Dynamics of polystyrene-block-poly(methylmethacrylate) (PS-b-PMMA) diblock copolymers and PS/PMMA blends: A dielectric study

Jin Liu a, Hanzheng Guo a, Xinchang Pang b, Xiaoli Tan a, Mufit Akinci a, Zhiqun Lin b, Nicola Bowler a,⁎

a Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, United States
b School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

Abstract

The dielectric relaxation properties of poly(methylmethacrylate) (PMMA), polystyrene-block-poly (methylmethacrylate) (PS-b-PMMA) diblock copolymers and PS/PMMA blends were investigated by broadband dielectric spectroscopy in the frequency range from 0.01 Hz to 1 MHz and temperature range from −40 to 150 °C. By parametric fitting techniques, an α relaxation process associated with the glass transition, the secondary β relaxation process due to localized motions of side groups, and the conductivity at low frequencies were identified and modeled for all samples. Based on the modeling results, the characteristic relaxation time, fragility index, activation energies, and relaxation strength of PMMA and PS-b-PMMA diblock copolymers were compared. It was found that the structural α relaxation of the copolymers was suppressed compared with that of PMMA. The covalent chemical bonds that link PS and PMMA blocks in the diblock copolymers are therefore assumed to dominate over the PMMA–PMMA, PMMA–PS and PS–PS bonds that exist in the PMMA and PS/PMMA samples, accounting for the suppression of the cooperative structural α relaxation and for larger activation energies of the localized β relaxation of the diblock copolymers. Further, the activation energy barriers of localized β relaxations in the copolymers are observed to increase, above the glass transition temperature.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The self-assembly of block copolymers into long-range ordered morphologies has been investigated for several decades [1]. Driven by the demand of miniaturization of devices in the microelectronics industry, they have become of great interest as a tool in nanomaterial fabrication in recent years [2,3]. For example, dielectric properties of different kinds of organo-metallic films and nanocomposites have been explored for potential applications in next-generation microelectronics [4–8]. Block copolymers possess favorable intrinsic properties such as long-range ordered phase separation and controllable morphology, and are relatively easy to synthesize, compared with other traditional patterning methods such as top-down lithography [9,10]. The use of block copolymer, instead of homopolymer counterparts, as the matrix in polymer-based nanocomposites affords opportunities to create tailored functional materials [11]. It is useful to understand the details of morphology changes in block copolymers under different conditions. Due to the accuracy and sensitivity of the dielectric spectroscopy technique, dielectric relaxation behaviors of copolymers are examined in this work to investigate their molecular dynamics.

Dielectric spectroscopy is a proven and sensitive technique for monitoring dynamics of polar materials over a broad temperature and frequency range, as the permittivity changes in response to phase transitions such as the glass transition [12,13]. By observing the dielectric relaxation behavior of polymers, their molecular dynamics can be studied. Dielectric spectroscopy is now widely used to investigate molecular dynamics of copolymers and nanocomposites [14–16].

The dielectric spectra of polystyrene (PS) do not exhibit strong dielectric relaxation behavior because the functional groups of PS are stable phenyl groups which are not characterized by a high local dipole moment. For poly(methylmethacrylate) (PMMA), on the other hand, there are two main dielectric relaxation mechanisms, namely, the structural α-type relaxation and localized β-type relaxation. The α relaxation arises from the motions of backbone chains, corresponding to the glass transition of the polymer. The β relaxation is due to the localized rotational moment of the dipole vector of the ester group (O==C–O–CH3). This localized β relaxation is the dominant relaxation process in PMMA. The dielectric strength of the β relaxation increases with temperature, which may be due to the increase of free volume, thereby leading to greater motion of dipoles [17]. The linear diblock copolymer, PS-b-PMMA, consists of PS and PMMA blocks covalently connected at one end. Depending on the molecular weight (MW) of the blocks and the polymerization process, linear diblock copolymers spontaneously phase-separate to form a wide range of morphologies, including: spherical,
lamellar, cylindrical and gyroid nanostructures. This phase-separation offers, in turn, opportunity to confine nanoparticles to a particular phase, thereby controlling spatial distribution of nanoparticles within the target domain [18].

In this paper, the molecular dynamics of linear diblock copolymer PS-b-PMMA are studied and compared with those of PMMA homopolymer and a PS/PMMA blend. To compare molecular dynamics of PMMA between the diblock copolymer PS-b-PMMA and the PS/PMMA blend, copolymer PS-b-PMMA samples and blended PS/PMMA samples were prepared. In both cases the MW of PS and PMMA was 50 k and 50 k, respectively. In order to investigate the molecular weight effect of PS on the molecular dynamics of copolymers, another copolymer sample PS-b-PMMA with the MW of PS and PMMA of 50 k and 130 k, respectively, was prepared. The frequency and temperature scans of dielectric measurements were conducted in a broad range, from 0.01 Hz to 1 MHz and from 40 to 150 °C, respectively.

The dielectric properties of the blends and copolymers are found to be dominated by the dielectric properties of PMMA, because PS is a non-polar polymer. The measured dielectric spectra are fitted by a sum of two Havriliak-Negami functions [19] and a conductivity term via the least-squares fitting technique [20,21]. The comparison between PS-b-PMMA copolymers and PMMA is conducted in terms of their characteristic relaxation time, fragility index, and relaxation strength for the α relaxation process, and characteristic relaxation time, activation energy, and relaxation strength for the β relaxation process. The study of dielectric relaxations of copolymers and homopolymers aims to explore the relaxation dynamics which depends on the morphology as well as the degree of polymerization of polymers.

2. Experiment
2.1. Sample preparation

PMMA homopolymer and PS-b-PMMA diblock copolymers were obtained from Polymer Source Inc. Disk-shaped samples for dielectric testing, approximately 20 mm in diameter and ranging from 0.5 to 1.25 mm thick, were formed as follows. PMMA was heated from room temperature to 150 °C, was die-pressed under 726 kg load for 5 min and was allowed to cool at room temperature without the load. PS-b-PMMA diblock copolymers were heated to 180 °C for 10 min, were die-pressed under 454 kg load and were allowed to cool at room temperature under a 136 kg load. The PS/PMMA blend was heated to 180 °C for 30 min, was die-pressed under 272 kg load for 5 min and was allowed to cool at room temperature under the same load. The heating rate was 10 °C/min, while the samples were cooled naturally at room temperature. Following the hot pressing processes, the samples were then polished and sputtered with Ag to form electrodes on both sides of the disk-shaped samples. The thickness of the samples was measured prior to sputter coating and their diameter was measured after sputter coating, using vernier calipers. In both cases, the average of 10 measurements was recorded.

The molecular weight, diameter, thickness, and volume fraction of the PS component in the samples are summarized in Table 1. The volume fraction of PS in each of PS-b-PMMA 50 k–50 k and 50 k–130 k is calculated based on the mass densities of PS and PMMA: 1.05 g/cm³ and 1.18 g/cm³, respectively. The electrode diameter (20 mm) is slightly larger than the sample diameter, which contributes to overall uncertainty of around 1% in measured permittivity (Table 1). The uncertainty introduced by the sample surface area being slightly smaller than the electrode, approximately 0.01%, was estimated by calculating the effect on the deduced sample permittivity of a parallel air capacitor with the appropriate area and thickness. The major contribution to the 1% overall uncertainty derives from the standard deviation of several repeated measurements.

2.2. Dielectric measurements

The complex permittivity of the samples was measured using a Novocontrol dielectric spectrometer with automatic temperature control from −40 to 90 °C with a 10 °C increment, and from 90 to 150 °C with a 5 °C increment over a frequency range from 0.01 Hz to 1 MHz. The temperature increment was reduced above 90 °C so that the glass transition could be investigated in detail. The experimentally measured imaginary parts of relative permittivity of PMMA and PS-b-PMMA, PS/PMMA samples (the MW of both PS and PMMA is 50 K; denoted 50 k–50 k) are shown in Figs. 1–3, respectively.

3. Spectral analysis

The α and β relaxation processes and a conductivity term of PMMA, PS-b-PMMA, and PS/PMMA samples are modeled by least squares fitting techniques [20,21]. The dielectric spectrum can be expressed as the sum of α and β relaxation and a conductivity term, as described by Eq. (1):

\[
\varepsilon'(\omega) - \varepsilon_\infty = \sum_{p=1}^{2} \frac{\Delta\varepsilon_p}{1 + i\omega\tau_p} = \sum_{p=1}^{2} \frac{\Delta\varepsilon_p}{1 + i\omega\tau_p} = \frac{i\sigma}{\varepsilon_0\omega}\]

where \(\omega\) is angular frequency, \(p = 1, 2\) denotes the two relaxation types, \(\Delta\varepsilon\) is the dielectric strength, \(\varepsilon_\infty\) is the permittivity well above the frequency of measurement, \(\sigma\) is the conductivity, \(\varepsilon_0\) is the permittivity of free space, and \(\tau_{HN}\) and \(\beta_{HN}\) are characteristic relaxation time and shape parameters that describe the Havriliak–Negami function [19]. The term containing the power A is due to conductivity and electrode effects. A is always smaller than 1. It is common to proceed by fitting

![Fig. 1. Experimentally measured imaginary relative permittivity \(\varepsilon'\), of PMMA (MW = 50 k).](image-url)
the imaginary part of the permittivity, \(\epsilon''(\omega)\). By using the least squares fitting techniques, the fitting parameters are determined such that the following criterion is satisfied:

\[
\sum_i \left[ \left( \frac{\epsilon''_{\exp}}{\epsilon''_i} \right) + \sigma_{DC} \sum_{p=1}^2 \epsilon_{\beta,HN}(\omega_i) \right]^2 \rightarrow \text{min}
\]  

where the sum is over the \(i\) experimental data points and

\[
\epsilon_{\beta,HN}(\omega_i) = \text{Im} \left\{ \frac{\Delta \epsilon_p}{1 + (i\omega \tau_{\beta,HN})^{1-\beta \alpha_HN}} \right\}
\]

An alternative approach was suggested by Turnhout and Wübbenhorst [21] in terms of the derivative \(\partial \epsilon''/\partial \omega\). This derivative method is based on the principle that each relaxation process described by Havriliak–Negami function can be decomposed into a series of Debye relaxation processes, while the relation

\[
\frac{\partial \epsilon''}{\partial \omega} = -\frac{\pi}{2} \epsilon''(\omega)
\]

holds for each Debye relaxation processes. This derivative method was adopted in the present study, because it eliminates the effect of Ohmic contacts and provides sharper peaks in the dielectric spectrum. The corresponding criterion to that stated in Eq. (2) is

\[
\sum_i \left[ \left( \frac{\partial \epsilon''_{\exp}}{\partial \omega} \right) + \sigma_{DC} \sum_{p=1}^2 \frac{\partial \epsilon_{\beta,HN}(\omega_i)}{\partial \omega} \right]^2 \rightarrow \text{min}.
\]  

Representative isothermal plots of PS-b-PMMA diblock copolymers (50 k–50 k and 50 k–130 k) are plotted at 105 °C in Fig. 4, where the \(\alpha\) and \(\beta\) relaxation processes and conductivity terms are identified. The superimposed relaxations and the conductivity term agree well with the experimental data, where the standard errors calculated according to Eq. (3) are \(2.38 \times 10^{-4}\) and \(9.89 \times 10^{-5}\) for the 50 k–50 k and 50 k–130 k diblock copolymers, respectively. Isothermal data sets were modeled at other temperatures with similar standard errors.

4. Results and discussion

4.1. Characteristic frequency

The isochronal plots of imaginary relative permittivity of PMMA, two PS-b-PMMA diblock copolymers, and the PS/PMMA blend at 25 Hz are shown in Fig. 5. The \(\alpha\) and \(\beta\) relaxation processes and the effect of conductivity emerge as the temperature increases. For temperatures ranging from −40 to 80 °C, PMMA, PS-b-PMMA, and PS/PMMA show similar \(\beta\) relaxation peaks as the \(\beta\) relaxation of PMMA dominates. As temperature increases, the corresponding \(\alpha\) relaxation peaks, associated with the glass transition temperature, \(T_g\), are visible for PS, PS-b-PMMA diblock copolymers and the PS/PMMA blends. The \(\alpha\) relaxation peaks of copolymers are almost undetectable and hard to separate from the conductivity effects at the highest temperatures studied.
For amorphous polymer PMMA, the dielectric β relaxation process arises from localized rotational fluctuations of side chains. The mechanisms of β relaxation were discussed by Goldstein and Johari [22,23], and they argued that the β relaxation universally exists in a great variety of amorphous polymers. The temperature dependence of the characteristic relaxation time of β relaxation follows the Arrhenius law:

$$f_{\beta,\text{max}} = f_0 \exp \left( -\frac{E_k}{k_B T} \right)$$

where the factor $f_0$ is on the order of the vibrational frequency of the localized motions, $E_k$ is the activation energy of the β relaxation, and $k_B$ is the Boltzmann constant. Above the glass transition temperature $T_g$, the glassy state is transformed to a rubbery state, which is also known as a super cooled liquid. When the temperature increases up to the melting temperature $T_m$, the super cooled liquid will transform to the liquid state. The segmental motions and chain connectivity of polymers both contribute to the dynamic glass transition by intramolecular and intermolecular cooperativity. The characteristic relaxation rate of α relaxation, which describes the viscosity and structural relaxation, obeys the Vogel–Fulcher–Tammann (VFT) law [21,24–26]

$$f_{\alpha,\text{max}} = f_0 \exp \left( -\frac{D T_0}{T-T_0} \right)$$

where $D$ is the strength parameter and the temperature $T_0$ is characteristic of static dipolar freezing of dipolar motion in the absence of long-range correlation. The fragility of polymers, with index $m$ [12], is related to the curvature in the plot of $\log_{10}(f_{\alpha,\text{max}})$ versus $1/T$, is thus a measure of the steepness of the temperature dependence, and is given by

$$m = \frac{d \log_{10}(f_{\alpha,\text{max}})}{dT/T_0} \bigg|_{T=T_g}$$

The fragility index $m$ of the sample can be described by the following formula [12] in terms of VFT parameters,

$$m = \frac{T_g}{10} \frac{DT_0}{(T_g-T_0)^2}$$

The relation between the maximum relaxation time and the corresponding Havriliak–Negami parameters $\alpha_{HN}$ and $\beta_{HN}$ in Eq. (1) are [12]

$$f_{\alpha,\text{max}} = f_0 \beta_{HN} \left[ \frac{\sin \left( \frac{\pi(1-\alpha_{HN})}{2}\beta_{HN} \right) - \sin \left( \frac{\pi\alpha_{HN}}{2}\beta_{HN} \right)}{\sin \left( \frac{\pi}{2}\beta_{HN} \right)} \right]^{-1/(1-\alpha)}$$

where $f_{\alpha,\text{max}} = 1/(2\pi \alpha_{HN})$ is the characteristic frequency of the α and β relaxations. Fig. 6 shows the Arrhenius diagram of α and β relaxations of the samples. The corresponding parameters are summarized in Table 2, wherein the glass transition temperatures were estimated as the temperature at which the characteristic relaxation time is 100 s. The values of $f_0$ and $D$ of the two diblock copolymers are much smaller than those of PMMA, which indicates the suppression of α relaxation in the copolymers as compared to PMMA. On the other hand, $f_0$ for the PS/PMMA blend is only a little less than that of PMMA. The fragility index of PS-b-PMMA (50 k–50 k) is similar to that of PMMA (50 k), because $m$ for PS and PMMA is similar [12]. The fragility index of PS-b-PMMA (50 k–50 k) is, however, smaller than that of PS-b-PMMA (50 k–130 k), because the fragility of PMMA generally increases with the molecular weight [17].

The temperature dependence of the α and β relaxations of samples extrapolated to higher temperature is shown in Fig. 7. For the PMMA sample, it can be seen that when the relaxation curves are extrapolated to higher temperature, the α relaxation and localized β relaxation merge to form the αβ relaxation, while the cooperative α relaxation of the PS/PMMA blend and of the PS-b-PMMA diblock copolymers (50 k–50 k and 50 k–130 k) eventually disappear when the dielectric strength associated with the α relaxation approaches

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_0$ (Hz)</td>
<td>$D$</td>
</tr>
<tr>
<td>$T_0$ (K)</td>
<td>$T_r$ (K)</td>
</tr>
<tr>
<td>PMMA</td>
<td>(4.0 ± 0.2) × 10^8</td>
</tr>
<tr>
<td>PS/PMMA blends</td>
<td>(1.68 ± 0.08) × 10^7</td>
</tr>
<tr>
<td>PS-b-PMMA (50 k–50 k)</td>
<td>(4.2 ± 0.2) × 10^2</td>
</tr>
<tr>
<td>PS-b-PMMA (50 k–130 k)</td>
<td>(2.7 ± 0.1) × 10^2</td>
</tr>
</tbody>
</table>

Uncertainties are estimated in accordance with the confidence level of the fit between the experimental data and the model, Eq. (1), which is around 5%.
zero. The significant suppression of the $\alpha$ relaxation in the copolymer samples is discussed in Section 4.2.

For the $\beta$ relaxation, all the samples show similar values of activation energy, because the dominant $\beta$ relaxation processes all arise from localized rotational motions of side chains of PMMA (Fig. 6). Fig. 8 shows the behavior of the $\beta$ relaxation above $T_g$. The $\beta$ relaxation activation energy of PMMA and PS/PMMA above $T_g$ is larger than that of the 50 k–50 k and 50 k–130 k diblock copolymers due to significant suppression of $\alpha$ relaxation in the dynamics of copolymers, which lowers the activation energy of the localized motions as seen clearly in Table 3.

4.2. Dielectric strength

The dielectric strength of $\alpha$ and $\beta$ relaxation processes as a function of temperature is shown in Figs. 9 and 10, respectively. Uncertainties were assumed in accordance with the confidence level of the fit between the experimental data and the model, Eq. (1), which is approximately 5%. It is noteworthy that the volume fraction of PS in the samples is 0.53 for both PS-b-PMMA (50 k–50 k) and PS/PMMA, and is

$$\Delta \varepsilon_{\alpha}$$

for PS-b-PMMA (50 k–130 k), Table 1. It is thus expected that $\Delta \varepsilon_{\alpha}$ for PMMA should be larger than for the other samples, which is indeed the case seen in Figs. 9 and 10.

The overall dielectric strength of the $\alpha$ relaxation, $\Delta \varepsilon_{\alpha}$ shown in Fig. 9, of the PS-b-PMMA diblock copolymers (50 k–50 k and 50 k–130 k) is smaller than that of PMMA and the PS/PMMA blend. This is because the $\alpha$ relaxation of the copolymers is suppressed due to the chemical connectedness of the PS and PMMA blocks.

The dielectric strength of the $\alpha$ relaxation decreases when the temperature goes up, indicating that the environment exerts weaker influence on the reorientation of the dipole in the cooperative regime of the $\alpha$ relaxation, as temperature increases. In one description, the $\alpha$ relaxation is related to an effective dipole moment $\mu_{eff}$ which decreases due to decrease of the size of the co-operatively rearranging regions [27] when temperature increases [28].

The $\beta$ relaxation is ascribed to the localized rotational fluctuations of the ester group and depends on the total number of contributing dipoles. The molecular weight of PMMA homopolymer and the PMMA block in PS-b-PMMA (50 k–50 k) diblock copolymer is the same, but $\Delta \varepsilon_{\alpha}$ of PS-b-PMMA (50 k–50 k) shown in Fig. 10 is approximately half of that of PMMA due to the reduced PMMA volume fraction in the copolymer. Similarly, the dielectric strength $\Delta \varepsilon_{\alpha}$ of PS-b-PMMA (50 k–130 k) is larger than that of PS-b-PMMA (50 k–50 k) due to the larger molecular weight of PMMA in the PS-b-PMMA (50 k–130 k) diblock copolymer (i.e., higher volume fraction), thereby increasing the number of dipoles that contribute to the $\beta$-relaxation. Comparing the behavior of PS/PMMA and PS-b-PMMA (50 k–50 k) in terms of the strengths of their $\beta$-relaxations, Fig. 10, that of PS/PMMA is higher than that of PS-b-PMMA because PS and PMMA are immiscible [28]. By contrast, in the case of the diblock copolymer, the PS and PMMA chains are covalently linked and, as a result, the strength of the $\beta$-relaxation of PS-b-PMMA (50 k–50 k) is weaker than that of PS/PMMA.

**Table 3**

Parameters of $\beta$ relaxation process of the samples used in the study, Eqs. (5)–(7).

<table>
<thead>
<tr>
<th>$\beta$ Relaxation</th>
<th>$E_a$ (kJ, $T&gt;T_g$)</th>
<th>$E_a$ (kJ, $T&lt;T_g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>106 ± 5</td>
<td>78 ± 4</td>
</tr>
<tr>
<td>PS/PMMA blends</td>
<td>106 ± 5</td>
<td>78 ± 4</td>
</tr>
<tr>
<td>PS-b-PMMA 50 k–50 k</td>
<td>89 ± 4</td>
<td>75 ± 4</td>
</tr>
<tr>
<td>PS-b-PMMA 50 k–130 k</td>
<td>88 ± 4</td>
<td>82 ± 4</td>
</tr>
</tbody>
</table>

![Fig. 7. Arrhenius diagrams showing the $\alpha$ relaxation at temperatures above $T_g$ and extrapolation to higher temperatures using the fitting model.](image)

![Fig. 8. Arrhenius diagram showing the $\beta$ relaxation above $T_g$.](image)

![Fig. 9. Dielectric relaxation strength of $\alpha$ relaxation of samples as a function of inverse temperature above $T_g$.](image)
The dielectric strength of the $\beta$ relaxation, $\Delta \varepsilon_{\beta}$, shows a mostly increasing trend with temperature, except in the region around $T_g$, which may be affected by the presence of the $\alpha$ relaxation. The $\beta$ relaxation is a thermally-activated process and the angular extension of the fluctuating ester group increases with temperature, thereby increasing $\Delta \varepsilon_{\beta}$.

### 5. Conclusion

The dielectric spectrum of PMMA homopolymer, and PS-b-PMMA diblock copolymers (50 k–50 k and 50 k–130 k) and a PS/PMMA blend was investigated by broadband dielectric spectroscopy. The experimental results were modeled as the superposition of $\alpha$ and $\beta$ relaxation processes and a conductivity term. The comparison of dielectric relaxation properties of PMMA and PS-b-PMMA diblock copolymers was conducted in terms of the characteristic relaxation time, fragility index, activation energies, characteristic relaxation time, and relaxation strength. It was found that $\alpha$ relaxation is greatly suppressed in PS-b-PMMA, due to the change of local molecular dynamics. By extrapolation, the $\alpha\beta$ merging process was observed only in the PMMA sample. To account for the different values of dielectric strength, changes of molecular dynamics of samples were discussed.

### Acknowledgment

We gratefully acknowledge funding support from the Air Force Office of Scientific Research (FA9550-09-1-0388).

### References