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Temperature dependence of the electrical conductivity of some conjugated polyazomenthines

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The temperature dependence of the electrical conductivity (σ) of six conjugated polyazomethines was studied in the temperature range (303-423 K). A plot of log(σ) versus (1/T) reveals two regions with an inflection point at the glass transition temperature T_g of the polymers. Below T_g the conductivity is not very sensitive to change in temperature, while the sensitivity increases above T_g. This behavior is explained as a consequence of the effect of the different types of motions of the polymeric chains below and above T_g on the conductivity of the polymers.

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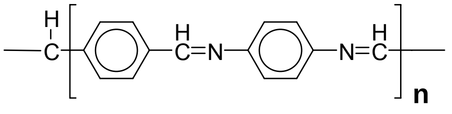
1. Introduction

M. Serin and co-worker [1] investigated the temperature dependence of the dark (d_c), conductivity of the polyester of bisphenol-A with tert-phthalic and isophthalic acid (ARDEL) in the temperature range of (300-520 K)[1]. A plot of log(σ) versus the inverse temperature shows two regions, a low-temperature region and a high-temperature region, with an inflection point at the (T_g) of the polymer. Thus, the authors suggested the measurement of temperature dependence of conductivity as a new method for the determination of (T_g) of these types of polymers.

In the present work we have measured the conductivity of six conjugated polyazomethines in the temperature range (303-423 K) in order to get insight into the nature of this behavior.

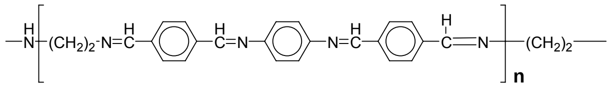
2. Investigated polymers

Polymer I was prepared via the polycondensation of p-phenylene diamine and terephthaldialdehyde, the anticipated structure of the polymer is as follows:



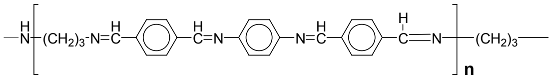
Scheme (I)

Polymer II was obtained through the polycondensation of terephthaldialdehyde, p-phenylene diamine, and 1,2-ethylene diamine in the molar ratio 2:1:1.The anticipated structure of the polymer is as follows:



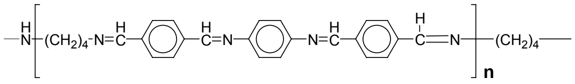
Scheme (II)

Polymer III was prepared through the polycondensation of terephthaldialdehyde, p- phenylene diamine and 1, 3-propane diamine in the molar ratio 2:1:1.The anticipated structure of the polymer is as follows:



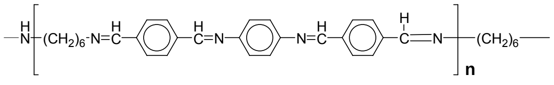
Scheme (III)

Polymer IV was obtained through the polycondensation of terephthaldialdehyde, p- phenylene diamine and 1,4- butane diamine in the molar ratio 2:1:1 . The ideal structure of the polymer is as follows:



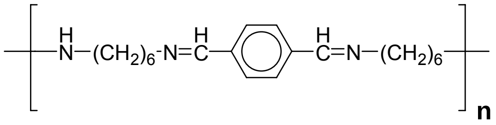
Scheme (IV)

Polymer V was prepared through the polycondensation of terephthaldialdehyde, p- phenylene diamine and 1, 6-hexane diamine in the molar ratio 2:1:1. The anticipated structure of the polymer is as follows:



Scheme (V)

Polymer VI was prepared through the polycondensation of terephthaldialdehyde, and 1, 6-hexane diamine in the molar ratio 1:1. The anticipated structure of the polymer is as follows:



Scheme (VI)

3. Results and discussion

Table (1) contains the values of the conductivities of polymers (I-VI) at different temperatures. The conductivity of the polymers in the first region, which covers the temperatures below (T_g) is not very sensitive to temperatures variations, while the other region which covers the temperatures above (T_g) exhibits a higher temperature dependence. These details are revealed in Fig. (1) For the case of polymer I. All other polymers behave similarly.

Table 1. Conductivities of pure polymers as a function of temperature.

Temp. (K)	Conductivity (S/cm)					
	Pol. I	Pol. II	Pol. III	Pol. IV	Pol. V	Pol. VI
303	4.18E-13	1.51E-13	1.544E-13	1.63E-13	1.82E-13	2.12E-13
313	5.83E-13	1.93E-13	1.83E-13	1.99E-13	2.25E-13	2.60E-13
333	7.70E-13	3.22E-13	2.95E-13	3.08E-13	3.58E-13	4.17E-13
353	1.89E-12	6.29E-13	5.39E-13	5.40E-13	6.87E-13	8.89E-13
373	3.88E-12	1.55E-12	9.70E-13	1.03E-12	1.55E-12	1.94E-12
393	1.33E-11	5.97E-12	6.63E-12	9.94E-12	9.98E-12	1.19E-11
423	9.07E-11	3.39E-11	3.08E-11	5.08E-11	4.07E-11	5.03E-11

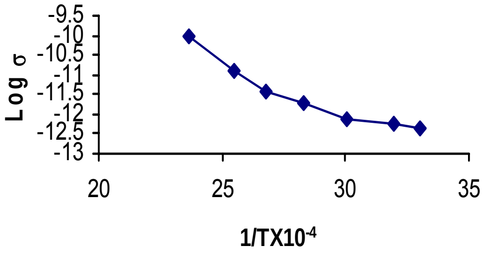


Fig. 1. Arrhenius plot of log σ versus 1/T for polymer.

M. Serin and Co-workers attributed the increase of conductivity with the elevation of temperature to the rise in population of electrons in the excited state (conduction band)[1]. This excitation involves the transfer of electrons from the HOMO to the LUMO of the organic semiconductor. For coloured compounds, which is the case in conjugated polymers, the excitation energy lies in the range of (1.5-2) eV.mol^{-1}. Activation energies determined by us for the studied polymers are in the range (0.1-0.13) eV.mol^{-1}for the region below T_g, and in the range (0.3-0.44) eV.mol^{-1} in the region above T_g .

In our opinion, the segmental motion of the polymeric chains provides a better explanation for the temperature dependence of the conductivity of conjugated polymers. Below Tg large-scale segmental motion of polymeric chains does not take place, only few types of restricted motions exist below this temperature [2]. In these types of motions the moving moieties (side-chains, methylene or phenylene groups in the main chain) do not change place, but rather rotate or carry on torsional motions around an equilibrium position. Above T_g a liquid-like motion of long segments of the polymeric chains becomes possible which gives rise to inter-chain collisions. These collisions are not expected to influence any intramolecular electronic excitation, but they enhance the inter-chain charge-carriers transfer.

At low temperatures and in the absence of segmental collisions the charge-carries have to traverse the space separating the chains and overcome potentials with high energy barriers. As the temperature increases and segmental collisions becomes possible, the inter-chains charge-carriers transfer becomes Feasible via a direct contact between the exchanging moieties. This approach is supported by the fact that all polymeric properties that are sensitive to segmental mobility suffer a change in their temperature dependence at the T_g of the polymers [3]. Specific heat capacities of polymers and their volume coefficient of expansion [4] are examples of such properties.

The process of the inter-chain charge-carriers transfer may be thought as a function of the strength of electronic donor-acceptor interactions between the exchanging chains moieties. This transfer is further facilitated by the chains collisions and the external electric field.

Table 2. Activation energies of the electrical conductivity of polymers (I-VI) eV.mol^{-1}.

	Pol. I	Pol. II	Pol. III	Pol. IV	Pol. V	Pol. VI
Ea_1	0.1086	0.1320	0.1105	0.1055	0.1222	0.1280
Ea_2	0.3017	0.3571	0.3890	0.4373	0.3674	0.3666

Table (2) gives the activation energies of the conductivity of polymers (I-VI) below (Ea_1), and above

(Ea_2) the glass transition temperature. These energies are obtained from the slopes of the lines resulting from plotting log (σ) of the polymers versus (1/T). The activation energies below T_g fall in the range of (0.1-0.13) eV and in the range of (0.3-0.44) eV above T_g. The types of molecular motions below T_g are mainly the torsion of phenylene or methylene groups along the main chains, which require less energy than the large-scale segmental motion that commences above T_g.

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