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The temperature dependence of the electrical conductivity of some unsaturated copoly (ester-amine) polymers

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The temperature dependence of the electrical conductivity (σ) of ten unsaturated copolymers of the (ester-amine) type was studied in the temperature range (303-373K). A plot of log (σ) versus (1/T) reveals two region 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. The Tg of the investigated polymers determined with this method is influenced by the nature of monomers constituting the polymers and their sequence distribution.

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Keywords: Unsaturated copoly (ester-amine) polymers, Electrical conductivity, Glass transition temperature, Molecular motion

1. Introduction

The effect of temperature on electrical conductivity of conjugated polymers have been studied by many authors [1,2]. A plot of log (σ) versus the increase temperature (1/T) show two regions with an inflection point at the glass transition temperature.

The segmental motion of the polymeric chains provides a reasonable explanation for the temperature dependence of the conductivity of conjugated polymers. The conductivity process is affected through transport of charge carries which traverse through the space separating the chains. Shahab and coworkers [2] pointed out that the inter-chain charge carriers transfer is a function of the strength of electronic donor-acceptor interaction between the exchainging chains moeities. This transfer is further facilated by the chains collosions and the external electric field.

In the present work we have measured the conductivity of ten different copolymers of the ester-amide structure in the temperature range (303-373 K) in order to study the influence of monomer sequence distribution, the nature of the constituting monomers, and the interruption of the conjugation of chains of the electrical conductivity process.

2. Experimental

Ten polymers have been prepared via the condensation of terephthaloyl dichloride, isophthaloyl dichloride, maleic anhydride and maleoyl dichloride as diacids with different diols and diamines. (Table 1).

Polymer I was synthesized by condensation polymeyization of terephthaloyl dichloride with a mixture of hydroquinone and *p*-phenylene diamine. Polymer II was prepared by reaction of terphthaloyl dichloride firstly with hydroquinone, then with terephthaloyl dichloride. Polymer III was obtained via polymerization of hydroquinone with isophthaloyl dichloride. Condensation polymerization of isophthaloyl dichloride with a mixture of hydroquinone and *p*-phenelene diamine gave polmer IV. Polmer V was prepared through transesterfication of 1,4-dimaleoyl hydroquinone and N,N\`-diacetoyl-*p*-phenylene diamine, and polymer VI was obtained by reaction of 1,5-dimaleoyl diethyleneglycol with N,N\`-diacetoyl-*p*-phenylene diamine.

Polymer VII was prepared by polycondensation of maleoyl dichloride with resorcinol and *p*-phenelene diamine using the same procedure for preparation of polymer II. Polycondesation of moleoyl dichloride with a mixture of hydroquinone and *p*-phenylene diamine delivered polymer VIII. Polycondensation of maleoyl dichloride with a mixture of diethylene glycol and *p*-phenylene diamine resulted in polymer IX. Finally, polymer X was synthesized via the condensation of maleoyl dichloride with hydroquinone and *p*-phenylen diamine following the procedure of preparing polymer II.

The T_g was measured according to the methods suggested by Serin and Co-worker.

Table 1. The monomers used for preparing the polymers.

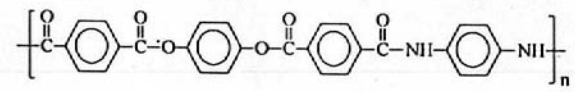
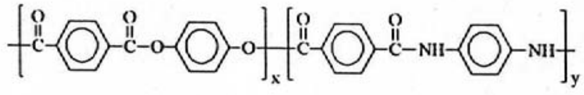
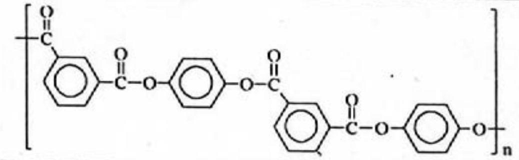
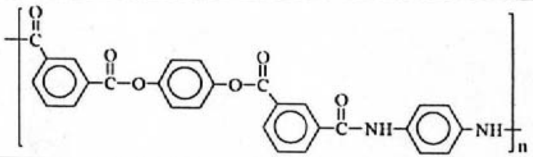
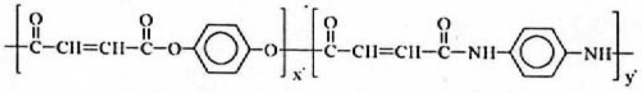
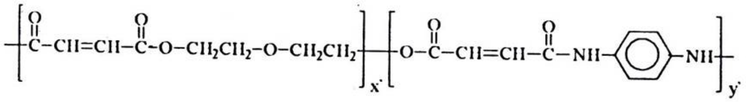
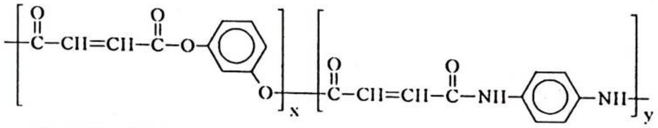
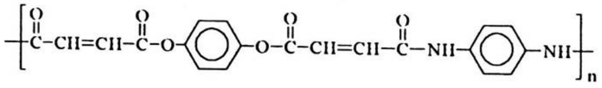
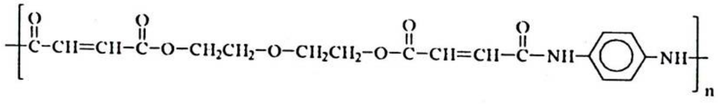
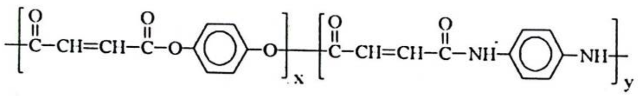
No.	Acid chloride	Anhydride	Diol	Diamine	Sequence distribution	Structure
I	Terephthaloyl dichloride	-	Hydroquinone	p-Phenylene diamine	Random	
II	Terephthaloyl dichloride	-	Hydroquinone	p-Phenylene diamine	Block	
III	Isophthaloyl dichloride	-	Hydroquinone	-	-	
IV	Isophthaloyl dichloride	-	Hydroquinone	p-Phenylene diamine	Random	
V	-	Maleic anhydride	Hydroquinone	p-Phenylene diamine	Alternating	

Table 1. continue.

No.	Acid chloride	Anhydride	Diol	Diamine	Sequence distribution	Structure
VI	-	Maleic anhydride	Diethylene glycol	p-Phenylene diamine	Alternating	
VII	Maleoyl dichloride	-	Resorcinol	p-Phenylene diamine	Block	
VIII	Maleoyl dichloride	-	Hydroquinone	p-Phenylene diamine	Random	
IX	Maleoyl dichloride	-	Diethylene glycol	p-Phenylene diamine	Random	
X	Maleoyl dichloride	-	Hydroquinone	p-Phenylene diamine	Block	

X = Large segment of ester unit.
Y = Large segment of amide unit.
X` = One segment of ester unit.
Y` = One segment of amide unit.

3. Results and discussion

3.1. Change of conductivity with temperature elevation

Table 2. shows the electrical conductivities (σ) of polymers (J-X) at different temperature. The plot of ln (σ) versus the inverse absolute temperature shows two regions. The first region, which covers the temperatures below Tg, is less sensitive to temperature variations, while the other region, which covers the temperature above T_g, exhibits a larger temperature dependence. Fig. 1 reveals these observation for polymer I. All other polymers behave similarly.

Table 2. The conductivities (S / m) of polymers (1-X) at different temperatures.

Polymer no.	303 K	313 K	323 K	333 K	343 K	353 K	363 K	373 K
I	3.01 E-11	3.28 E-11	3.97 E-11	4.43 E-11	4.77 E-11	5.54 E-11	8.38 E-11	1.5 E-10
II	5.67 E-11	6.72 E-11	9.86 E-11	1.21 E-10	3.11 E-10	6.03 E-10	6.86 E-10	1.00 E-9
III	3.14 E-10	3.49 E-10	4.10 E-10	5.24 E-10	6.28 E-10	8.57 E-10	9.43 E-10	1.00 E-9
IV	4.52 E-11	5.47 E-11	6.86 E-11	8.49 E-11	1.13 E-10	2.09 E-10	6.17 E-10	1.00 E-9
V	7.86 E-12	8.00 E-12	1.26 E-11	1.43 E-11	1.29 E-11	1.2 E-11	1.42 E-11	1.55 E-11
VI	1.31 E-11	1.58 E-11	1.62 E-11	1.77 E-11	1.81 E-11	1.88 E-11	2.06 E-11	2.39 E-11
VII	8.62 E-11	1.31 E-10	1.49 E-10	1.97 E-10	1.22 E-10	1.53 E-10	1.49 E-10	4.00 E-10
VIII	2.13 E-11	2.33 E-11	2.62 E-11	2.78 E-11	3.95 E-11	4.97 E-11	6.5 E-11	6.89 E-11
IX	1.2 E-11	1.25 E-11	1.61 E-11	1.73 E-11	1.94 E-11	2.03 E-11	2.53 E-11	3.12 E-11
X	9.8 E-8	1.17 E-7	1.92 E-7	3.27 E-7	6.48 E-7	4.15 E-6	2.07 E-5	2.07 E-5

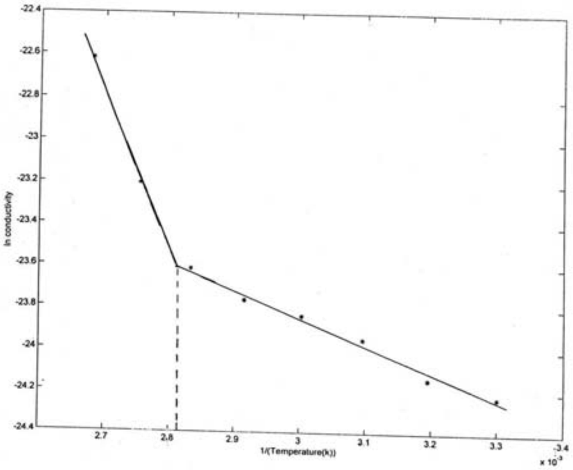


Fig. 1.Tthe relation between ln (conductivity) and the inverse absolute temperature for polymer (I).

The activation energies for the temperature dependence of the conductivity of different polyazomethines determind by shahab and Co-workers lie in the range (0.1-0.49) $eV.mol^{-1}$. M. Serin and Co-workers attributed the increase of conductivity with the elevation of temperature to the rise in population of electrons in the exited 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 for conjugated polymers. The excitation energy lies in the range of (1.5-2) $eV.mol^{-1}$. therefore, Shahab and co-workers explained this behaviour in terms of the increase of the mobility of chain segments with the increase in the temperature.

Below T_g large-scale segmental motion of polymeric chains does not take place, only few types of restricted motions exist below this temperature. In these types of motions the moving moieties (side-chains, phenylene or methylene groups in the main chain) do not change place, but rathor or carry torsional motions around an equilbrium position. In this case the charge with the necessity to overconme high energy barriers due to the existence of electric fields.

Above T_g, a liquid like motion of long segments of the polymeric chains becomes possible which gives rise to inter-chain collosions, and enables the electron to jump from one chain to another.

Some of the polymers containing maleic anhydride units (V-X) show irregularity in the temperature-conductivity dependece curve near the T_g. This behaviour is due to the isomerization of maleic to fumaric units with a change of the position of the T_g.

The population of electrons from HOMO to LUMO by increasing temperature is very limited in this case due to the high energy gap separating these energy levels. Therefore the contribution of the electronic excitation to the increase of conductivity due to temperature elevation is minor compared with the contribution arising from the increase in the mobility of chains.

The activation energies determined in this work for the invistigated polymers (Table 3) lie in the range (0.11-0.74) eV.mol^{-1} which is very close to those obtained by shahab and co-workers for conjugated polyazomethines. Hence, we think that the increase in chains segmental mobility at elevated temperature is also in this case responsible for the conductivity enhancement.

Table 3. The activation energies of the electrical conductivity of polymers (1-X) before and after transition temperature (Ea$_1$) and (Ea$_2$).

Polymer	Ea$_1$ / eV.mol^{-1}	Ea$_2$ / eV.mol^{-1}
I	0.11	0.33
II	0.21	0.33
III	0.25	0.066
IV	0.19	0.67
V	0.17	0.11
VI	0.05	0.12
VII	0.23	0.34
VIII	0.07	0.29
IX	0.091	0.12
X	0.74	0.69

3.2 Effect of the structure of polymer on Tg

There are many factors which influence the Tg of the polymers. The most important of these factors are the nature of monomers constituting the polymers and their sequence distribution [3]. However the existence of strong hydrogen bonding in the investigated copolymers leads to certain irregularities and unexpected results.

Table 4 gives the Tg of the studied polymers. Tg of polymers I, IV and VIII decrease from 354 to 344 to 333 K as the acidic units change form terephthalic to isophthalic to maleic.

Table 4. The glass transition temperature of polymers (I-X).

Polymer	Tg (K)
I	354
II	337
III	347
IV	344
V	353
VI	358
VII	342
VIII	333
IX	357
X	347

The aromatic groups introduce stiffness in the polymeric chains [4] with a larger effect of the para terephthalic acid compared with meta isophthalic acid, since the former can give trans extended structure of polymeric chains, that possess great tendency to crystallization.

Polymers V, VIII and X are all composed of the same monomeric units, but they differ in the sequence distribution. They are alternate, random and block respectively. The T_g if these polymers have the order:

V > X > VIII

This can be rationalized in terms of the regularity and associated tendency to crystallization of the chains which is largest with polymer V and smallest with oplymer X. these results indicate that the sequence distribution of the monomers in the chains strongly effect the T_g and in the order:

Alternate > random > block

This behaviour was noticed clearly with polymers I and II, which are composed of other monomer units.

The values of the Tg of polymers VIII and IX are also surprising; They are both random and different only in the diol units. Contrary to exception, the replacement of hydroquinone with diethylene glycol raised the Tg instead of lowering it. Diethylene glycol is an aliphatic ether. Ethers are known to be very flexible due to the ease of rotation around the ether linkage. Apparently, the rotation is restricted in this case because of the involvement of the ether linkage with hydrogen bonding.

References

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