

Molecular Dynamics of Biomimetic Ionomers Studied by Dielectric Spectroscopy on the Nanometer Length Scale

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ABSTRACT

Information about the dynamic molecular processes in materials is important for understanding the material's functionality in biotechnological applications, and in the present work we show the potential of dielectric spectroscopy in providing such information.

In this study, dielectric spectroscopy is used to study the bulk properties of the phosphoryl choline (PC) functionalized poly (trimethylene carbonate) (PTMC), ionomer compared to the unfunctionalized PTMC_{diol}. The data clearly shows the presence of the polar PC end groups and the diffusion constant of these moieties is calculated. This information indicates the ability of the material to function as a controlled drug release vehicle in which drug molecules are incorporated within the PC aggregates to create a drug reservoir in the material bulk.

Keywords: biomimetic, ionomer, dielectric spectroscopy

1 INTRODUCTION

New biomimetic materials are being developed which show great promise for applications such as hemocompatible coatings and controlled release vehicles for drug delivery. A deeper understanding of the relationship between the material structure and its function is important in order to be able to tailor specific properties of these materials to fit the various biotechnological applications.

The biomimetic ionomer studied is a phosphoryl choline (PC) functionalized poly (trimethylene carbonate) (PTMC), which has recently been shown to exhibit dual activity with the biomimetic PC group forming physical cross-links in the bulk, as well as providing a hydrophilic and hemocompatible surface [1].

The purpose of this study is to study the bulk dielectric properties of the PC functionalized ionomer in comparison to the unfunctionalized PTMC_{diol} and thus gain information about the molecular dynamics of the ionomer.

2 EXPERIMENTAL

2.1 Materials

Two materials were used in this study. First, a low molecular weight bifunctional poly (trimethylene

carbonate) (PTMC_{diol}) was used as a reference sample. The second material studied was the phosphoryl choline (PC)-functionalized PTMC ionomer. ¹H NMR end group analysis of both materials revealed a molecular weight of ~3900 g/mol. Details of the synthesis of both PTMC_{diol} and PC-PTMC-PC can be found elsewhere [1], while their structures are presented in Fig. 1.

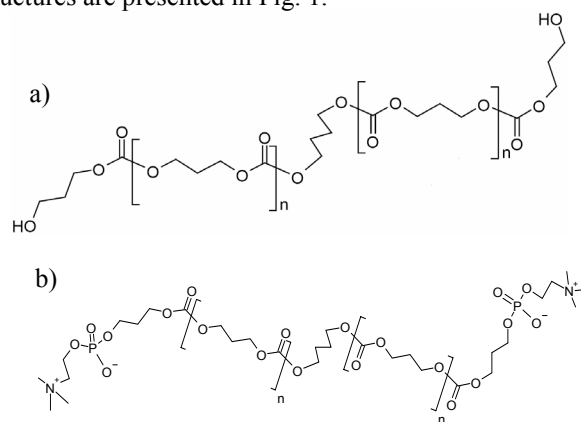


Figure 1: Structure of a) PTMC_{diol} and b) PC-PTMC-PC

The mechanical properties of these two materials were previously investigated through rheology measurements [1], as shown in Fig. 2. This data shows that at ambient and physiological temperatures the PTMC_{diol} behaves as an amorphous melt and has no mechanical integrity, whereas the ionomer behaves like a rubber with a shear modulus of ~2 MPa.

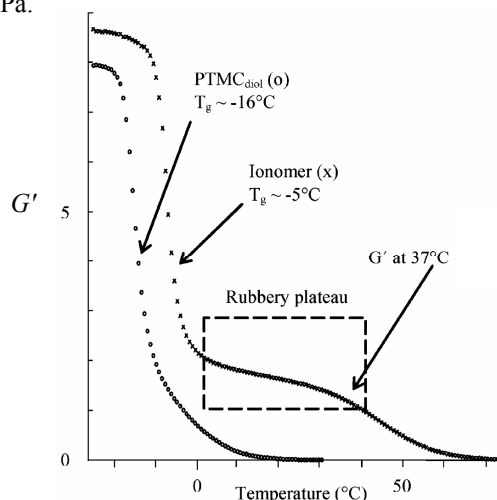


Figure 2: Shear Modulus G' of PTMC_{diol} and ionomer

2.2 Dielectric Spectroscopy

Dielectric spectroscopy measurements were carried out with an Alpha-A dielectric measurement system (Novocontrol Technologies GmbH & Co. KG). The samples were placed between two brass electrodes at a separation of 100 μm . A guard ring was incorporated around the signal electrode and the entire electrode arrangement was enclosed in a sealed stainless steel container to provide an electrically shielded environment in which the humidity could be controlled. The humidity was maintained at a constant level of 37% by the presence of a saturated NaI solution.

Dielectric measurements were taken at 5, 22, and 40°C, which span the “rubbery plateau” temperature range of the ionomer (see Fig. 2).

3 THEORY

In dielectric spectroscopy, a sinusoidal voltage is applied across the sample situated between two electrodes and the frequency of this voltage excitation is stepped through the frequencies of interest. The current response due to charged species present in the sample is then measured and can be interpreted in terms of several frequency dependent quantities such as impedance, conductance, and dielectric permittivity. In this work we have chosen to work with the real part of the frequency dependent conductivity, σ^* , as well as with the complex permittivity, ε^* , where

$$\sigma^* = \sigma' + i\sigma'' \text{ and } \varepsilon^* = \varepsilon' - i\varepsilon'' . \quad (1)$$

The real part, σ' , of the conductivity is related to the imaginary part, ε'' , of the dielectric permittivity as

$$\sigma' = \omega\varepsilon_0\varepsilon'' \quad (2)$$

where ω is the angular frequency and ε_0 is the permittivity of free space ($8.854 \cdot 10^{-14}$ F/cm).

At high frequencies, charged molecules or groups of molecules in a sample will only have time to move a very short distance in response to the applied electric field before the sign of the sinusoidal field is changed and the moieties are forced to change their direction of motion. Thus, at high enough frequencies, the groups will be able to move unhindered by any blocking material structures/interfaces (on the mesoscopic scale) or electrodes (on the macroscopic scale), as if they were in a homogeneous medium. The conductivity associated with this motion can be expressed as

$$\sigma_{hf} = nq\mu , \quad (3)$$

where n is the concentration of the charged groups, q is the elementary charge and μ is the mobility which is related to the diffusion coefficient D and the thermal energy kT according to

$$D = \frac{\mu kT}{q} . \quad (4)$$

At lower excitation frequencies, when the charged molecules or groups move in one direction long enough to be blocked either by microscopic obstacles inherent in the material's structure or by the external electrodes, the distance d between the blocking features is related to the molecular diffusion coefficient D and the angular frequency ω_0 , which signifies the lower limit of the frequency region for unhindered motion, according to

$$d = \sqrt{\frac{D \cdot \sigma'_{hf}}{\varepsilon \cdot \varepsilon'_{hf}}} \cdot \frac{1}{\omega_0} . \quad (5)$$

Here ε'_{hf} denotes the real part of the relative dielectric permittivity in the frequency region for unhindered ionic motion, i.e., where $\sigma' = \sigma_{hf}$. The above equation is obtained by equating the imaginary part of the relative dielectric permittivity in the high frequency region,

$$\varepsilon''_{hf} = \frac{\sigma_{hf}}{\omega\varepsilon_0} , \quad (6)$$

with the imaginary part of the ion-blocking low-frequency relative permittivity [2]

$$\varepsilon''_{lf} = \frac{\omega\varepsilon'_{hf}d^2}{D} \quad (7)$$

at the angular frequency $\omega = \omega_0$.

4 RESULTS AND DISCUSSION

The dielectric spectroscopy data presented in Fig. 3 clearly shows on significant changes upon the addition of the polar PC zwitterion. Whereas the PTMC_{dioI} polymer spectrum is dominated by a thermally activated dipolar relaxation at high frequencies, as well as a dc-like conduction process at lower frequencies, the PC-PTMC-PC ionomer has two additional features.

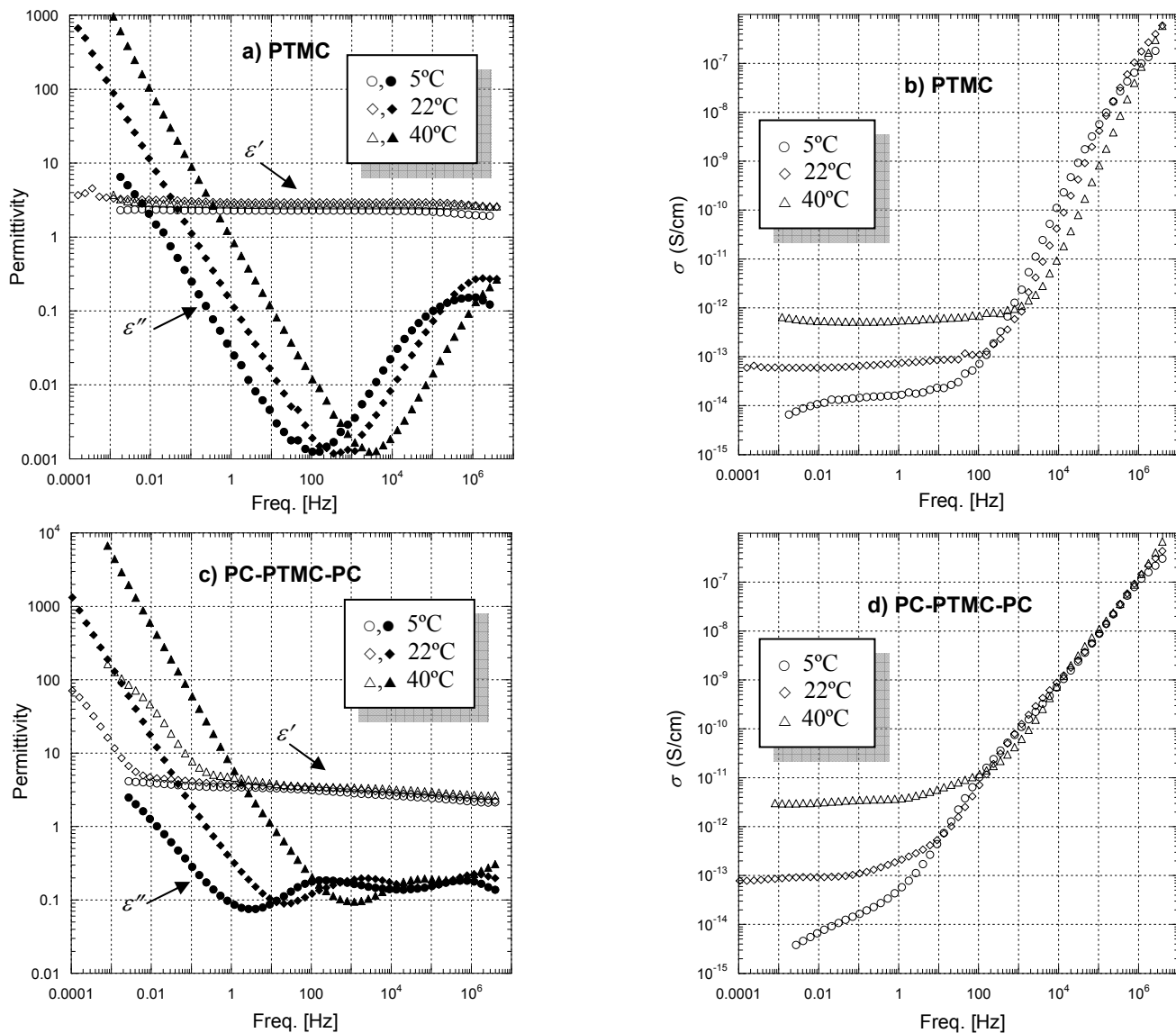


Figure 3: a) permittivity and b) conductivity spectra for PTMC_{diol.} and c) permittivity and d) conductivity spectra for PC-PTMC-PC

The real and imaginary parts of the permittivity as well as the real part of the conductivity for the PTMC polymer (a,b) and the PC-PTMC-PC ionomer (c,d) are displayed at three different temperatures.

At frequencies lower than that of the visible PTMC relaxation frequency, the ionomer exhibits a dielectric relaxation probably related to the vibrational motion of the polar PC end groups. The activation energy associated with this process is ~ 1.5 eV as obtained from an Arrhenius plot of the relaxation peak frequency versus the inverse thermal energy.

In the low-frequency part of the PC-PTMC-PC dielectric spectra recorded at 22°C and 40°C, a significant increase in the real part of the permittivity, ϵ' , towards

lower frequencies is visible. This behavior is most likely caused by the blocking of movable groups in the material. If we assume that these groups are identical to the polarized constituents of the ionomer, Fig. 1b, we get from a molecular mass and density calculation that there are $\sim 1.5 \cdot 10^{20}$ ionomers/cm³ present in the material. From Fig. 3d we obtain that σ_{hf} is equal to $\sim 1 \cdot 10^{-13}$ S/cm and $\sim 3 \cdot 10^{-12}$ S/cm for 22°C and 40°C, respectively. The diffusion coefficient D is calculated from Eqs. (3) and (4) to be approximately $1 \cdot 10^{-16}$ cm²/s and $3.3 \cdot 10^{-15}$ cm²/s, for 22°C and 40°C, respectively.

Estimating a value of the distance the moieties are able to move in this process from Eq. (5), we obtain a d value of ~ 80 nm for both temperatures. This number is, interestingly enough, of the same order of magnitude as the average spacing between the center points of two adjacent ionomers. Furthermore, the obtained diffusion coefficient values indicate that the diffusion process is thermally

activated with an activation energy similar to that found for the PC-PTMC-PC relaxation process. This finding speaks in favor of the assumption that both processes are linked to the movement of the same entity.

5 CONCLUDING REMARKS

The values of the diffusion coefficients as well as their temperature dependence are important parameters to take into consideration when optimizing the ionomer as a controlled drug delivery vehicle in which drug molecules are incorporated within the PC aggregates to create a drug reservoir in the material bulk.

To be able to support the dielectric spectroscopy results presented in this work, a non-linear optical technique utilizing second harmonic generation from a femtosecond laser pulse will be soon used for the first time to study the molecular dynamics at the surface of the ionomer.

REFERENCES

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