Molecular Motions and Transitions in a Poly(*p*-hydroxystyrene) Derivative

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ABSTRACT: The dielectric relaxation mechanisms in a poly(*p*-hydroxystyrene) derivative have been studied by Thermally Stimulated Depolarization Currents (TSDC) in the temperature range between -160 and 130° C. A broad relaxation was observed at low temperatures, from -160 up to 0°C, which obeyed to the zero entropy approximation. In contrast, the glass transition relaxation showed the usual behavior, a strong departure to the zero entropy prediction. Both relaxations have been studied in detail by the technique of thermal sampling. The thermal behavior of this poly(*p*-hydroxystyrene) derivative was also studied by Differential Scanning Calorimetry in the temperature range between 20 and 200°C. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1921–1926, 1999

Key words: relaxations; glass transition; thermally stimulated currents; TSC; TSDC; DSC.

INTRODUCTION

The technique of Thermally Stimulated Depolarization Currents (TSDC) has been extensively used to study relaxation mechanisms in polymeric materials.^{1,2} This technique has proven to be a very suitable tool to detect and characterize the dipolar relaxations and the corresponding distributions of relaxation time. It was found that amorphous polymeric materials show essentially two main types of relaxation mechanisms: (1) relaxations below the glass transition temperature (frequently called β -relaxations), which are broad and are often characterized by low activation enthalpies and negligible activation entropies, i.e., obey the so-called zero entropy prediction. The molecular motions at the origin of these relaxations are believed to be low amplitude, local motions, which occur in a large variety of local environments, leading to a distribution of relaxation times responsible for the broadness of the depolarization peaks in the TSDC spectrum. (2) The glass transition relaxation (often called α -relaxation), which shows a strong departure from the zero entropy prediction, and is characterized by a distribution of relaxation time arising from a wide distribution of activation enthalpies and entropies (or, in the terminology of Arrhenius, of activation energies and preexponential factors). This relaxation is generally ascribed to the microbrownian motions of the segments (of variable length) of the main chain.

In the present work we present the results obtained in a TSDC study of a poly(*p*-hydroxystyrene) derivative, and we report the parameters that characterize the α - and the β -relaxations in this polymer. The thermal behavior observed by Differential Scanning Calorimetry (DSC) above room temperature is also reported.

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EXPERIMENTAL

The polymer studied in the present work is poly{4-hydroxy-3-[1'-(4-hydroxyphenyl)ethyl]styrene} (see structure below). It is produced by Hoechst Celanese with the commercial name of poly(*p*-hydroxystyrene)-polymer grade (PHS-PG). The studied samples had mean molecular weight $\overline{M_m} = 3880$ and polydispersity of 1.68.



The samples used in the TSDC measurements were discs of 0.8-mm thickness, which were shaped under a pressure of ~ 75 Mkg m⁻². Before the measurements, the sample was kept in a vacuum oven at 70°C for several days. It was shown³ (for a different material: pentachloronitrobenzene) that the influence of pressure (or density of the disc) on the dielectric relaxation behavior was such that the strength of the relaxation increased with increasing density, but that its basic features such as the frequency location, the activation energy and the spread of relaxation times were not affected by the density of the disc. The TSDC measurements performed on a PHS-PG sample that was obtained by cooling down from the melt also showed that the essential features of the dielectric behavior are independent of the compacity of the sample.

Thermally Stimulated Depolarization Current (TSDC) experiments were carried out with a TSC/ RMA spectrometer (Solomat Instruments, Stamford, CT) covering the range of -170 to $+400^{\circ}$ C. The parallel electrode assembly has an effective area of 38 mm². A Faraday cage shields the sample. Prior to the experiments the sample, located between parallel plate electrodes, is evacuated to 10^{-4} mbar and flushed several times with 1,1 bar of high-purity helium. To analyze specific regions

of the TSDC spectrum, different methods of polarising the sample were used, namely, the socalled TSDC global experiment and the thermal sampling (or cleaning, or windowing) experiment.⁴ The technique of thermal sampling, TS, allows the polarization of specific segments of a complex global relaxation or, otherwise stated, it allows the resolution of a global peak into its individual relaxation modes. Performing different TS experiments with polarization temperature, T_p , varying in the global peak's temperature region allows the selective activation of the different fractions or segments of the global peak, i.e., the separation of a broad distribution of relaxations into its narrowly distributed components. This is indeed one of the advantages of the technique, and the experimental strategy to be implemented in a TSDC study is such that the global experiments are used to detect and localize the different relaxations in the TSDC spectrum, whereas the TS experiments are performed to study the detail of each complex relaxation (distribution of energy and/or relaxation time). Readers who are not familiar with the TSDC technique and data treatment can find useful information about this subject elsewhere.⁵⁻⁷

If we assume that the peaks obtained from a TS experiment can be described by a Debye relaxation function, we have:

$$\frac{dP}{dt} = -\frac{P}{\tau} \tag{1}$$

where *P* is the remaining polarization and τ the relaxation time. The depolarization current (*I*(*t*) = -dP/dt) measured as a function of temperature is used to calculate the relaxation time at given temperature:⁸

$$\ln(\tau(T)) = \ln \int_{T}^{\infty} I(t)dt - \ln(I(T))$$
(2)

Differential scanning calorimetry (DSC) measurements were performed with a Setaram DSC-121 calorimeter, in the temperature range of $20-200^{\circ}$ C, using a heating rate of 10 K min⁻¹ and argon as a purge gas.

RESULTS AND DISCUSSION

The TSDC global experiments (Fig. 1) showed a broad and low-intensity relaxation extending



Figure 1 TSDC global spectrum of PHS-PG. The experimental conditions were: polarization temperature, $T_P = 90^{\circ}$ C; freezing temperature, $T_0 = -160^{\circ}$ C; final temperature, $T_f = 130^{\circ}$ C; electric field strength, E = 100 V/mm and heating rate, $r = 8^{\circ}$ C/min. The dashed line corresponds to the starting up of the experiment, and it does not represent any lower temperature limit of the low-temperature relaxation.

from -160° C up to $\sim 0^{\circ}$ C. Above this temperature, a higher intensity relaxation was also observed (see Fig. 1) whose maximum intensity ocurred at temperatures higher than 100°C.

It was observed that the sample undergoes a transformation at 130-135°C, which prevented the analysis of the whole higher temperature relaxation spectrum due to the loosing of electric contact between the sample and the electrodes. In fact, if the sample is heated up to 130-135°C, it becomes dark brown and brittle. As pointed out before, the TSDC analysis of a sample obtained by cooling down from the melt leads to results that are similar to those obtained from the compressed powder. This suggests that the transformation occuring at 130-135°C does not influence the dielectric relaxation behavior of the sample.

The relaxations observed in the TSDC spectrum of PHS-PG were analyzed in the temperature range from -160 °C up to ~ 100 °C using the thermal cleaning procedure. Figure 2 shows some thermally cleaned peaks obtained in the temperature region between -160 and 0 °C, while Figure 3 shows results obtained in the temperature region where the higher temperature relaxation appears.

It is observed that the lower temperature components of the TSDC spectrum obey to the zero entropy prediction^{5,9,10} (see Fig. 4), i.e., they show low activation enthalpies that increase with in-



Figure 2 Thermally cleaned components of the lower temperature relaxation of PHS-PG. The polarization temperature, T_P , varied from -140 to -20°C (the temperature of maximum intensity of the peaks, T_m , increases with increasing T_P). The other experimental conditions were: window width, $\Delta T = 2$ °C; electric field strength, E = 400 V/mm, and heating rate, r = 4°C/ min.

creasing temperature (from 40 kJ mol⁻¹ up to 80 kJ mol⁻¹ in the temperature region between -160 and 0°C) and negligible activation entropies. This relaxation was observed by dielectric relaxation spectroscopy (frequency range 10^2-10^6 Hz) in the temperature region between -40 and $+40^{\circ}$ C (nonpublished results).



Figure 3 Thermally cleaned components of the higher temperature relaxation. The polarization temperature, T_P , varied from -5 to 85° C (the temperature of maximum intensity of the peaks, T_m , increases with increasing T_P). The other experimental conditions were: window width, $\Delta T = 2^{\circ}$ C; electric field strength, E = 400 V/mm and heating rate, $r = 4^{\circ}$ C/min.



Figure 4 Representation of ΔH^{\neq} vs. T_m for the thermally cleaned components of the relaxations observed in the TSDC spectrum of PHS-PG. The continuous line corresponds to the "zero entropy prediction."

On the other hand, the components of the TSDC spectrum above 0°C show activation enthalpies that increase significantly with increasing temperature (from 80 kJ mol⁻¹ up to 280 kJ mol^{-1} in the temperature region from 0°C up to 100°C) and strongly deviate from the line describing the zero entropy prediction. This behavior, often referred as compensation behavior, appears as a feature of the glass transition,^{11,12} and suggests that the peak in the right-hand side of Figure 1 (whose components are shown in Fig. 3) is the glass transition peak. The glass transition temperature can be defined as the temperature of maximum intensity of the glass transition peak obtained in a TSDC global experiment or, alternatively, as the temperature of maximum intensity of the TS peak that shows higher activation enthalpy. In the present study we are not able to determine the glass transition temperature of PHS-PG owing to the transformation previously reported that occurs in the vicinity of 130°C and precludes the complete analysis of the glass transition relaxation. Because the higher temperature component of the glass transition relaxation shown in Fig. 3 is probably not that showing a maximum activation enthalpy (see Fig. 4), the conclusion we can draw from our results is that T_{σ} is somewhat above 100°C. [This glass transition relaxation, which appears at $\sim 100^{\circ}$ C in TSDC, would appear at higher temperatures in dielectric relaxation spectroscopy (in the frequency range of 10^2-10^6 Hz). Because the sample undergoes a physical transformation at about 135°C and becomes instable above this temperature, it becomes impossible to analyze this relaxation with this technique. Nevertheless, the fact that differential scanning calorimetry detects the glass transition at 90–95°C, make us confident that the TSDC relaxation at 100°C is indeed the glass transition and not any kind of space charge phenomena.]

It has been pointed out in previous studies¹³ that an important feature of the TSDC technique is that the activation Gibbs energy of the different individual components (TS peaks) of the whole TSDC spectrum shows an universal linear dependence on the temperature that is the same for all materials and relaxation processes:

$$\Delta G^{\neq} = \alpha \ T_m \tag{3}$$

where T_m is the temperature of maximum intensity of the TS peak and α is a constant whose value was found to be 280 J K⁻¹ mol⁻¹ on the basis of the study of a very large number of materials and relaxations. Figure 5 shows the representation of ΔG^{\neq} as a function of T_m for all the individual components of the TSDC spectrum of PHS-PG, and we observe that the expected linear relationship is confirmed.

The intercept of the representation in Figure 5 is near zero, and the slope is 288 J K⁻¹ mol⁻¹, in very good agreement with the value of 280 J K⁻¹ mol⁻¹ previously reported. The existence of such a relationship implies that the values of ΔG^{\neq} are restricted to moderate values, which in turn, im-



Figure 5 Plot of ΔG^{\neq} vs. T_m for the thermally cleaned components of the different relaxations observed in PHS-PG. The intercept of the representation is near zero and the slope is 288 J K⁻¹ mol⁻¹.



Figure 6 DSC thermograms of the as-received material: (1) first heating; (2) second heating.

plies that any strong variation of the activation enthalpy, ΔH^{\neq} , as that observed in the right-hand side of Figure 4, is accompanied by a concomitant increase of the activation entropy, ΔS^{\neq} .^{10,13} This behavior, which is currently designated as compensation behavior, seems to be a general feature of the glass transition relaxation but, as clearly demonstrated before,¹² it does not imply the existence of any physically significant compensation point.

The as-received material was also analyzed by differential scanning calorimetry (DSC). The thermogram obtained between 20 and 200°C is shown in Figure 6 (curve 1). The abrupt change in the slope of the heat flow vs. temperature curve is typical of the glass transition, and it can be observed that the onset temperature of this transition occurs at 93° C.

Above this temperature a broad and small endothermic peak is observed, which shows a maximum at 134°C. If the sample is now heated for a second time in the same temperature range (after cooling down naturally from 200 to 20°C), this small endothermic peak disappears and a very clean thermogram is obtained (Fig. 6, curve 2). This second thermogram shows an abrupt change in the heat flow curve similar to that observed in the first heating, and the onset temperature is now at 90°C. If the same sample is scanned in a similar way for a third time, the thermogram does not change, and reproduces closely what was observed in the second heating. These experiments clearly point out to the existence of a glass transition at $T_g = 90-95$ °C. This calorimetric glass transition temperature is slightly lower than the

 T_g predicted from our TSDC results. In contrast, the nature of the second transition observed in the as-received material is not clear. As previously mentioned, the sample becomes dark brown and brittle when treated above 135–140°C. If this dark-brown sample is analyzed in the DSC, a transition is observed above 120°C and extending up to 200°C (see Fig. 7, curve 1) and, at the same time, the T_g is slightly depressed to ~ 88°C.

It is interesting that this transition disappears, and the original thermogram is obtained (with T_g \approx 95°C), if the sample is heated up to 200°C, cooled down and scanned again (Fig. 7, curve 2).

CONCLUSIONS

From the previous discussion we can draw the following conclusions:

- 1. The present study of PHS-PG shows the presence of two distinct relaxation mechanisms.
- 2. One of them, appears in the TSDC spectrum as a broad relaxation extending from -160° C up to 0°C, is characterized by low activation enthalpies and obeys to the zero entropy prediction. It corresponds to local molecular motions, which occur in a large variety of local environments, leading to a distribution of relaxation times (responsible for the broadness of the relaxation).
- 3. The other relaxation which is present in PHS-PG extends from 0 up to 100°C in the



Figure 7 DSC thermograms of the sample treated at temperatures above 135-140 °C: (1) first heating; (2) second heating.

TSDC spectrum, and its activation parameters show a strong departure from the zero entropy prediction. This behavior indicates that it corresponds to the glass transition relaxation.

- 4. The sample undergoes a transformation in the temperature region of 130–135°C, which prevented the complete analysis by TSDC of the glass transition relaxation. This transformation, which makes the sample dark brown and brittle, may be related to the transition that appears in the DSC thermogram of the as-received sample as an endothermic peak, which disappears in subsequent scans. The nature of this transformation is not completely elucidated, but it was observed that it does not change the general features of the dielectric behavior of the sample.
- 5. The DSC results suggest that PHS-PG has a glass transition temperature at 90–95°C that is slightly lower than the glass transition temperature predicted by the TSDC results.

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REFERENCES

- Bernes, A.; Boyer, R. F.; Chatain, D.; Lacabanne, C.; Ibar, J. P. In Order in the Amorphous State of Polymers; Keimath, S. E.; Miller, R. L.; Rieke, J. K., Eds.; Plenum: London, 1987.
- 2. Lavergne, C.; Lacabanne, C. IEEE Electr Insulat Magazine 1993, 9, 5.
- Hall, P. G.; Horsfall, G. S. J Chem Soc Faraday Trans 1973, 69, 1071.
- Dias, A. B.; Moura Ramos, J. J.; Williams, G. Polymer 1994, 35, 1253.
- Correia, N. T.; Campos, J. M.; Moura Ramos, J. J. J Chem Soc Faraday Trans 1997, 93, 157.
- 6. van Turnhout, J. Thermally Stimulated Discharge of Polymer Electrets; Elsevier Sci. Pub. Co.: Amsterdam, 1975.
- 7. Chen, R.; Kirsch, Y. Analysis of Thermally Stimulated Processes; Pergamon Press: Oxford, 1981.
- 8. Bucci, C.; Fieschi, R.; Guidi, G. Phys Rev 1966, 148, 816.
- 9. Sauer, B. B.; Avakian, P.; Starkweather, H., Jr.; Hsiao, B. S. Macromolecules 1990, 23, 5119.
- 10. Sauer, B. B.; Avakian, P. Polymer 1992, 33, 5128.
- 11. Moura Ramos, J. J.; Mano, J. F. Thermochim Acta 1996, 285, 347.
- 12. Sauer, B. B.; Moura Ramos, J. J. Polymer 1997, 38, 4065.
- Moura Ramos, J. J.; Mano, J. F.; Sauer, B. B. Polymer 1997, 38, 1081.