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Polymer 43 (2002) 5175–5179

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# TSC study of length ester side group effect on sub-vitreous relaxations in poly(*n*-alkyl methacrylates)

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Received 10 December 2001; received in revised form 17 June 2002; accepted 19 June 2002

## Abstract

A comparative study by thermo-stimulated currents (TSC) of three poly(*n*-alkyl methacrylates) is performed. TSC complex spectra exhibit two dipolar relaxations considered in the following: the glass relaxation and a secondary relaxation related to motion of ester side groups. For each sample, the fractional polarisations protocol is applied to describe the fine structure of these complex spectra. It allows us to define the evolution of activation parameters with temperature. The influence of side chain architecture is then considered. It emphasises that the  $\beta$  mode is independent of the ester group length. On the contrary, the  $\alpha$  mode is highly sensitive to structural change. These results are finally explained in terms of molecular mobility. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Thermo-stimulated currents; Poly(*n*-alkyl methacrylates); Dielectric relaxations

## 1. Introduction

The glass transition has been highly studied in various areas: enthalpic, mechanic, dielectric [1]. In spite of these works, the molecular mobility is not well defined.

There are several ways of studying this molecular mobility. One of them is to make polymer chain architecture vary. That is why we studied the influence of ester chain length of poly(*n*-alkyl methacrylates) on dielectric relaxations by thermo-stimulated currents (TSC). This series of amorphous polymers has been the subject of dynamic dielectric spectroscopy experiments, more particularly by Garwe et al. [2]. They determined the evolution with temperature and frequency of relaxations. Nevertheless, these relaxations are complex: they result from a distribution of relaxation times. On the one hand, the TSC technique has a great resolution power thanks to his low equivalent frequency ( $10^{-3}$ – $10^{-2}$  Hz). On the other hand, the fractional polarisations protocol allows us to describe experimentally this distribution of relaxation times, which provides us new elements for describing the molecular mobility.

In this paper, we will first present the TSC complex spectra of poly(ethyl methacrylate) (PEMA), poly(*n*-butyl

methacrylate) (PnBMA) and poly(*n*-hexyl methacrylate) (PnHMA) to establish the influence of ester group length on temperature positions of relaxations. Then the evolution of activation parameters deduced from the analysis of fine structure of complex spectra will be reported. In the last part, a molecular interpretation of these results will be given.

## 2. Experimental section

### 2.1. Materials

PEMA, PnBMA and PnHMA were furnished by PolymerExpert.

They were synthesised by anionic polymerisation, which permitted to obtain amorphous samples with constant tacticity (85% syndiotactic, 10% atactic, 5% isotactic), and polydispersity index close to 1.

In order to avoid effect of molecular weight on glass transition temperature, we chose number average molecular weight close to  $100\,000\text{ g mol}^{-1}$ . It should be noted that the molecular weight of PnHMA is a bit higher in order to enhance the mechanic behaviour.

Samples were pressed under a pressure of 1 bar for 2 min at temperature above  $T_g$  in order to prepare them in the form of films.

Differential scanning calorimetry (DSC) experiments

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Table 1  
Characterisation of the samples

Materials	$M_n$ (g mol <sup>-1</sup> )	$M_w$ (g mol <sup>-1</sup> )	$I = M_w/M_n$	$T_g$ (°C)
PEMA	98 000	104 000	1.06	82 ± 1
PnBMA	105 000	117 000	1.11	34 ± 1
PnHMA	93 000	207 000	2.22	-5 ± 1

were carried out in a DSC 2920 instrument from T.A. Instrument at 10 °C min<sup>-1</sup>. The glass transition was determined by the inflexion point method.

Features of each sample are reported in Table 1.

## 2.2. Methods

In the TSC technique [3], a sample is polarised by an electrical field  $E$  at a temperature  $T_p$  for a time  $t_p$  ( $t_p = 2$  min), long enough to orient all dipolar units having relaxation time  $\tau(T_p)$  lower than  $t_p$ . The sample is then quenched to a temperature  $T_0 \ll T_p$  with liquid nitrogen, which freezes the orientation of dipoles. At this temperature, the electrical field is removed and the sample is short-circuited for  $t_0$  ( $t_0 = 2$  min). Upon heating at 7 °C min<sup>-1</sup>, dipolar units return to equilibrium and a depolarisation current is recorded with a Keithley 642 electrometer with a precision of 10<sup>-16</sup> A.

These spectra are generally complex because they result from the distribution of species with different relaxation times. To resolve this wide distribution, different approaches exist: an analytical one with the use of function fits with continuous parameters (for example, a Kohlrausch–Williams–Watts function [4]) and an experimental one, namely, the fractional polarisations protocol [3], which permits to resolve experimentally the fine structure of the complex spectra. For this work, we chose the last one. In this procedure, after polarisation at  $T_p$  for  $t_p$  ( $t_p = 2$  min), the sample is short-circuited for  $t_d$  ( $t_d = 2$  min) at  $T_d$ , some degrees below the polarisation temperature. So dipolar units characterised by relaxation times  $\tau$  such that  $\tau(T_p)$  is lower than  $t_p$  and  $\tau(T_d)$  is higher than  $t_d$ , are oriented and experimentally isolated. The film is then quenched and, as for the TSC experiment, the depolarisation current is recorded upon a linear increase of temperature. By shifting the polarisation window ( $\Delta T = T_p - T_d = 5$  °C) along the temperature axis, a series of elementary spectra is obtained.

A Debye type process characterised by a single relaxation time  $\tau(T)$  can be associated to each elementary spectrum. These  $\tau(T)$  are calculated from the recorded depolarisation current  $I(T)$

$$\tau(T) = \frac{1}{qI(T)} \int_T^\infty I(T)dT$$

where  $q = dT/dt$  is the heating rate.

## 3. Results

### 3.1. Complex spectrum

Complex TSC spectrum was recorded for each sample.

Spectra obtained for PEMA are represented in Fig. 1 as an example. The sample of 150  $\mu\text{m}$  thickness was polarised by an electric field of  $1.1 \times 10^6$  V m<sup>-1</sup> at polarisation temperatures varying from 50 to 105 °C. Spectra were recorded from -150 to 125 °C.

On this figure, two relaxation modes can clearly be seen: one at approximately -30 °C, labelled  $\beta$ , and the other at 105 °C, labelled  $\alpha'$ . Under this latter, another peak appears around 80 °C and is progressively hidden by the  $\alpha'$  mode as the polarisation temperature increases (cf. insert of Fig. 1). The maximum temperature of this peak is in agreement with the glass transition estimated from the DSC experiment. Consequently, this mode has been associated with the dielectric manifestation of the glass transition. It will be labelled  $\alpha$ .

The  $\beta$  mode is a secondary relaxation that has been attributed by some author like Kulik et al. [5] or Kuebler et al. [6], to a flip motion of the side group around the carbon–carbon bond that links it to the main chain, accompanied by a small rotation of the chain backbone around its local chain axis to avoid steric clashes.

The existence of these three dipolar relaxation modes was established from the TSC experiments for all samples. For more details on analysis of PnBMA or PnHMA TSC spectra, readers are invited to refer to Refs. [7,8]. Results concerning the  $\alpha'$  mode will not be considered in this paper but they will be the subject of a future publication.

The normalised complex spectra of each sample are reported in Fig. 2.

On this figure, it appears that whatever the sample is, the

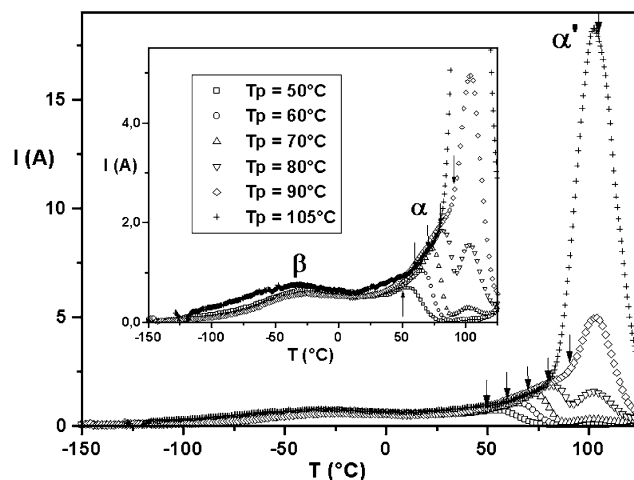


Fig. 1. Influence of polarisation temperature on TSC complex spectrum of PEMA. The sample was polarised by an electrical field of  $1.1 \times 10^6$  V m<sup>-1</sup> at polarisation temperatures varying from 50 to 105 °C (indicated by arrows).

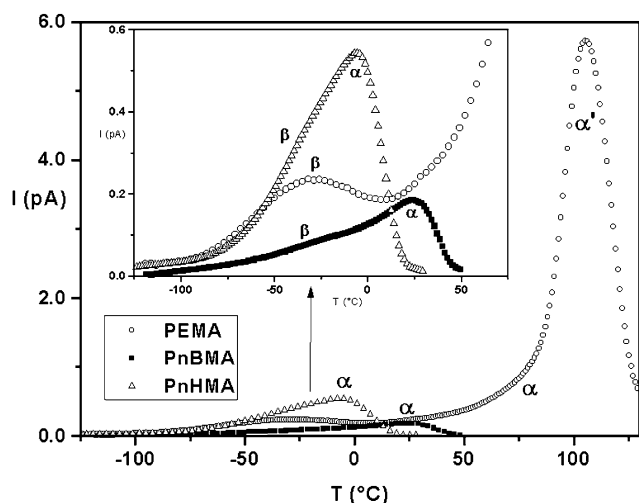


Fig. 2. Normalised complex TSC spectra of PEMA, PnBMA and PnHMA.

position in temperature of the  $\beta$  mode is nearly constant and equal approximately at  $-30$  °C. This result is in agreement with dynamic dielectric [2] and mechanical [9] studies of poly(*n*-alkyl methacrylates) or previous TSC studies of poly(methyl *n*-alkylacrylates) of Godard et al. [10].

As far as the  $\alpha$  mode is concerned, its maximum temperature decreases as the length of the ester side group increases. It evolves from approximately  $80$  °C for PEMA to, respectively,  $30$  °C for PnBMA and  $-5$  °C for PnHMA. This mode, contrary to the  $\beta$  mode, is thus influenced by the chain architecture. Since the  $\beta$  relaxation appears at the same temperature, the gap between the  $\alpha$  and  $\beta$  modes decreases with increasing ester chain and these relaxations merge.

### 3.2. Fine structure of complex spectrum

The resolution of the fine structure of the complex TSC spectra of polymers has been performed by fractional polarisations.

As an example, the series of elementary spectra obtained for PnBMA is reported in Fig. 3 (for PnHMA, see Ref. [8]). For each sample, the shape of this series follows complex spectrum's one. Elementary spectra isolated for  $\beta$  and  $\alpha$  modes are shifted to higher temperatures on a large scale with increasing polarisation temperature, which highlights a wide distribution of relaxation times.

In a heterogeneous approach [11], these elementary spectra can be analysed by assuming a single relaxation time. This allows us to define, for each isolated process, the relaxation time variation as a function of temperature. These variations of  $\tau(T)$  are reported in an Arrhenius diagram in Fig. 4 in the case of PnBMA.

These relaxation times obey an Arrhenius equation

$$\tau(T) = \tau_{0a} \exp\left[\frac{\Delta H_a}{RT}\right]$$

where  $\tau_{0a}$  is the pre-exponential factor which can be related

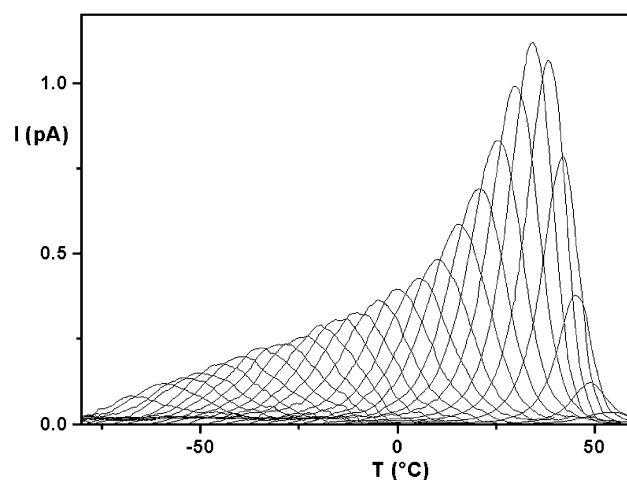


Fig. 3. Series of elementary spectra obtained for a sample of PnBMA of  $110$   $\mu\text{m}$  thickness. The applied electrical field is  $1.1 \times 10^6$   $\text{V m}^{-1}$ . The polarisation window ( $5$  °C wide) is shifted by  $5$  °C between  $-75$  and  $50$  °C.

to the activation entropy,  $\Delta H_a$  is the activation enthalpy and  $R$  is the perfect gas constant.

Moreover, in the case of PEMA and PnBMA, for the  $\alpha$  mode, relaxation times isolated till the mode maximum obey a compensation law [3]

$$\tau(T) = \tau_c \exp\left[\frac{\Delta H_a}{R} \left(\frac{1}{T} - \frac{1}{T_c}\right)\right]$$

where  $\tau_c$  is the compensation time and  $T_c$  is the compensation temperature. They are the coordinates of the point where the extrapolations of these  $\tau(T)$  converge (in dashed lines of Fig. 4).

This phenomenon indicates a linear relation between activation enthalpy and entropy.

More details of the analysis of PnBMA can be found in Ref. [7].

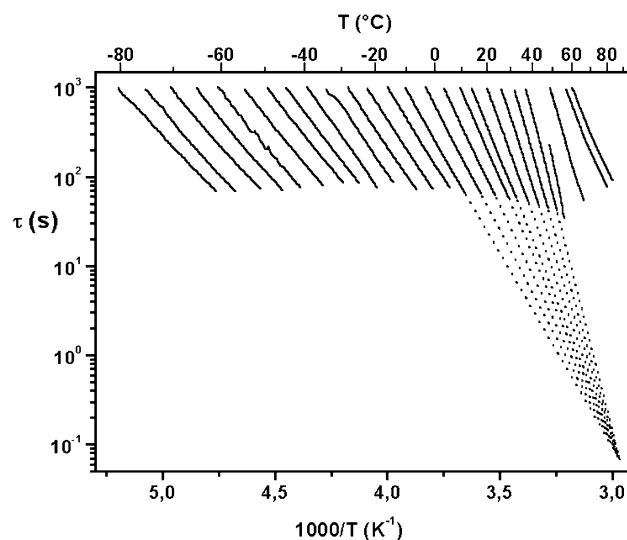


Fig. 4. Arrhenius diagram of relaxation times isolated by fractional polarisations for PnBMA. The dashed lines represent the extrapolation which gives rise to the compensation point ( $T_c$ ,  $\tau_c$ ).

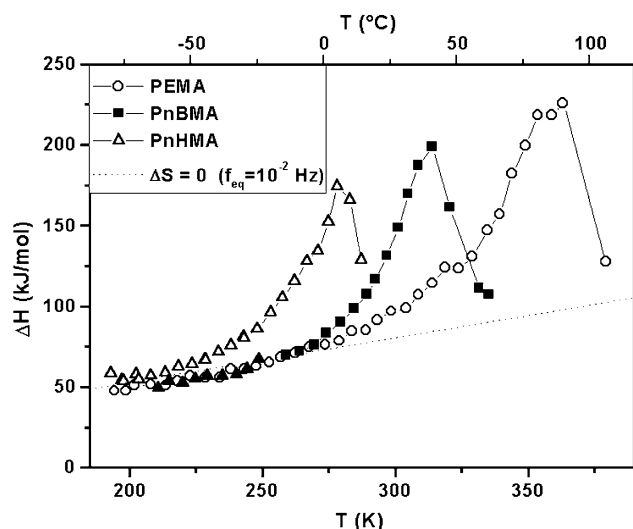


Fig. 5. Comparison of the activation enthalpies evolutions with temperature from PEMA, PnBMA and PnHMA. The dot line represents the Starkweather's line of null activation entropy calculated for an equivalent frequency of  $10^{-2}$  Hz.

It should be noted that, in the case of PnHMA, any compensation phenomenon was observed.

For each sample, the evolution with temperature of activation enthalpy of elementary processes has been studied. They are reported in Fig. 5.

The Starkweather's 'line' has been added. It expresses the theoretical activation enthalpy  $\Delta H_0$  associated with null activation entropy. It is expressed [12,13] as

$$\Delta H_0 = RT \left[ 1 + \ln \left( \frac{kT}{2\pi h f_{\text{eq}}} \right) \right]$$

where  $k$  is the Boltzmann's constant,  $h$  is the Planck's constant and  $f_{\text{eq}}$  is the equivalent frequency set to  $10^{-2}$  Hz.

The evolution of activation enthalpy is the same for all poly( $n$ -alkyl methacrylates). In the  $\beta$  mode temperatures range, activation enthalpy of elementary processes increases slightly and follows the Starkweather's line: the activation entropy is close to zero.

As for the  $\alpha$  mode, on the low temperatures side, activation enthalpy increases strongly and departs from the Starkweather's line: the activation entropy increases till the maximum of the mode. From the  $\alpha$  mode maximum, activation enthalpy and entropy decrease and reach the Starkweather's line.

Nevertheless, as the length of the ester side group increases, the value of the activation enthalpy reached at the  $\alpha$  mode maximum, decreases. On the contrary, the one of the  $\beta$  mode is constant.

## 4. Discussion

### 4.1. Influence of the ester group length on $\beta$ mode

The comparison of TSC complex spectra of PEMA,

PnBMA and PnHMA indicates that the temperature position of the  $\beta$  mode is approximately constant ( $-30$  °C) when length of the ester side group increases. Moreover, the study of the evolution of activation enthalpy shows that this relaxation occurs with an activation enthalpy approximately constant and at null activation entropy. This indicates that motions are localised and non-cooperative. Indeed, according to nuclear magnetic resonance results [5,6], the  $\beta$  mode is due to rotations of ester side groups. Since the ester chain is rather flexible, movement of the COO group is not hindered by the alkyl part of the ester group. Consequently, this relaxation is not dielectrically or mechanically influenced by the structure of the ester side chains.

### 4.2. Influence of the ester group length on $\alpha$ mode

The study of TSC complex spectra of PEMA, PnBMA and PnHMA shows that the  $\alpha$  mode is shifted to lower temperatures with increasing side ester group length. When the length of side chains increases, main chains move apart from each other. There are fewer interactions between them and the glass transition decreases. This effect is known as internal plasticisation. Consequently the glass relaxation mode is shifted to lower temperatures.

Moreover, according to Starkweather's criterion for cooperativity [13,14], the activation enthalpy departure from the null activation entropy line, establishes that this mode is cooperative. It should be noted that the existence of a compensation phenomenon was found for PnBMA [7] and PEMA in agreement with the work of Sauer and Avakian [15]. According to Hoffman, Williams and Passaglia's interpretation [16], it reveals the involvements of longer and longer sequences of the chain. Thus, when temperature increases till the  $\alpha$  mode maximum, the movement is more and more delocalised along the chains and needs more and more energy to occur. With increasing ester chains length, gap between main chains being larger, sequences are less hindered by neighbouring main chains: movement is less cooperative and need less activation enthalpy, which explains the decrease of the maximum value of the activation enthalpy. This can also explain the absence of compensation phenomenon in the case of PnHMA: movements could be enough cooperative to make the activation enthalpy depart from the Starkweather's line, but not enough cooperative to generate a compensation phenomenon. This is both in agreement with Dargent's conclusions on compensation law [17] and Donth and coworkers' conclusions on the cooperativity of the  $\alpha$  mode [18]. Indeed, Garwe et al., showed by dynamic dielectric spectroscopy experiments that when alkyl chain length increases, the merging zone of the  $\alpha$  and  $\beta$  modes is shifted towards lower temperatures and frequencies [2]. At fixed frequency (like in TSC experiments), the longer the length of the alkyl chains, the nearer the merging zone is approached. Or, according to Donth, cooperativity of the  $\alpha$  mode decreases when this

merging zone is approached [18]. Thus, the  $\alpha$  mode of PnHMA is less cooperative than the one of PEMA.

## 5. Conclusion

This study of three poly(*n*-alkyl methacrylates) by TSC permits us to show the existence of two relaxations modes: the  $\beta$  mode, associated principally with motion of ester side groups, and the  $\alpha$  mode, attributed to the dielectric manifestation of the glass transition. The use of fractional polarisations allows us to analyse their fine structure.

This set of experiments establishes that, on the one hand, the  $\beta$  mode, since it is localised, is not influenced by the chain architecture. On the other hand, the  $\alpha$  mode involves molecular motions, more and more delocalised with increasing temperature. Thereby, this relaxation is very sensitive to the length of the ester chain and the amount of free volume. It induces an internal plasticisation and a decrease of cooperativity.

## References

- [1] McCrum NG, Read BE, Williams G. Anelastic and dielectric effects in polymeric solids. New York: Wiley; 1991.
- [2] Garwe F, Schönhals A, Lockwenz H, Beiner M, Schröter K, Donth E. *Macromolecules* 1996;29:247–53.
- [3] Teyssedre G, Mezghani S, Bernes A, Lacabanne C. Thermally stimulated currents of polymers. In: Runt JP, Fitzgerald JJ, editors. *Dielectric spectroscopy of polymeric materials: fundamentals and applications*. Washington: ACS; 1997. p. 227–58.
- [4] Alegria A, Goitiandia L, Colmenero J. *J Polym Sci, Part B: Polym Phys* 2000;38:2105–13.
- [5] Kulik AS, Beckham HW, Schmidt-Rohr K, Radloff D, Pawelzik U, Boeffel C, Spiess HW. *Macromolecules* 1994;27:4746–54.
- [6] Kuebler SC, Schaefer DJ, Boeffel C, Pawelzik U, Spiess HW. *Macromolecules* 1997;30:6597–609.
- [7] Dudognon E, Bernès A, Lacabanne C. *Macromolecules* 2001;30:3988–92.
- [8] Dudognon E, Bernès A, Lacabanne C. *Macromolecules*, in press.
- [9] Heijboer J. *J Stat Dyn Prop Polym Solid State* 1982;94:197–211.
- [10] Godard ME, Burel F, Saiter JM, Grenet J. *J Therm Anal* 1998;51:897–903.
- [11] Richert R. *J Non-Cryst Solids* 1994;172–174:209–13.
- [12] Starkweather Jr. HW. *Macromolecules* 1981;14:1277–81.
- [13] Starkweather Jr. HW. *Macromolecules* 1988;21:1798–802.
- [14] Starkweather Jr. HW. *Polymer* 1991;32:2443–8.
- [15] Sauer BB, Avakian P. *Polymer* 1992;33:5128–42.
- [16] Hoffman JD, Williams G, Passaglia E. *J Polym Sci: Polym Symp* 1966;14:173–235.
- [17] Dargent E, Kattan M, Cabot C, Lebaudy P, Ledru J, Grenet J. *J Appl Polym Sci* 1999;74:2716–23.
- [18] Donth E. *J Polym Sci, Part B: Polym Phys* 1996;34:2881–92.