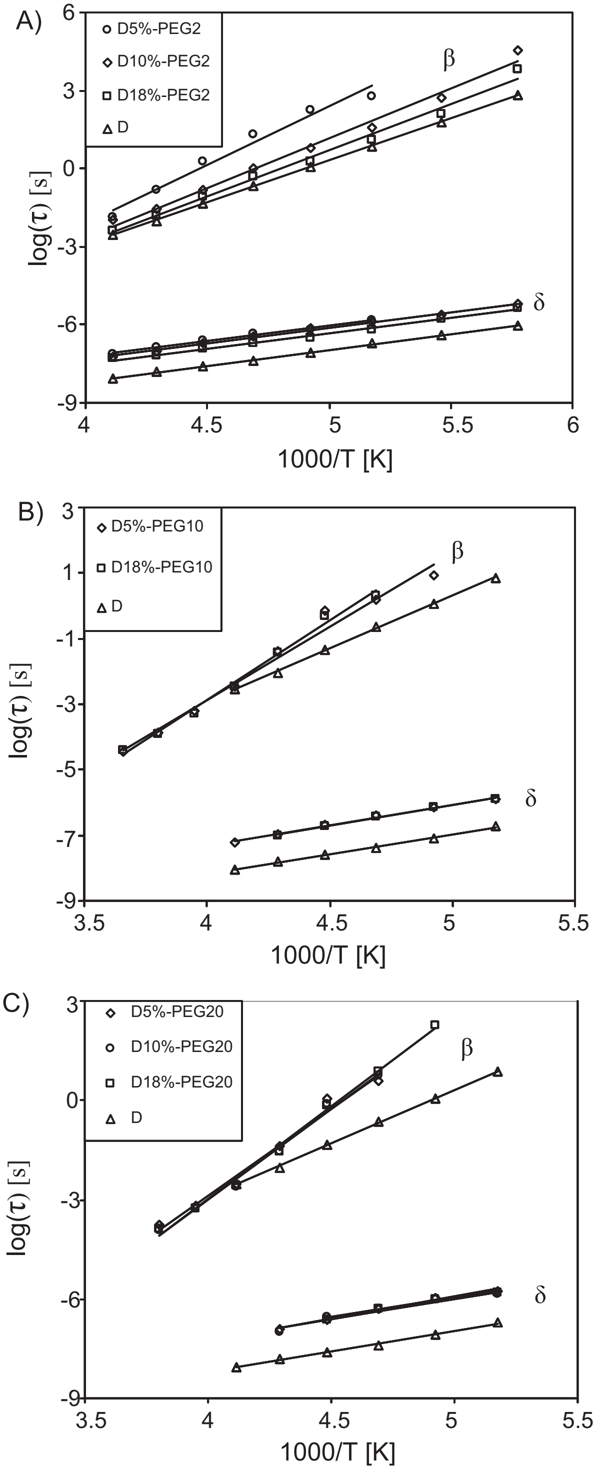

Figure 10.
Average relaxation time as a function of reciprocal temperature for D-PEG2 blends for the β and the δ process.

ture in Figure 7. Part A of Figure 7 describes the results for the β process ($\Delta\varepsilon_\beta$) and part B for the δ process ($\Delta\varepsilon_\delta$). An examination of the trends in the dielectric relaxation strength leads to two principal observations: 1) $\Delta\varepsilon_{\beta,}$ $\Delta\varepsilon_\gamma$ and $\Delta\varepsilon_\delta$ increase with increasing dendrimer concentration in all blends; and 2) $\Delta\varepsilon_\beta$ and $\Delta\varepsilon_\gamma$ in D-PEG2 and $\Delta\varepsilon_\delta$ in all blends increase with increasing temperature which is a typical characteristic of local processes. However, $\Delta\varepsilon_\beta$ in D-PEG10 and D-PEG20 blends decreases with increasing temperature, as in the case of neat PEGs.

The Average Relaxation Time and its Dependence on Concentration, Temperature and molecular Weight of PEG

The average relaxation time for the segmental process in the amorphous phase was calculated from the frequency of the maximum loss modulus. In Figure 8 we show τ_M as a function of dendrimer concentration at 293 K for D-PEG2, D-PEG10 and D-PEG20 blends. The time scale of the α_A process increases with increasing dendrimer concentration at a given temperature. The increase is initially strong, but above around 23 wt%, independently of molecular weight of PEG, a further increase in dendrimer concentration has limited effect on the relaxation time. Analogous trend was observed at other temperatures in the range between 263 and 323 K.

The temperature dependence of τ_M for all blends at temperatures below Tm is presented in Figure 9. The data were fitted to the VFT equation. The observed increase in the time scale of relaxation with respect to dendrimer concentration is due to two factors: (1) the Tg of the blend is the average of the Tg of blend components, weighted by their mass fractions as described by the Fox-Flory equation[33]; and (2) the restriction of mobility caused by H-bonding that forms between dendrimers and PEG.

Finally, we focus attention on the temperature dependence of the average relaxation time for local processes. Figure 10 shows the average relaxation time for the β and the δ process, obtained from the HN fits, as a function of temperature for the following blends: DX-PEG2 (Figure 10A), DX-PEG10 (Figure 10B) and DX-PEG20 (Figure 10C) where x = 5, 10 and 18%. The solid lines in these figures are Arrhenius fits. The activation energy for the β process varies as follows: in DX-PEG2 blends is: 90.8 kJ/mol for D5%-PEG2, 73.1 kJ/mol for D10%-PEG2 and 68.0 kJ/mol for D18%-PEG2; in DX-PEG10 blends: 92 kJ/mol for D5%-PEG10 and 91.5 kJ/mol for D18%-PEG10; and in the D-PEG20 blends is: 91.5 kJ/mol for D5%-PEG20, 91.3 kJ/mol for D10%-PEG10, 90.6 kJ/mol for D18%-PEG20 and 61.5 kJ/mol for D. The activation energy for this process decreases with increasing dendrimer concentration in all blends. The calculated value of the activation energy for the δ process is: in DX-PEG2: 24.0 kJ/mol for D5%-PEG2, 23.0 kJ/mol for D10%-PEG2 and 22.4 kJ/mol for D18%-PEG2; in DX-PEG10: 23.7 kJ/mol for D5%-PEG10 and 24.0 kJ/mol for D18%-PEG10; and in the DX-PEG20: 24.9 kJ/mol for D5%-PEG10, 23.6 kJ/mol for D10%-PEG20, 22.5 kJ/mol for D18%-PEG20 and 23.4 kJ/mol for D. Interestingly, both processes slow down with decreasing dendrimer concentration and we ascribe that to H-bonding between PEG oxygen and amino groups on the dendrimer surface, which are involved in both β and δ processes. Thus H-bonding in these blends affects the dynamics of both local and segmental processes.

Conclusion

We have completed an investigation of the dynamics of a series of blends of Polyethylene Glycol (PEG) with PAMAM dendrimers. The effect of temperature, concentration and molecular weight of PEG on various relaxation processes in blends was probed by dielectric relaxation spectroscopy (DRS) over the frequency range from 10^{-1} to 10^6 Hz and at temperatures from 193 to 343 K. The principal conclusions are as follows.

Neat PEG is semicrystalline polymer that exhibits three relaxation processes: the segmental process in the amorphous phase and two local processes due to the localized motions in the amorphous regions and the rotation of hydroxyl end groups. PEG molecular weight does not have an effect on the average relaxation time for either segmental or local relaxation, though, interestingly, the segmental process slows down with increasing degree of crystallinity.

Interesting observations were made about blend dynamics. The three processes observed in the neat dendrimers (β, γ and δ) are also seen in D-PEG2 blends. In D-PEG10 and D-PEG20, however, only the β and the δ process were observed. Both processes are characterized by an increase in the time scale of relaxation with decreasing dendrimer concentration as a result of H-bonding between PEG oxygen and amino groups on the dendrimer surface.

The time scale of the segmental process in the amorphous phase increases with increasing dendrimer concentration. We believe that the reason is twofold: (1) the Tg of the blend is the average of the Tg of blend components weighted by their mass fractions, as described by the Fox-Flory equation; and (2) the restriction of mobility caused by H-bonding between dendrimers and PEG.

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