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Dielectric study of local relaxations in dendritic macromolecules

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Abstract

The aim of this work is to characterize the dielectric properties of amorphous dendritic macromolecules as a function of architectural complexity. By combining thermostimulated currents and dynamic dielectric spectroscopy, the dielectric permittivity has been obtained as a function of temperature, in a very broad frequency range (10^{-4} – 10^6 Hz). Generations $g = 0$ to $g = 2$ were investigated. The molecular origin of the quasi-Debye mode observed for $g = 0$ at low temperature is common to all generations: localized reorientations of aldehyde end groups. The interactions with the phosphorus/sulfur (P = S) dipoles are probably responsible for the broadening pointed out in upper generations.

1. Introduction

Phosphorus-containing dendrimers have been chosen as a complex polymeric model to investigate the relationship between complex relaxation processes associated with specific architecture. Dendrimers are characterized by a self-similar architecture (tree-like architecture). The architectural effect on the dielectrical properties of non-conductive materials, such as phosphorus-containing dendrimers, has been investigated by dynamic dielectric spectroscopy (DDS) and thermostimulated currents (TSC). Dielectric losses associated with localized molecular relaxations have been analysed at low frequency and low temperature.

Secondary β relaxation modes, generally characteristic of the chemical structure in the glassy state, have been considered. The influence of generation evolution and the modification of the chemical nature of the core and end groups have been followed.

2. Materials and methods

2.1. Materials

The synthesis of phosphorus-containing dendrimers has been described previously [1, 2]. Numbering of these compounds hereafter will be as $[G'_g]$, in which g is the number of the

generation—here $g = 0$ and $2 - G'$ correspond to a dendrimer with terminal aldehyde groups and a P = S core. Phosphorus-containing dendrimers of generation 0 with a P = O core will be designated as $[G'_0(\text{P} = \text{O})]$ for chemical species with an aldehyde end group and $[G_0(\text{P} = \text{O})]$ for chemical species without an aldehyde end group. The molecular structure of phosphorus-containing dendrimers is illustrated in figure 1. All the samples studied are available as powder. For $[G'_0]$, no calorimetric manifestation of glass transition has been pointed out; for $[G'_2]$, the glass transition temperature T_g is 122 °C.

2.2. Methods

Broadband dielectric measurements were performed using a Novocontrol BDS400 covering a frequency range of 10^{-2} Hz/ 10^6 Hz with 10 points per decade. Experiments were carried out within a temperature range -150 °C/ 100 °C. Dielectric isotherms were measured every 5 °C. Before each frequency scan, the temperature was kept constant to within ± 0.2 °C. The real ϵ'_T and imaginary ϵ''_T parts of the relative complex permittivity ϵ_T^* , were measured as a function of the frequency F at a given temperature T . The experimental data were fitted by the Havriliak–Negami (HN) function [4, 5] without any additional conductivity term

$$\epsilon_T^*(\omega) = \epsilon_\infty + \frac{\epsilon_{st} - \epsilon_\infty}{[1 + (i\omega\tau_{HN})^{\alpha_{HN}}]^{\beta_{HN}}}$$

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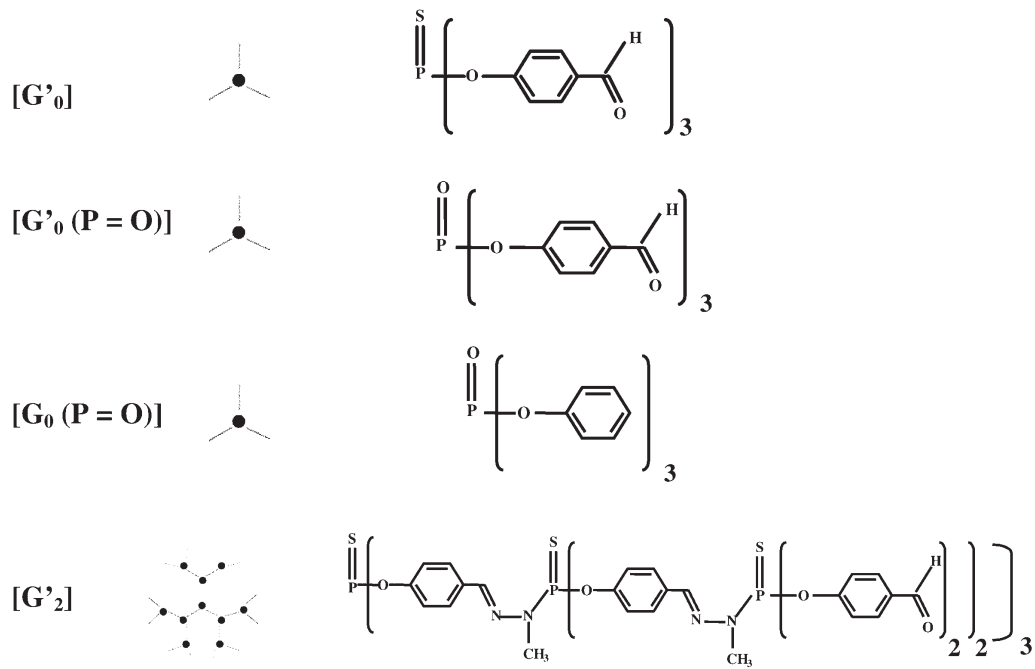


Figure 1. Scheme of phosphorus-containing dendrimer architectures (points (●) symbolize P = S or P = O groups) and molecular structures for $g = 0$ and $g = 2$.

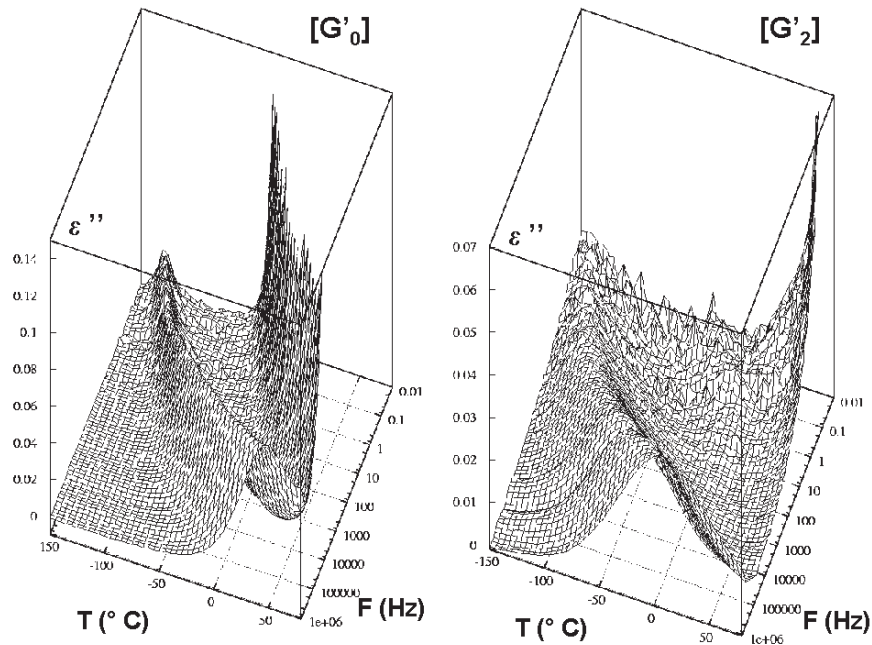


Figure 2. Frequency and temperature dependence of the dielectric loss for the β -mode of $[G'_0]$ and $[G'_2]$.

where ϵ_∞ is the relative real permittivity at infinite frequency, ϵ_{st} is the relative real permittivity at null frequency, τ_{HN} is the relaxation time, ω is the angular frequency, and α_{HN} and β_{HN} are the HN parameters. TSC spectra were recorded on a Thermold TSC/RMA spectrometer. The sample was polarized by an electrostatic field $E_P = 400 \text{ kV m}^{-1}$ during $t_p = 2 \text{ min}$ over a temperature range from the polarization temperature $T_P = -100^\circ\text{C}$ down to the freezing temperature $T_0 = -180^\circ\text{C}$. Then, the field was turned off and the depolar-

ization current was recorded with a constant heating rate ($q_h = +7^\circ\text{C min}^{-1}$), so that the equivalent frequency of the TSC spectra was $f_{eq} \sim 10^{-3}-10^{-4} \text{ Hz}$. TSC experiments are complementary to DDS spectroscopy on the low-frequency side.

3. Results and discussion

Evolution of the generation allowed us to follow the relaxational complexity and molecular structure relationships.

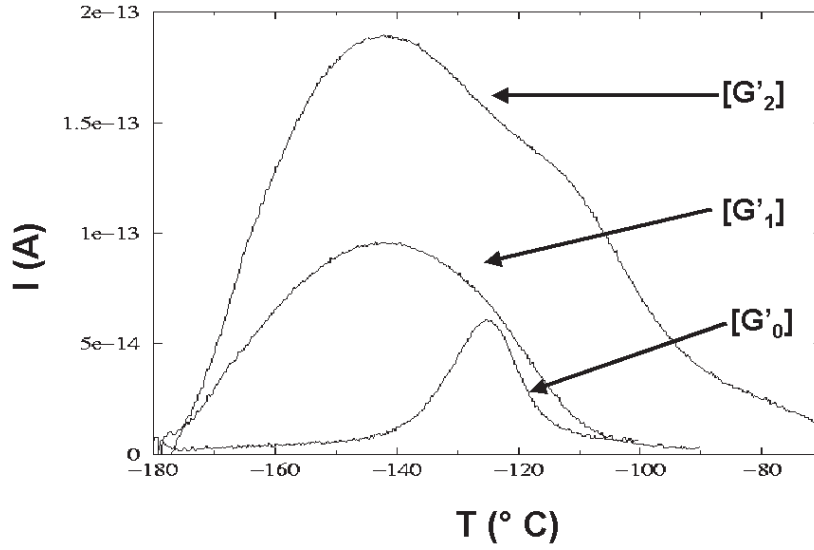


Figure 3. TSC spectra of P = S core dendrimers $[G'_0]$, $[G'_1]$ and $[G'_2]$.

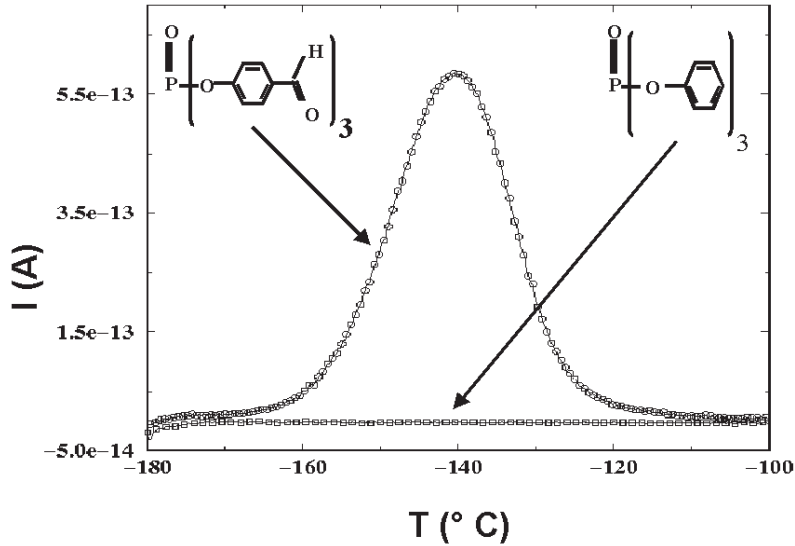


Figure 4. TSC spectra of P = O core dendrimers $[G'_0(P=O)]$ and $[G_0(P=O)]$.

For $[G'_0]$, the sample exhibiting no glass transition, no α dielectric relaxation was observed. However, the dielectric loss profile confirms previous data on different dendritic macromolecules [3]: a quasi-Debye mode $\beta^{[G'_0]}$ (figure 2), confirmed by HN parameters [4,5], is observed at low frequency and low temperature. The numerical values of the HN parameters are reported in table 1. Since the isotherm $T = -25^\circ\text{C}$, the contribution of electrical conductivity σ appears on the low-frequency tail of $\epsilon''_T(\omega)$. Nevertheless, it does not modify HN fitting. Details of the dielectric data analysis have been published elsewhere [6]. By TSC [7], the depolarization current exhibits a narrow (quasi-non-distributed) β relaxation mode. Its maximum is located at -124°C (figure 3). For $[G'_2]$, two relaxation regimes are revealed by TSC: the α relaxation mode observed at higher temperature is due to the dielectric

manifestation of the glass transition; at lower temperature, the β mode due to localized molecular mobility is characterized by relaxation times with an Arrhenius-like temperature dependence

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta H}{RT}\right)$$

where R is the ideal gas constant, τ_0 is the pre-exponential factor, and ΔH is the activation enthalpy. τ_0 is of the order of magnitude of $\sim 10^{-13}$ s.

According to the Eyring relationship

$$\tau_0 = \frac{h}{k_B T} \exp\left(-\frac{\Delta S}{R}\right)$$

where h is the Planck constant, k_B is the Boltzmann constant, and ΔS is the activation entropy. For $[G'_0]$ and $[G'_2]$, ΔS is near

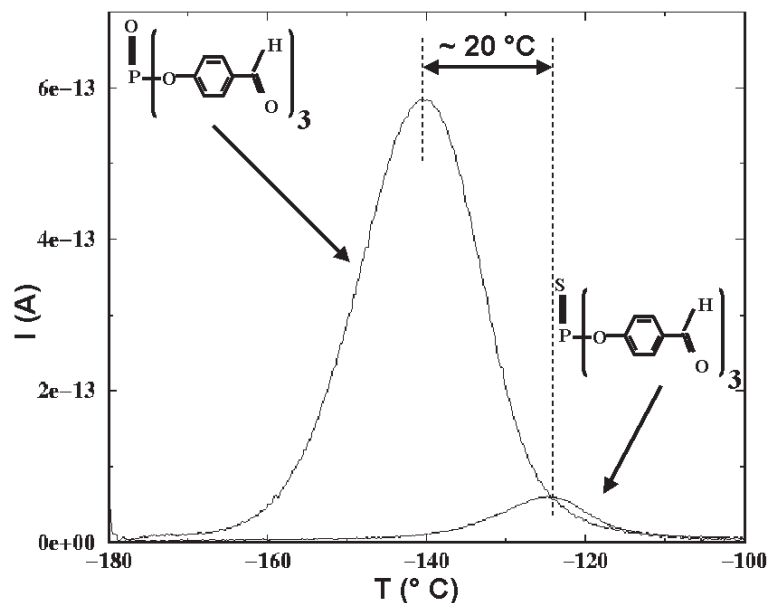


Figure 5. Comparison of TSC spectra of $[G'_0(\text{P} = \text{O})]$ and $[G'_0]$.

Table 1. Evolution of HN parameters (α_{HN} and β_{HN}) with temperature for generation $g = 0$ and $g = 2$ (extracted from a series of isotherms from $T = -150^\circ\text{C}$ to $T = 50^\circ\text{C}$).

HN parameters	$g = 0 [G'_0]$	$g = 2 [G'_2]$
α_{HN}	0.90–0.971	0.28–0.41
β_{HN}	0.912–1.0	1.0

zero, and ΔH takes the values $\Delta H = 40.4$ and 34.9 kJ mol^{-1} , respectively.

The low-temperature mode $\beta^{[G'_2]}$ occurs in the same temperature range as $\beta^{[G'_0]}$ (figure 3), but its half-width increases (HN parameters related to mode width). The hypothesis of an additional dipolar relaxation is proposed in order to explain this broadening.

Considering the mobility and the polarity of the aldehyde groups, they might be responsible for the β relaxation modes. To check this hypothesis, a TSC comparative study of dendrimers without aldehyde end groups ($G_0(\text{P} = \text{O})$, figure 1) was performed: it was found that the β mode is divided by a factor higher than 500; in practice, this β mode does not exist (figure 4). The quasi-Debye β mode was therefore assigned to local movements of the aldehyde end groups. The increase of complexity of the β relaxation mode upon generation indicates the existence of interactions with other dipolar species, most probably $\text{P} = \text{S}$. The substitution of a $\text{P} = \text{S}$ core by a $\text{P} = \text{O}$ core for $g = 0$ (respectively $[G'_0]$ and $[G'_0(\text{P} = \text{O})]$) shows that there is a significant interaction with this group. Indeed, TSC experiments indicate a low-temperature shift of $\sim 20^\circ\text{C}$ of the narrow mode (figure 5).

4. Conclusion

Dendrimers are good models for analysing the molecular origin of broad relaxation modes observed in complex systems. Starting with dendrimers of generation $g = 0$ with a $\text{P} = \text{O}$ core, the comparative study of molecules with and without aldehyde end groups allows us to attribute the low-temperature relaxation mode to reorientations of aldehyde end groups. This is a quasi-Debye mode, characteristic of a localized molecular mobility. The substitution in the phosphorus core of $\text{P} = \text{O}$ by $\text{P} = \text{S}$ is reflected in the TSC spectrum: the β peak is shifted towards higher temperatures by 20°C and its magnitude is divided by a factor of six. This evolution might be explained by a stronger interaction of the core with the end groups. For $\text{P} = \text{S}$ phosphorus core dendrimers, when generation increases ($g = 1$ and 2), a broadening of the β relaxation mode is observed: it has been associated with the broad distribution of interactions with the dipolar species.

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