THERMAL AND ELECTRICAL TRANSPORT PROPERTIES OF SOME POLYMER MATERIALS FOR MANUFACTURING ELECTRONIC DEVICES

Andreea Irina Barzic[1], Raluca Marinica Albu[1], Razvan Florin Barzic[2]

[1] "Petru Poni" Institute of Macromolecular Chemistry, Iasi, 700487, Romania, e-mail: irina_cosutchi@yahoo.com
[2] "Gheorghe Asachi" Technical University, Faculty of Mechanics, Iasi, 700050, Romania

Abstract: *A series of imidic polymers were investigated with respect to their transport properties. Molecular modeling was employed to evaluate their chain conformation. The type of functional groups that are present in the backbone affected thermal conductivity. Heat conduction ranged in a similar manner as the electrical resistivity. The potential energy of interaction with copper oxide, titanium oxide and chromium nitride was assessed. All polymers interacted better with the last two metallic compounds, aspect that is favorable for the development of components based on organic dielectrics with medium heat conduction for electronic devices.*

Keywords: *polymer, thermal conductivity, electrical resistivity, metal interaction*

1. Introduction

Polymers are materials of great importance in electronic domain since they are low cost and easy to process in elements of different shapes and sizes. However, they need to exhibit good thermal, electrical and mechanical properties in order to be implemented in devices. For instance, enhanced thermal transport properties of polymers are essential for avoiding the overheating issues often encountered in electronic circuits [Tong, 2011]. On the other hand, good charge transport in organic materials is widely exploited in electronics, for example in manufacturing organic electrodes [Bueppelmann, 1994]. Among the criteria to accomplish good conduction characteristics one must be focused on lowering the ionization potential and augment the electron affinity. For polymers with periodic structures, the difference between the highest occupied electronic levels and the lowest unoccupied levels is reduced. It is known that the energy gaps for semiconductors are narrow and become larger for conducting macromolecular systems [Drobny, 2012].

Having all these in view, one can conclude that the materials must have some structural peculiarities to satisfy such conduction demands. For single polymer systems, the increase of main and side chain conjugation is a good solution [Albu, 2014a], while for multicomponent systems addition of micro- or nano-scale fillers is useful for increasing the transport properties [Barzic, 2014]. Also, good adhesion at polymer/metal interface is desirable [Albu, 2014b].

In this study, some polymer materials with new structures are investigated from the point of view of their transport abilities. Thermal transport in the samples is determined through the formalism of connectivity indices. The permittivity and electrical resistivity of the analyzed polymers are obtained using the group contribution method and molecular modeling experiments. The ability of the samples to interact with several materials (particularly metals) with which are often in contact in electronic devices is determined.

Thus, the adhesion implication of the specimens to other metallic parts of circuits is analyzed. The obtained results have a great impact for sorting the adequate materials for implementation in electronic instruments.

2. Experimental

2.1 Materials

The study is focused on some imidic polymers, which are constructed from aromatic monomers. Both dianhydride and diamine reactants contain similar functional groups, such as: ether bridges (polymer 1), carbonyl (polymer 2), sulfone (polymer 3), and a combination of ether linkages, sulfur atoms and heterocyclic moieties (polymer 4). Monomers used to design these imidic polymers are commercially available [Banerjee, 2015]. The chemical structures used in this investigation are new (as far as we know) and are presented in **Figure 1**.

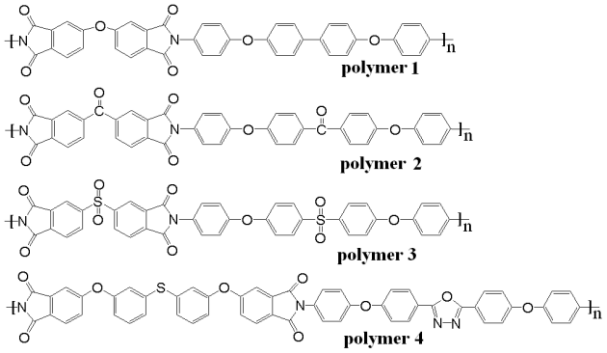

Figure 1: *The chemical structures of the aromatic imidic polymers.*

The building units were chosen so that the backbone is characterized by a certain degree of conjugation, which is sustained by both bulky aromatic rings and functional groups with high polarity. This is expected to favor the electrical and thermal transport properties along the main chain.

2.2 Simulation experiments

Simulations were performed to preview the molecular conformation of the structural units corresponding to the imidic polymers (see **Figure 2**). For computation of the optimal chain geometry in conditions of minimized energy, the HyperChem 8.0 program (Demo Version) was utilized. The molecular mechanics force field was employed to assess the conformational changes induced by each monomer combination. The termination condition was chosen to be 2000 cycles. Mean chain polarizability for each structural unit from **Figure 1** was also evaluated from QSAR approach.

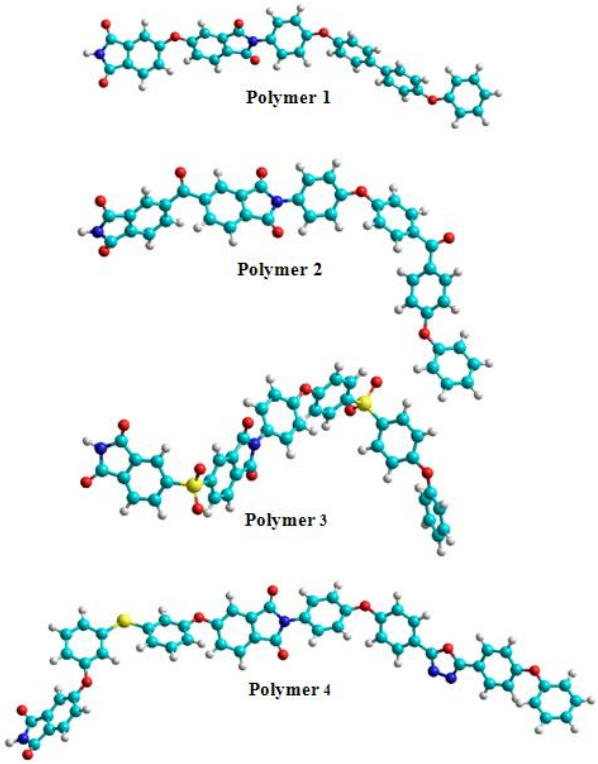

Figure 2: *The conformation of the aromatic imidic polymers computed for one structural unit.*

3. Results and discussion

The ability of the suggested polymers to conduct heat was determined through the connectivity indices formalism. The thermal conductivity (λ) at room temperature can be estimated by taking into consideration the contribution of the bonds between pairs of atoms present in the main chain and also the amount of some specific atoms. Bicerano [Bicerano, 1996] developed the expression used in our calculations:

$$\lambda = 0.135614 + 0.126611 \cdot {}^{1}\chi^{BB}/\mathrm{N} + \\ + 0.108563(N_N + N_O - 0.125N_H)/\mathrm{N} \quad (1)$$

where ${}^{1}\chi^{BB}$ is the first-order connectivity index which accounts for the atom bonds that contribute to the transport property, N is the number on non-hydrogen atoms, while N_N, N_O and N_H represent the number of nitrogen, oxygen and hydrogen atoms, respectively.

The results achieved based on equation (1) for all specimens are displayed in **Table 1**.

Table 1: The values of the first-order connectivity index and thermal conductivity of examined polymers

Sample	${}^{1}\chi^{BB}$	λ (J/m·K·s)
Polymer 1	21.247	0.204
Polymer 2	21.431	0.203
Polymer 3	21.252	0.212
Polymer 4	33.879	0.211

The thermal conductivity values are influenced by the chemical structure of the imidic polymers. The samples containing sulfone groups (polymer 3) or heterocyclic moieties (polymer 4) are able to conduct better heat, comparatively with the other two examined materials. It seems that these structural peculiarities are favoring the transport of carriers (electrons and phonons) in the specimens at room temperature. This result recommends these imidic compounds for applications in high power electronics, where heat conduction and resistance at elevated temperatures are required.

Other important properties in electronics are based on the dielectric performance of the material [Ghosh, 1996]. This can be further related in a certain manner to the volume resistivity of the polymer. For the studied samples, the group contribution method was applied. The mean polarizability of the samples was assessed using this principle and HyperChem. The Lorentz-Lorenz equation was used for refractive index estimation (2):

$$\frac{n^2 - 1}{n^2 + 2} V = \frac{4\pi N_A}{3} \alpha \quad (2)$$

where n is the dielectric constant, V is molar volume, N_A is Avogadro's number and α is the mean polarizability.

The dielectric constant (ε) can be estimated by applying the Maxwell equation that includes the infrared contribution. It was observed that the samples with higher mean polarizability present the highest dielectric constant values, namely 3.59 (polymer 3) and 3.19 (polymer 4), comparatively with 3.07 and 3.08 for polymers 1 and 2, respectively. The volume resistivity was also affected by the dielectric behavior of studied compounds. **Figure 3** reveals that the samples 3 and 4, characterized by the highest permittivity, present the highest electrical conductivity.

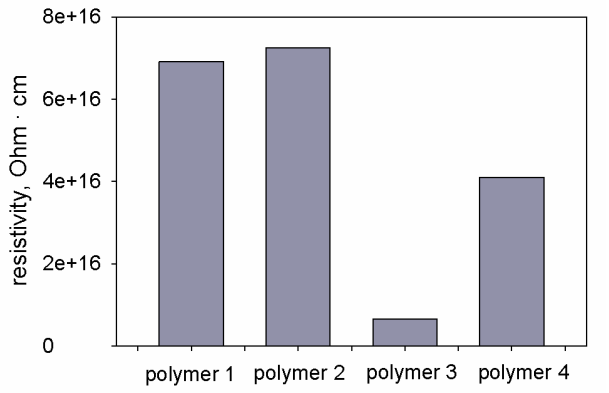

Figure 3*: The variation of volume resistivity with the chemical structures of the samples.*

The result is in good agreement with obtained data for thermal conductivity. However, the level of conductivity is still low and it is not in the range of semiconducting samples. Therefore, in order to enhance this property, a good alternative would consist in addition of conductive nano-sized filler particles, like carbon nanotubes, fullerene or graphene.

Given the values for transport properties for the studied imidic polymers, the results recommend their utilization in manufacturing parts of electronic circuits that require components with insulating features, medium heat dissipation and high thermal resistance (considering their aromatic structure they would a high glass transition temperature above 350°C).

A further step in this study was to evaluate the potential energy of interaction (V) with some metal oxides or nitrides used in electronic industry. In printed circuit boards, a polymer is faced with metallic parts and their good interaction is important for good operation of the whole device. As seen in **Figure 4**, the potential energy of interaction was determined for analyzed imidic polymers and copper oxide (CuO), titanium oxide (TiO) and chromium nitride (CrN).

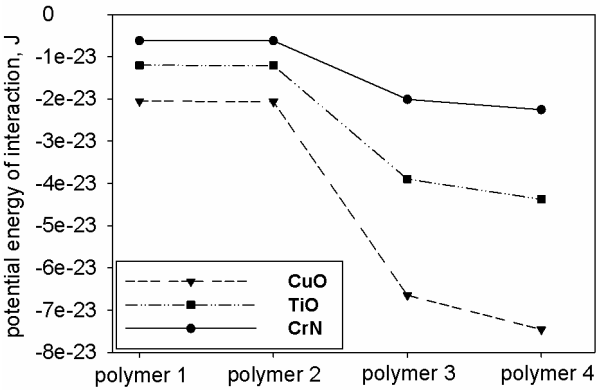

Figure 4*: Potential energy of interaction of the polymer samples with different metal oxides.*

All macromolecular specimens exhibit a potential energy of interaction of about the same order of magnitude (10^{-23} J). It can be noticed that regardless the sample structure, this parameter ranges in the following order: $V_{CuO} < V_{TiO} < V_{CrN}$.

The obtained data is important in selecting the polymers with optimum balance between transport properties and potential energy of interaction with metallic parts of circuits.

4. Conclusions

A series of four imidic polymers with aromatic structures were evaluated from the point of view of their transport properties. Thermal conduction was highest for the sample containing sulfone groups and lowest for specimen derived from ether bridges. The same tendency was observed concerning the electric resistivity. The potential energy of interaction with metal oxides or nitrides was determined. All samples interact better with chromium nitride and titanium oxide. This result is favorable for manufacturing components for electronic circuits that are compatible with such metallic parts. Given the electrical insulation level and permittivity values, the samples would be good candidates for capacitors based on organic dielectrics.

Acknowledgements: This work was supported by a grant from the Romanian National Authority for Scientific Research and Innovation, CNCS–UEFISCDI, project PN-II-RU-TE-2014-4-2976, no. 256/1.10.2015.

References

1. Tong, X. C., *Advanced materials for thermal management of electronics packaging*, New York, Springer, 2011.
2. Bueppelmann, K. and Weber K, *Electrically conductive materials based on graft copolymers*, Plast. Rubber Compos. Process. Appl., 22, 47, 1994.
3. Drobny, J.G., *Polymers for electricity and electronics: Materials, properties, and Applications*, Hoboken, Wiley, 2012.
4. Albu, R.M., Avram, E., Musteata, V.E. and Ioan, S., *Dielectric relaxation and AC conductivity of modified polysulfones with chelating groups*, J. Solid State Electrochem., 18, 785, 2014a.
5. Barzic, R.F., Barzic, A.I. and Dumitrascu, Gh., *Percolation network formation in poly(4-vinylpyridine)/aluminum nitride nanocomposites: rheological, dielectric, and thermal investigations*, Polym. Compos., 35, 1543, 2014.
6. Albu, R.M., Stoica, I., Avram, E., Ioanid, E.G. and Ioan, S., *Gold layers on untreated and plasma-treated substrates of quaternized polysulfones*, J. Solid State Electrochem., 18, 2803, 2014b.
7. Banerjee, S., *Handbook of specialty fluorinated polymers- preparation, properties, and applications*, Elsevier, Amsterdam, 2015.
8. Bicerano, J., *Prediction of the properties of polymers from their structures*, J.M.S.-Rev. Macromol. Chem. Phys., 36, 161, 1996.
9. Ghosh, M.K. and Mittal, K.L., *Polyimides: fundamentals and applications*, Marker Dekker, New York, 1996.