Dielectric properties of thermoplastic polyimide R-SOD at low temperatures

T H Dao¹, R A Castro¹

¹Herzen State Pedagogical University of Russia, St. Petersburg, 191186 Russia.
Email: honghip2012@gmail.com

Abstract. Molecular mobility and charge transport in R-SOD aromatic thermoplastic polyimide was studied by dielectric method. Dielectric spectra of all PI samples in the examined temperature and frequency range revealed one region of dipole polarization relaxation. The γ-process can be linked to the local mobility of phenylene rings in the diamine part of a macromolecule. The dependence of the σ’~ω-s type was observed in the studied temperature range (s<1.0), which indicates the existence of hopping mechanism of charge transport.

1. Introduction.
Polyimides (PIs) feature good physical and chemical properties, a stable structure, high thermal and chemical resistance, and are therefore widely used as insulating materials in aircraft and space engineering, where extreme conditions are common. Thermoplastic aromatic PIs are of special interest, since they are easily processed and can provide the basis for nanocomposites of new generation with improved mechanical, electrical and membrane properties.

PIs have been studied by different methodology including relaxation methods (dielectric, mechanical, and nuclear magnetic resonance). Relaxation methods provide diversified information about the structure and molecular mobility of a polymer at all levels of the molecular organization. Thus, regions of the maximum dielectric loss (processes of dipole polarization relaxation) can be observed on the dielectric spectra; these are determined by both the local molecular mobility of certain groups, and the cooperative movement of large kinetic segments and even of the macromolecule as a unit. Relaxation time and activation characteristics of molecular motion depend on molecular interactions, which are determined by the chemical structure and intermolecular interactions [1,2].

The objective of this study was to identify the features of dielectric relaxation and charge transport in thin layers of the aromatic thermoplastic polyimide R-SOD by the dielectric spectroscopy (DS) method. The DS method provides us a tool to discover specific features of polarization processes and their relationships with structural features of the studied material [3-5]. In this method the basic operation is to create a sine wave at the frequency of interest, apply it to the sample and measure the sample voltage U(t) and result current I(t). From this, the amplitude I0 and phase angle of the current harmonic base component I*(ω) is calculated by complex Fourier transform (FT) of I(t). In addition to the phase detection, the FT suppresses all frequency components in I(t) except a narrow band centered around the generator frequency. This improves accuracy and reduces noise and DC drifts by several orders of magnitude. E.g. measuring a signal covered by a noise signal of 1000 times larger is possible. Finally, the impedance Z(ω) and material parameters ε*(ω) and σ*(ω) are calculated [6].

2. Experimental details.
Under this study, molecular mobility of the thermoplastic polyimide R-SOD (Fig. 1) was examined by dielectric spectroscopy method.
Polyimide R-SOD was manufactured via two-stage synthesis. The first stage (polycondensation reaction) – obtaining polyamide acid (PAA) – was performed in equimolar solution of aromatic dianhydride and aromatic diamine in dimethylacetamide, at room temperature. Films were poured from PAA solution onto the glass. The second stage (thermal treatment of PAA films) resulted in PI production.

Dielectric spectra were obtained with “Concept 81” broadband dielectric spectrometer (Novocontrol Technologies GmbH), with ALPHA-ANB automatic high-resolution frequency spectrum analyzer. Films of 25…40 μm thickness, compressed between brass electrodes (diameter of the upper electrode – 20 mm) at a temperature of ~300°C above the glass transition temperature, were taken as samples. Temperature-frequency dependences of dielectric permittivity ε', dielectric loss factor ε'', dielectric loss tangent tgδ, and conductivity σ were obtained for all PI samples in the frequency range 10¹ Hz …10⁶ Hz and the temperature range 173K...323K.

Dielectric spectra were analyzed with the Havriliak-Negami (HN) two-parametric empirical function [7] using the Novocontrol Winfit software. Based on these approximations, positions of the dielectric loss maxima were identified and the HN parameters were determined for the studied relaxation processes:

\[
\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta \varepsilon}{1 + (i\omega \tau)\alpha_{HN}^\beta_{HN}}
\]

where, \(\varepsilon_{\infty}\) is the high-frequency limit of the real part of dielectric permittivity, \(\Delta \varepsilon\) is the dielectric increment (the difference between the low- and high-frequency limits), \(\omega = 2\pi f\), \(\alpha_{HN}\) and \(\beta_{HN}\) are shape parameters that describe the symmetric (β = 1, the Cole-Cole distribution) and asymmetric (α = 1, the Cole-Davidson distribution) expansion of the relaxation function, respectively.

3. Results and discussion

Temperature and frequency dependences of \(tg\delta\) and \(\varepsilon''\) were essentially similar for all tested samples. To visualize the dielectric behavior over the entire temperature range, the temperature dependence of \(\varepsilon'\) and \(tg\delta\) is presented in fig. 2,3. These dependences show a region of the maximum within the studied temperature and frequency range, which are determined by the process of dipole polarization relaxation (γ relaxation process), since the position of \(tg\delta_{max}\) and \(\varepsilon'_{max}\) is shifted towards higher temperatures against the change in frequency.

Fig. 4 demonstrates the frequency dependence of dielectric loss factor in the temperature regions corresponding to γ relaxation process. The received HN parameters values allow to concluding that in the studied interval of frequencies and temperatures in layers of R-SOD polyimide non-Debye relaxation process with relaxation time distribution according to Cole-Davidson model is observed.

Dependences \(-\log\tau_{max} = f(1/T)\) for γ-process can be described by the Arrhenius equation:

\[
\tau(T)_{max} = \tau_0 \exp\left(\frac{E_a}{RT}\right)
\]

where, \(\tau_0 = \tau_{max}\) at \(T \to \infty\), \(E_a\) is the activation energy, \(R\) is the universal gas constant (\(R = 8.314 J/mol\cdot K\)) (fig. 5). The linearity of \(-\log\tau_{max} = f(1/T)\) dependence is typical for the local forms of molecular mobility described by the Debye model. This model assumes the absence of intermolecular interactions and here the activation energy does not depend on temperature. The equation parameters (2) for this process are presented in table 1.
According to the Debye model, a charged particle (dipole) bounded by the potential barrier $E_a=8\ldots12$ kcal/mol oscillates with a frequency $f_0=10^{12}\ldots10^{13}$ Hz ($-\log t_0=13\ldots14$ s). Data from Table 1 allows us to conclude that parameters of the equation (2) for $\gamma$-process conform to the characteristics of the local process. At the same time, $-\log t_0$ values for all samples are greater than those predicted for the local mobility by the Debye theory. This fact can be explained if we assume the presence of intermolecular interaction.

Several explanations were proposed for high-frequency $\gamma$-process. Specifically, it was demonstrated that this process was determined by the local mobility of ether groups adjacent to the flexible parts and bonded water molecules. At the same time, the intensity of $\gamma$-process correlated with the bound water content [8-12]. As a rule, $\tan \delta_{\text{max}}$ temperature (at 10 Hz) in $\gamma$-process was independent of the PI structure and made $\sim 185$ K. In our case, we can suggest that the molecular mechanism of the fastest $\gamma$-process is determined by the mobility of phenylene rings with adjacent ether groups in the diamine part of a PI macromolecule. Dielectric losses of a PI in glassy state are small for $\gamma$ process and in the region of $\tan \delta$ maximum stay within $2.10^{-3}\ldots2.10^{-2}$ (Fig. 4).
Figure 4. Frequency dependence of dielectric loss factor $\varepsilon''$ at different temperatures. Symbols are experimental points, lines are of the HN fits. $T = 173K…213K$

Table 1. Parameters of the Arrhenius equation (2) for $\gamma$-process

| Sample | $-\log \tau_0$, c | $E_a$, kcal/mol | $E_a$, eV |
|--------|-----------------|----------------|-----------|
| R-SOD  | 14.92           | 11.02          | 0.48      |
| Error (±)| 0.09            | 0.07           | 0.003     |

Frequency dependence of the real part of the complex conductivity $\sigma'$ is presented in fig. 6. The dependence of the $\sigma'$--$\omega$ type was observed in the studied temperature range, with values of the exponent $s<1.0$, which indicates the existence of hopping mechanism of charge transport.

Different theories for AC conduction in amorphous semiconductors have been proposed such as the quantum mechanical tunneling (QMT) model, the overlapping–large–polaron tunneling (OLPT) model, the correlated barrier hopping (CBH) model [13].

According to the overlapping–large–polaron tunneling (OLPT) model, the frequency exponent $s$ is given by equation:

$$s = 1 - \frac{4}{[\ln(1/\omega \tau_0) - W_H/k_BT]}$$

(3)

where $W_H$ is the polaron hopping energy, $k_B$ is the Boltzman constant, $T$ is the temperature. The OLPT model predicts that frequency exponent $s$ should be both temperature and frequency dependent, $s$ decreases with increasing temperature from unity at room temperature to a minimum value at a certain temperature and then it increases with increasing temperature [13]. Therefore, OLPT model is applicable to the obtained results in our experiment.
Figure 5. Temperature dependence of the most probable relaxation time $\tau_{\text{max}}$.

Figure 6. Frequency dependence of conductivity $\sigma'$ at different temperatures. $T = 173\text{K}…313\text{K}$ (step 10K).

Two sections can be distinguished for the temperature dependence $\sigma'$ (fig. 7). At a “critical” temperature, the type of the system conductivity changes (at $T = 206\text{ K}$ for the frequency $f = 10^4\text{ Hz}$). With increase in frequency the value of the “critical” temperature increases. The change of conductivity mechanism is consistent with the presence of certain features in the relaxation also allows to make a conclusion about possible transition from dielectric to conductive state in studied thin polymer films. For full understanding of this behavior of system it is necessary to conduct additional researches.

4. Conclusion.
Molecular mobility of the ODPA-OOD aromatic thermoplastic polyimide was studied by dielectric method. Dielectric spectra of all PI samples in the examined temperature and frequency range were essentially similar and revealed one region of dipole polarization relaxation. The $\gamma$-process can be linked to the local mobility of phenylene rings in the diamine part of a macromolecule.
The dependence of the $\sigma' \sim \omega_s$ type was observed in the studied temperature range, with values of the exponent $s<1.0$, which indicates the existence of hopping mechanism of charge transport. Two sections can be distinguished for the temperature dependence of $\sigma'$, at a "critical" temperature, the type of the system conductivity changes. We can make a conclusion about possible transition from dielectric to conductive state in studied thin polymer films.

Acknowledgments. The reported study was supported by the Ministry of Education and Science of the Russian Federation (project № 3.5005.2017/BY).

Figure 7. Temperature dependence of conductivity $\sigma'$ at frequency $f=10^3$ Hz.

References
[1] McCrum N G, Read B E, Williams G 1967 Anelastic and dielectric effects in polymeric solids (John Wiley and Sons: London).
[2] Hedvig P 1977 Dielectric Spectroscopy of Polymers pp 18-22.
[3] Avanesyan V T, Bordovskii G A and Castro R A 2000 Glass Physics and Chemistry vol. 26(3), pp 257-259.
[4] Castro R A, Bordovsky G A, Bordovsky V A, Anisimova N I 2006 Journal of Non-crystalline solids vol 352(9-20), pp 1560-1562.
[5] Castro R A, Bordovsky V A, Grabko G I 2009 Glass Physics and Chemistry vol 35(1), pp 43-46.
[6] Schaumburg G 1999 Dielectric Newsletter (5), pp 4-6.
[7] Havrilak S, Negami S 1967 Polymer vol 8, pp 161-210.
[8] Bryant R G 2002 Polymides (John Wiley & Sons: New York)
[9] Sroog C E 1969 Encyclopedia of Polymer Science and Technology (John Wiley & Sons, Inc.) vol.11, pp. 247-272.
[10] Kase Y 2008 Advanced Membrane Technology and Applications pp 581-598.
[11] Chisca S, Musteata V E, Sava I, Bruma M 2011 European Polymer Journal vol 47, pp 1176-1197.
[12] Bas C, Pascal T, Alberola N D 2003 Polymer Engineering & Science vol 43, pp 344-355.
[13] Chisca S, Musteata V E, Sava I, Bruma M 2011 European Polymer Journal vol 47, pp 1176-1197.