

# Thermally stimulated depolarization of poly(ether block amide) copolymer

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Phase segregation in poly(ether block amide) copolymer has been studied by thermally stimulated depolarization (TSD). Well-defined, complex and partial phase segregation were observed depending on the molecular mass of each segment of the copolymer. A new glass transition peak appeared were broadened. Soft-segment component poly(tetramethylene glycol) (PTMG), with a lower molecular mass, was found to be completely amorphous. No additional Maxwell-Wagner-Sillers (MWS) effect peak at the phase boundaries was detected.

## 1. Introduction

Poly(ether block amide) copolymers (PEBAX) are thermoplastic elastomers with a two-phase system. The soft segment is generally formed from a polyether of molecular weight between 600 and 2000 and the hard segment is a polyamide having molecular weight between 600 and 4000. The present study deals with the phase segregation in PEBAX whose hard segment is polyamide 12 (PA 12) and whose soft segment is poly(tetramethylene glycol) (PTMG). At service temperature, the soft segment PTMG is above its glass transition and is semicrystalline, and the hard segment PA 12 is below its glass transition and is also semicrystalline.

The copolymer used in this study is designated in the following manner: sharp phases (polytetramethylene glycol  $\bar{M}_n > 2000$  and polyamide 12  $\bar{M}_n < 2000$ ); broad phases (polytetramethylene

glycol  $\bar{M}_n > 2000$  and polyamide 12  $\bar{M}_n > 2000$ ); and narrow phase (polytetramethylene glycol  $\bar{M}_n < 2000$ ). For narrow phases, amalgamation of glass transitions will be observed in the spectrum and these cannot be resolved. If the phases are sharp, the molecular relaxation spectrum can be described by a superposition of the spectra of the two pure homopolymers. When phases are broad, the influence of one particular material on the other's relaxation will cause a new glass transition peak. This may appear due to melting of the crystalline phase of polytetramethylene glycol [1] or trapping of charge carriers at the phase boundaries [2]. Defects, such as missing atoms and dislocations, occur in a phase-separated polymer system and one or more of the few free electrons moving in the field may be trapped near the phase boundary by such a defect. This results in localized accumulation of charge, including an image

charge, in the phase which leads to an effective dipole. It can cause the appearance of a charge on a capacitor immediately after it has been discharged. This is because free charges within the dielectric may take several seconds to escape from traps after the applied field has been removed. The trapped electrons may be considered to form a conducting layer within the dielectric which effectively divides the capacitor into two regions represented by capacitances  $C_1$  and  $C_2$ , each associated with high resistances  $R_1$  and  $R_2$ , respectively. If the terminals are short-circuited, the charge leaks away with time constant,  $\tau$ , can be expressed as

$$\tau = (C_1 + C_2) \frac{R_1 R_2}{R_1 + R_2} = \frac{\tau_1 R_2 + \tau_2 R_1}{R_1 + R_2} \quad (1)$$

The admittance of the circuit,  $Y$ , is given by

$$Y = j\omega C_0(\epsilon'_r - j\epsilon''_r) \\ = \frac{1 + \omega^2 \tau_1 \tau + \omega^2 \tau_2 \tau - \omega^2 \tau_1 \tau_2 + j[\omega(\tau_1 + \tau_2) - \omega\tau + \omega^3 \tau_1 \tau_2 \tau]}{(R_1 + R_2)(1 + \omega^2 \tau^2)} \quad (2)$$

where  $\epsilon$  is the dielectric constant.

Therefore

$$\epsilon'_r = \frac{\tau_1 + \tau_2 - \tau + \omega^2 \tau_1 \tau_2 \tau}{C_0(R_1 + R_2)(1 + \omega^2 \tau^2)} \quad (3)$$

and

$$\epsilon''_r = \frac{1 - \omega^2[\tau_1 \tau_2 - \tau(\tau_1 + \tau_2)]}{\omega C_0(R_1 + R_2)(1 + \omega^2 \tau^2)} \quad (4)$$

At high frequencies

$$\epsilon'_r = \frac{\tau_1 \tau_2}{C_0(R_1 + R_2)\tau} = \epsilon_\infty \quad (5)$$

and at low frequencies, the interfacial polarization of the Maxwell-Wagner-Sillers type leads to a relative permittivity

$$\epsilon'_r = \frac{\tau_1 + \tau_2 - \tau}{C_0(R_1 + R_2)} = \epsilon_s \quad (6)$$

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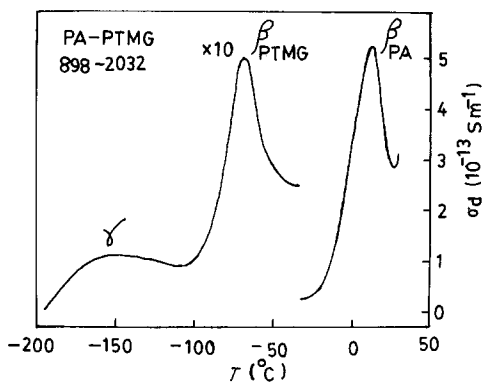


Figure 1 TSD spectrum of poly(ether block amide) copolymer PA 12-898 block PTMG 2032).

Ultimately we can write

$$\epsilon_r' = \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} + \epsilon_\infty \quad (7)$$

and

$$\epsilon_r'' = \frac{1}{\omega C_0 (R_1 + R_2)} + \frac{(\epsilon_s - \epsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2} \quad (8)$$

The frequency variation of  $\epsilon_r'$  has the same form as for orientational polarization. However, in the expression for  $\epsilon_r''$ , the second term is similar to orientational polarization but the first term becomes very large as frequency is reduced. The dielectric loss conductance,  $\omega C_0 \epsilon_r''$ , thus becomes independent of frequency and takes a value of  $1/(R_1 + R_2)$  at low frequencies. As the losses due to the Maxwell-Wagner-Sillers effect are only apparent for low measuring frequencies, the thermally stimulated depolarization method (working at  $10^{-3}$  Hz) was chosen to study the relaxation properties of poly(ether block amide) copolymer.

## 2. Experimental materials

All the samples of poly(ether block amide) copolymer were supplied by Drs J. M. Glotin and J. M. Mery of ATOCHEM Industry, France. The synthesis of this copolymer was performed by polycondensation of dicarboxylic terminated aliphatic polyamide oligomer and polyether diol oligomer. The polycondensation kinetics were studied by Deleens [3]. The characteristics of polyamide elastomers used in this study are described in Table I. Samples 575 K, 569 K and 564 K represent a series having a stoichiometric constant. Experiments were carried out by placing the sample between copper electrodes in a cryostat under a vacuum of  $10^{-6}$  torr with a constant supply of helium gas. A detailed account of this technique is given elsewhere [4, 5], so a brief experimental procedure is described here. All the samples (size  $64 \times 10^{-6}$  m<sup>2</sup>, thickness 2.5 mm) were polarized at 70°C by 500 V d.c.

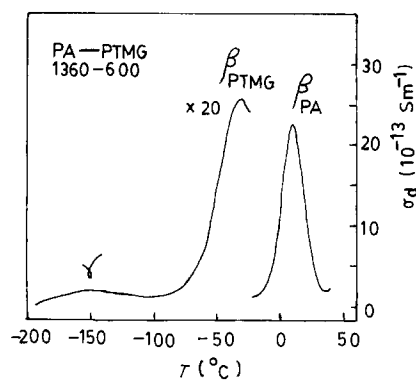


Figure 2 TSD spectrum of poly(ether block amide) copolymer (PA 12-1360 block PTMG 600).

for 2 min to allow complete alignment of any dipole and drift of the free charges. The polarization thus acquired was congealed with electric field by lowering the temperature to  $-194^\circ\text{C}$ . The sample was then short-circuited for 2 min to remove stray surface charges. The sample was then connected to an electrometer and the depolarization current was recorded as a function of increasing temperature with a constant heating rate of  $7.5^\circ\text{C min}^{-1}$ . For comparative studies of the amplitude of the spectra, the intensity of the current was normalized with respect to unity dipolar conductivity,  $\sigma_d$ , and expressed in  $\text{S m}^{-1}$  by the relation

$$\begin{aligned} \sigma_d (\text{S m}^{-1}) &= \frac{J}{E} \\ &= \frac{I/S}{V_p/d} = \frac{Id}{SV_p} \end{aligned} \quad (9)$$

where  $I$  is the depolarization current in (A),  $S$  the surface area of the specimen (m<sup>2</sup>),  $V_p$  the d.c. polarizing voltage (V) and  $d$  the thickness of specimen (m).

## 3. Results and discussion

Figs 1 to 4 show the TSD spectra of samples 552 K, 575 K, 569 K and 564 K. The temperature and amplitude of the relaxation peaks of poly(ether block amide) copolymer are reported in Table II. The expected TSD peak, corresponding to the glass transition of polyamide 12 phase, results from large-scale motion of molecular dipoles, recombinations of ions previously trapped in the crystallites during the cooling process, and sometimes also from space charge polarization. This peak is obviously masked by  $\beta_{PA}$ . Slow cooling does not affect the mode of crystallization nor thus the dipolar mobility in or around the crystallites [6], but changes the ionic and space charge polarization markedly by allowing a more effective charge separation. To investigate the effect of slow cooling on hard-segment molecules, polarization for

TABLE I Structural parameters of poly(ether block amide) copolymer

Sample	$\bar{M}_n$ (PA 12)	$\bar{M}_n$ (PTMG)	Molar ratio PA : PTMG	$W_{PA}/W_{PTMG}$	Inherent viscosity, $\eta$ (dl g <sup>-1</sup> )
552 K	898	2032	1 : 1	31/69	1.35
575 K	1360	600	1 : 1.14	67/33	1.30
569 K	2135	1000	1 : 1	68/32	1.37
564 K	4200	2032	1 : 1	67/33	1.35

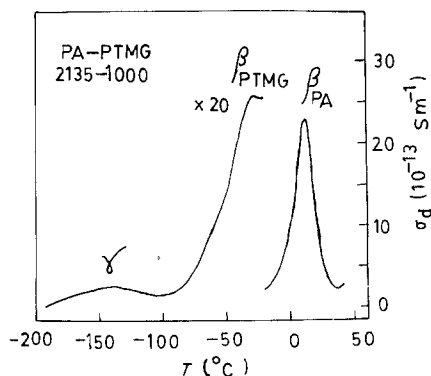


Figure 3 TSD spectrum of poly(ether block amide) copolymer (PA 12-2135 block PTMG 1000).

the sample 564 K was obtained by slow cooling at  $2^\circ\text{C min}^{-1}$  from  $80^\circ\text{C}$  to  $-50^\circ\text{C}$ , followed by a rapid cooling ( $40^\circ\text{C}^{-1} \text{min}^{-1}$ ) down to  $-194^\circ\text{C}$ . The glass transition of the hard segment has been split into three parts as shown in Fig. 5. The first peak can be ascribed to a dipolar relaxation mechanism, the second enhanced peak to an ionic process, and the third peak may be correlated to space charge polarization.

The relaxation,  $\beta'$ , is attributed to melting of the crystalline phase of polytetramethylene glycol. Long sequences of polyamide 12 reduce the molecular mass of polytetramethylene glycol, and a new glass transition appears (Fig. 4 and [7]). For short sequences of polyamide 12, the molecular mass of polytetramethylene glycol is not reduced much, and the melting of the crystalline phase has been blocked by the formation of chain entanglements associated with more molecular mass. Thus, no new glass transition is observed (Fig. 1 and [8]).

The relaxation involving ionic charge carriers is attributed to interfacial polarization (Maxwell-Wagner-Sillers effect) resulting from the existence of well-separated phases, rather than to space charge polarization, but no additional MWS peak is apparent as the constituent phases possess similar electrical conductivities.

The peak  $\beta_{\text{PTMG}}$  is attributed to the micro-Brownian motion of the chain in the amorphous region of the soft segment. This peak, in general, appears to be influenced by the hard-segment content, but not by hard-segment molecular weight, when the phases are sharp or broad [9, 10]. A significant shift of this peak is apparent only in the amorphous sample with a polytetramethylene glycol content of  $\bar{M}_n = 600$  and  $\bar{M}_n = 1000$  (Figs 2 and 3). As higher temperatures are

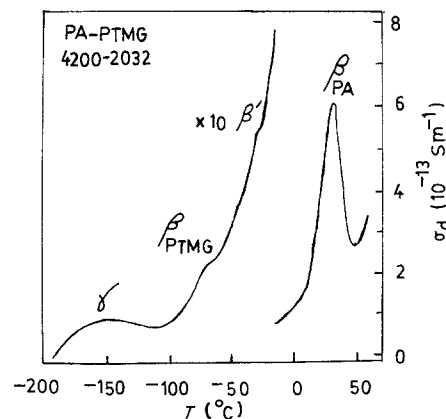


Figure 4 TSD spectrum of poly(ether block amide) copolymer (PA 12-4200 block PTMG 2032).

approached, the shift cannot result from a decrease in molecular mixing of the two phases but rather must result from the drastic decrease in crystallinity of the polytetramethylene glycol phase. The position of the peak  $\beta_{\text{PA}}$  also shifts to a lower temperature. The approach of these two peaks explains the diminution of segregation between the amorphous phases of polytetramethylene glycol and polyamide 12. The displacement of the position of the peaks compared to their homopolymer peaks [11, 12] shows that there exists an interaction between the amorphous chains of polytetramethylene glycol and polyamide 12. Also, the absence of the  $\beta'$  peak reveals that the polytetramethylene glycol with a lower molecular mass is completely amorphous.

The relaxation,  $\gamma$ , is due to the motion of  $\text{CH}_2$  sequence. Both the soft and hard segments contain the  $\text{CH}_2$  sequence, but the major contribution to the  $\gamma$  relaxation comes from the soft segment, because of its relatively high content in the polymer. The position of the  $\gamma$  peak seems to be little affected by the copolymer structure while the amplitude is a decreasing function of polyamide 12 content and an increasing function of PTMG content. This is further confirmation of this assumption.

#### 4. Conclusion

The TSD peaks associated with the glass transitions of PTMG and PA 12 sequences appear unresolved for the narrow phase while for sharp or broad phases, they are resolved. Owing to the similar electrical conductivities of the constituent phases for PTMG and PA 12, no MWS peak is observed, but as a result of melting of the crystalline phase of PTMG a

TABLE II The relaxation characteristics of poly(ether block amide) copolymer

Sample	Conductivity, ( $10^{-14} \text{ S m}^{-1}$ ) $\sigma_{\beta_{\text{PTMG}}}$	$T_{\beta_{\text{PTMG}}} (^\circ\text{C})$	$T_{\beta'} (^\circ\text{C})$	Conductivity, ( $10^{-13} \text{ S m}^{-1}$ ) $\sigma_{\beta_{\text{PA}}}$	$T_{\beta_{\text{PA}}} (^\circ\text{C})$
552 K*	5.0	-70		5.2	13
575 K†	12.8	-31		22.1	10
569 K†	13.0	-28		23.0	12
564 K‡	2.3	-66	-30	6.0	31

\*Well-defined two-phase segregation observed.

†Partial phase segregation observed.

‡Complex phase segregation observed.

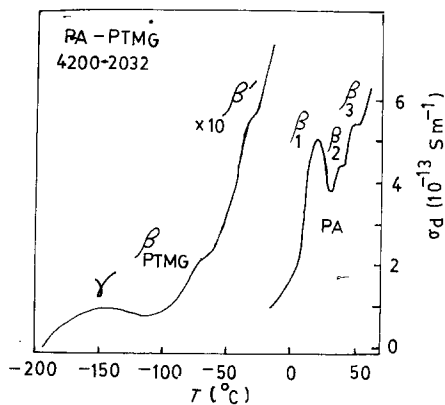


Figure 5 TSD spectrum of poly(ether block amide) copolymer (PA 12-4200 block PTMG 2032) indicating the effect of slow cooling.

new glass transition appears when transitions are broadened. The PTMG with  $\bar{M}_n \leq 1000$  is completely amorphous as the  $\beta_{\text{PTMG}}$  peak shifts significantly towards higher temperature. The role of the polytetramethyleneglycol chain inside the polyamide matrix is to have a plasticizing effect, and to increase disorder in the amorphous phase.

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