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d.c. CONDUCTIVITY AND STRUCTURE OF NYLON 6-LiCl MIXTURES

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Abstract—d.c. Conductivity experiments have been performed for a wide range of temperature under a constant voltage application for nylon 6 and its mixture with 4% w/w LiCl. The data confirm previous indications of decrease of crystallinity and increase of glass transition due to lithium halides. Support is also given to previous interpretations of the conduction mechanism for polyamides, i.e. essentially electronic below 80° but essentially ionic above 110°.

INTRODUCTION

Polymeric materials have been extensively studied for their electric behaviour especially because of their interesting properties as insulators. In particular the dependence of electric characteristics on temperature, pressure, moisture, applied field strength and on physical ageing has been carefully examined [1, 2]. These experiments have shown in many cases different behaviour between polymers and other materials e.g. the negative temperature coefficient of the resistivity and the non-linear (non-ohmic) current–voltage dependence. Moreover much work has been performed to elucidate the influence of structural characteristics like crystallinity [3], anisotropy [4], presence of ions [5], metal powder [6], plasticizers [5, 7] on electric properties. It is possible, at least in principle, to get informations on the structure of polymers through electrical measurements. The present work has this objective and d.c. conductivity results are used to confirm previous indications on changes in polyamide structure due to lithium halides [8, 9]. These inorganic salts have been shown to play an important role by breaking hydrogen bonds and inducing a pseudo-crosslinking between lithium ions and the carbonyl–oxygen groups. The effects are depression on the melting point, increases of the glass transition, density and melt viscosity, and decreases of crystallization rate and degree of crystallinity [8–10].

The data are also used to elucidate further the peculiar resistivity–temperature relationship for polyamides with respect to other polymers. It is known for instance that these polymers have at room temperature a very high resistivity, comparable with that for other organic insulators, but it decreases very quickly with rising temperature. This phenomenon is at present explained on the basis of proton mobility of amide groups, which is possible at high temperature. In a detailed study of nylon 66 Seanor [4] has found that above 90° the conduction has to be considered both electronic and with proton transfer, as also indicated by gas evolution, with the two conduction types being quantitatively comparable around 120°; below 90°, the conduction is only electronic as confirmed by Baird [12].

EXPERIMENTAL

The polymer used in the experiments was a nylon 6 manufactured by SNIA, stabilized at $T = 260°$ for ~5 hr. Its mixture with 4% w/w LiCl was also tested. The preparation of such mixtures has been described [8].

Disc shaped samples, ~8 cm dia, were cut from compression moulded sheets, 0.5 mm thick. The moulding temperature was 230° for pure nylon and 210° for the salted polymer. The samples were kept in a vacuum desiccator with silica gel for at least three days prior to the experiments which were conducted in a moisture-free atmosphere. The sample surfaces were covered with aluminium paste to ensure good electric contact with the electrodes. A three-electrode arrangement was used, with dimensions according to ASTM D257/72, in order to obtain the volume resistivity of the material, excluding any contribution of the surfaces.

The circuit employed in the measurements included also a Trygon low voltage power supply, a Keithley mod. 610 low current measuring electrometer, a digital voltmeter to check the applied voltage and a recorder inserted on the electrometer output.

All the measurements were performed with an applied voltage of 50 V, at temperatures between 25 and 160°, achieved by putting the electrodes and the sample into an oven. A slight dry nitrogen flow was blown throughout the tests, which lasted in most cases about 1000 sec although much longer experiments have also been carried out. Samples were used only once for the high temperature tests, because of possible degradation and especially of the crystallization of salted nylon and recrystallization of pure polymer; samples were used a few times at lower temperatures. In this case, after one test and before starting another, the electrodes were short-circuited for about 24 hr to discharge any residual current.

RESULTS AND DISCUSSION

Consider first the current-time curves reported in Figs 1 and 2 for pure nylon and for the nylon/4% LiCl system respectively. The pure polymer shows a slowly decreasing behaviour and never reaches a steady state. For nylon in presence of the salt, the behaviour changes very clearly with temperature: in particular the transient curves experimentally obtained above 77° attain a steady state. It has been already found [13–16] that, for crystalline polymers and for amorphous polymers below their glass

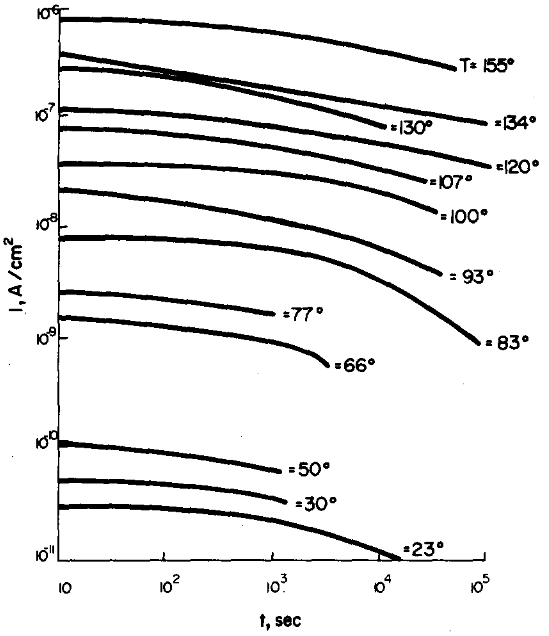

Fig. 1. Transient d.c. current after application of a 50V step voltage for pure nylon 6.

transition, the transient current curves never reach a steady state while such a value is attained by molten polymers and by amorphous polymers above T_g. It has already been shown by various measurements [8, 10] that, while nylon 6 is a typical semicrystalline polymer (degree of crystallinity about 30%; T_g between 50 and 60°; T_m 225°) the polymer with 4% w/w LiCl is almost fully amorphous, melts at 206° and has a glass transition temperature around 83° as seen from mechanical measurements [10].

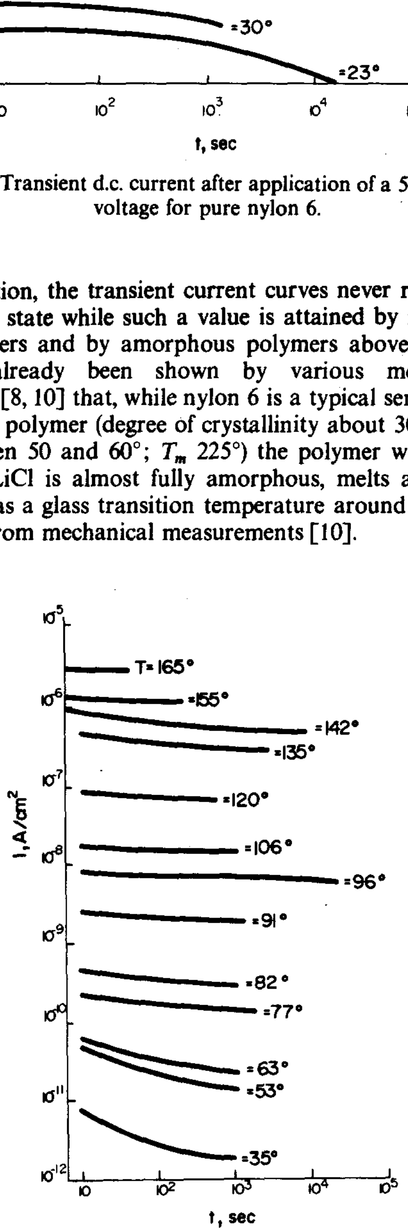

Fig. 2. Transient d.c. current after application of a 50V step voltage for the nylon 6/4% LiCl system.

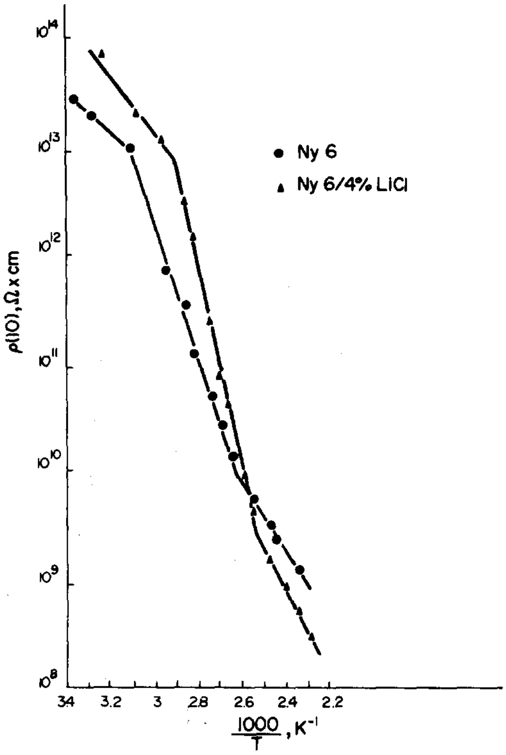

Fig. 3. Arrhenius plot of 10 sec resistivity.

For better evaluation of the glass transition temperature, isocronal resistivity values (at 10 sec) as taken from previous curves have been plotted in Fig. 3 vs (temperature)$^{-1}$ [7]. For each polymer three zones with different temperature coefficients can be seen. The first break point is at 52° for pure nylon and at 73° in the case of Ny/4% LiCl. Such values are very similar to those found from isocronal relaxation moduli (59 and 83° respectively) [10]. Of course when resistivity values taken at different times are plotted in the same way, the break points are found at different temperatures: again there is a correspondence in the mechanical and dynamic-mechanical response [17, 18]. As for the break points at higher temperatures, they may be perhaps understood in terms of conduction mechanisms. In this connection, some other interesting features of the curves in Fig. 3 should be noted. In the low temperature region, the salted polymer has a resistivity higher than pure nylon; at the other end of the explored range of temperatures, the inverse is true and the pure polymer has a resistivity higher than the salted material. Seanor [4] showed and Baird [12] confirmed that, in the low temperature region (below 80°), the conduction is essentially electronic probably involving as perhaps in the case of proteins [19], the electrons of the carbonyl group. This could well explain the higher resistivity of the salted samples for which the electrons of the double bond in the carbonyl group have been shown to be involved in a binding with Li^+ ions [8–11]. Of course on increasing the temperature, due to the increasing relative influence of the ionic conduction mechanism, the resistivities are not so different and eventually that of the pure nylon becomes higher due to a higher degree of crystallinity [3]. Above 110° in particular, the conduction mechanism is perhaps essentially ionic in character and therefore the slopes of the curves become almost the same. Also the slight differences in slope, i.e. in activation energies, are in line with the lower degree of crystallinity of the salted samples compared with that of the pure nylon. The obtained values for such a polymer are similar to others reported in literature, at least in the intermediate range of temperature [4, 6, 12].

CONCLUDING REMARKS

The transient d.c. results here reported for the nylon 6 and its mixture with 4% LiCl confirm the structural changes induced in the salted samples, viz the low degree of crystallinity and the increased glass transition temperature. The derived transition values compare well with those obtained in related work. Support is also given to previous interpretations on the conduction mechanism for polyamides: it is shown that conduction is essentially electronic at low temperatures (below 80°) but essentially ionic above 110°. The different resistivities and some differences also in their temperature dependence again confirm the binding action of the Li^+ ions and the decrease in crystallinity in the salted samples.

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REFERENCES

1. L. T. Yu, M. Jozefowicz and R. Buvet, *Chimie Macromoleculaire* Herman, Paris (1970).
2. D. A. Seanor, *Polymer Science*. Amsterdam, North-Holland (1972).
3. L. E. Amborsky, *J. Polym. Sci.* **62**, 331 (1962).
4. D. A. Seanor, *J. Polym. Sci. C* **17**, 195 (1967).
5. R. E. Barker and C. R. Thomas, *J. appl. Phys.* **35**, 87 (1964).
6. T. Czekaj and J. Kapko, *J. appl. Polym. Sci.* **21**, 2475 (1977).
7. A. Lupu, M. Giurgea, I. Baltog and P. Gluck, *J. Polym. Sci. Phys. Ed.* **12**, 2399 (1974).
8. B. Valenti, E. Bianchi, G. Greppi, A. Tealdi and A. Ciferri, *J. phys. Chem.* **77**, 389 (1973).
9. E. Bianchi, A. Ciferri, A. Tealdi, R. Torre and B. Valenti, *Macromolecules* **7**, 495 (1974).
10. D. Acierno, F. P. La Mantia, G. Titomanlio and A. Ciferri, *J. Polym. Sci. Phys. Ed.* In press.
11. D. Acierno, E. Bianchi, A. Ciferri, B. De Cindio, C. Migliaresi and L. Nicolais, *J. Polym. Sci. Polym. Symp.* **54**, 259 (1976).
12. M. E. Baird, *J. Polym. Sci. A2*, **8**, 739 (1970).
13. G. Stetter, *Kolloid Z.* **215**, 112 (1967).
14. A. E. Binks and A. J. Sharples, *J. Polym. Sci. A-2* **6**, 407 (1967).
15. V. Adamec, *Koll. Polymer.* **249**, 1085 (1971).
16. F. P. La Mantia and D. Acierno, *Polymer* **19**, 851 (1978).
17. J. D. Ferry, *Viscoelastic Properties of Polymers*. Wiley, New York (1970).
18. T. Murayama, *Dynamic Mechanical Analysis of Polymeric Material*. Elsevier, Amsterdam (1978).
19. D. D. Eley and D. I. Spivey, *Trans Faraday Soc.* **56**, 1439 (1960).