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The influence of pressure-induced structural changes on the ionic conductivity and dielectric relaxation in zwitterionic polymers

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In this work, the effect of the compacting pressure (that required to mould the samples for conductivity measurements) upon the ionic conductivity of two polymers, each with the same macromolecular backbone but with different lateral groups (N-oxide and carboxylic), is studied in detail. A comparative analysis shows that conductivity presents a maximum at a specific value of the compacting pressure (critical pressure) for both polymers, but the largest magnitude corresponds to the amorphous sample (that with a carboxylic group in the lateral pendant structure). The large variations in the conductivity as a function of the compacting pressure contrast to those observed in the relaxation times, where the effect of temperature is dominant. We obtain a single curve for both polymers when the shifting factor (i.e. ratio of relaxation times) in the Williams–Landel–Ferry (WLF) equation is plotted with reduced temperatures for all samples compacted at different pressures. When the reduced temperature is referred to that of the onset point for conductivity of both polymers, we found similar values of the fractional free volume and hence similar mobility at the critical pressure. © 1997 Elsevier Science Ltd.

(Keywords: zwitterionic polymers; compacting pressure; ionic conductivity)

INTRODUCTION

In a previous article[1], it was shown that the ionic conductivity of polymers with zwitterionic structures can be profoundly affected by the pressure used to mould and compact the samples for these studies. Results have illustrated a strong variation of the conductivity for different values of the compacting pressure, with the presence of a maximum in conductivity at a specific critical pressure. It was further pointed out that the changes in conductivity upon pressing the polymer samples may be best interpreted to arise from modifications of the original polarization state due to morphological changes in the structure of these polymers. The zwitterionic polymers studied in the mentioned work comprised N-oxide derivatives of the methacrylic acid, which along the synthesis process were neutralized with sodium hydroxide.

Several studies have examined the effect of pressure upon dielectric relaxation in various polymeric systems[2–7]. Throughout those studies, experiments have been conducted on bulk amorphous samples on which measurements of the dielectric functions are made under pressure. In this work, on the other hand, we perform measurements at atmospheric pressure upon powder samples which are compacted and shaped under pressure. We call this a ‘compacting pressure’, to differentiate this quantity and the ‘hydrostatic pressure’ mentioned before.

In this work we compare the results obtained from the N-oxide derivatives with those from other type of zwitterionic moieties: a carboxybetaine derivative of the same parent polymer. In this regard, we intend to analyse the effect of two kinds of lateral ionic groups on the observed conductivity as a function of the compacting pressure, keeping the same structure of the macromolecular backbone. This study will indicate the form the compacting pressure affects the conductivity through the contributions of the amorphous main polymer chain and lateral groups. A striking result shows that the critical pressure at which the conductivity exhibits a maximum is the same for both polymers when experiments are performed at specific temperatures.

Simultaneously, a dielectric relaxation analysis is carried out to study the variation of the relaxation times with compacting pressure and temperature for both polymers. Through comparisons with predictions of the WLF equation, we intend to give an explanation of the observed dielectric behaviour in terms of variation of the relaxation times due to the morphological changes in the structure of these polymers and modifications of

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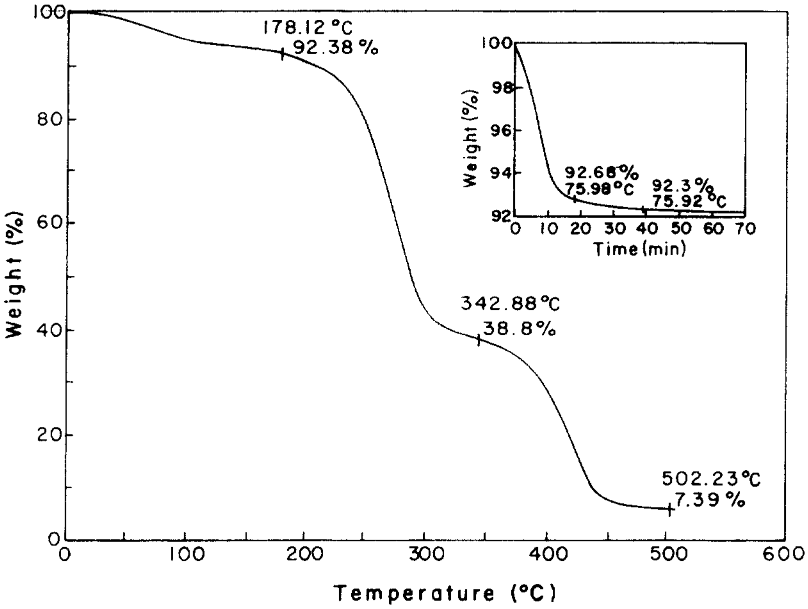


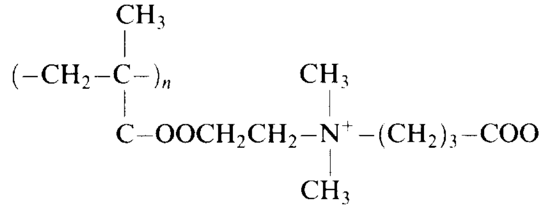
Figure 1 Thermogravimetry results for the carboxybetaine polymer. Weight loss with temperature. Insert: isothermal weight loss with time

the original polarization state brought about by the compacting pressure.

EXPERIMENTAL

Synthesis and characterization of the carboxybetaine polymer

The quaternization reaction to introduce the zwitterionic groups into the poly(N,N'-dimethylaminoethyl methacrylate) was carried out at 82°C in acetonitrile. 1.1 equivalents of 1,4-butyl lactone were added under nitrogen atmosphere. The quaternized polymer was precipitated, filtered and dried in a vacuum oven at 60°C for 24 h. The resulting polymer presents the structure



$$\begin{array}{l} \quad\; CH_3 \\ \quad\;\; | \\ (-CH_2-C-)_n \qquad\qquad CH_3 \\ \quad\;\; | \qquad\qquad\qquad\qquad\; | \\ \quad\; C-OOCH_2CH_2-N^+-(CH_2)_3-COO^- \\ \qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\; CH_3 \end{array}$$

I.r. spectroscopy (Nicolet 710 *FT*i.r. Spectrometer) identified the relevant bands of the precursor polymer and those of the quaternized polymer (1607–1638 cm^{-1}) corresponding to the ionized carbonyl group.

Elemental analysis (Desert Labs. Tucson, AZ) gives 41% of ionic groups or quarternization degree. Molecular weights (M_w) were determined by light scattering (Wyatt), g.p.c. (Waters 6000 A) and viscometry (Ubbelhode-type viscometer) using the universal calibration curve (with polystyrene standards). A molecular weight of 90 000 for the precursor polymer was obtained. The intrinsic viscosity value was 60 mg l^{-1}.

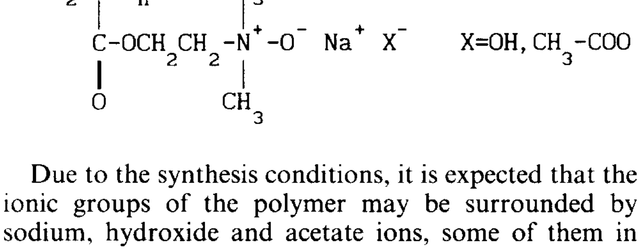
Thermal analysis (TA Instruments, 2100) provided a T_g of 67°C, which is near to the onset point for ionic conductivity given by the a.c. spectroscopy technique (around 83°C, see *Figure 3*). The same features were observed in other zwitterionic polymers (ref. 11) and showed that ionic conductivity was closely related to the mobility of the polymer chains above T_g.

Thermogravimetric analysis shows an initial decrease in sample weight prior to the main stages of chemical decomposition (see insert in *Figure 1*). This drop is related to water loss as the sample is heated (5°C min^{-1} from ambient temperature to 76°C in N_2 atm.). As observed, isothermal measurements show a water loss of around 8% up to 15 min. For times larger than 15 min weight loss due to water content is almost negligible. From these data it was possible to control the humidity content in the dielectric measurements shown later.

Finally, the amorphicity of the sample was estimated by X-ray diffraction (Siemens refractometer d-500, adapted with a heating system under vacuum). Results show that the carboxybetaine polymer is amorphous with negligible crystalline content.

Synthesis and characterization of the N-oxide polymer

The synthesis procedure has been described elsewhere[9]. The precursor polymer ($M_w = 90 000$) is the same as in the carboxybetaine case. The oxidation reactions render N–O structures in every side group (100% of ionic groups). Since the reaction takes place in acid solution, the product was neutralized with NaOH in the presence of acetic acid. The resulting polymer presents the structure



$$\begin{array}{l} \quad\; CH_3 \\ \quad\;\; | \\ (-CH_2-C-)_n \qquad CH_3 \\ \quad\;\; | \qquad\qquad\qquad\; | \\ \quad\; C-OCH_2CH_2-N^+-O^- \; Na^+ \; X^- \qquad X=OH, CH_3-COO \\ \quad\;\; \| \qquad\qquad\qquad\; | \\ \quad\; O \qquad\qquad\quad\;\; CH_3 \end{array}$$

Due to the synthesis conditions, it is expected that the ionic groups of the polymer may be surrounded by sodium, hydroxide and acetate ions, some of them in coordination with the oxygen and nitrogen atoms. To test this hypothesis, elemental analysis was carried out in triplicate and results show that the repeat unit of the polymer is surrounded by hydrated sodium acetate

Table 1 Results of elemental analysis determinations. The calculated values assume the structure described in the text

Element	% Calculated	% Experimental
C	33.84	33.60
H	4.53	4.7
N	1.41	1.2
O	37.06	—
Na	23.16	20.64

structures which comprise 10 sodium atoms together with their respective counterions. *Table 1* shows the calculated content of the elements assuming such structure and the experimental determined contents.

One of the intentions of the present work is the analysis of the effect of varying sodium concentration on the observed ionic conductivity. This was achieved by changing the neutralization degree of the compound using a column filled with a cationic interchange resin.

The sodium-free polymer, on the other hand, was obtained without the neutralization step previously mentioned. Rather, the product mixture was circulated through an anionic interchange resin to eliminate the acetic acid excess. Subsequently, the above procedure to prepare the polymer was followed. Molecular weights of the resulting polymers ranged between 95 000 and 115 000.

The sodium content of the polymer was quantified by fluorescence using SEM. The spectra showed a decreasing sodium content for higher resin amounts. Fully neutralized polymers (studied in ref. 1) presented a crystalline content of 90%. In ref. 1 (*Table 1*) decomposition temperatures and activation energies of fully neutralized samples as functions of the compacting pressure are given.

In the preparation of conductivity experiments, water content was carefully controlled. Water content produces a steep decrease in the glass transition temperature, inducing a lower T_g when the crystalline content is high. For example, the sample with 100% neutralization presents a crystalline content of 90% with a T_g of 270 K, which is in contrast to that of the amorphous sodium-free sample (348 K). The latter presents a T_g value close to that of the amorphous carboxylic polymer (340 K). On the other hand, samples with intermediate sodium concentrations (70%), where humidity can be easily reduced, show higher onset values for conductivity than the amorphous sample (383–393 K). Special care was given to the sample with the highest crystallinity to control water content.

X-ray diffraction (Siemens refractometer D-500, adapted with a heating system under vacuum) determined the crystalline content. The diffraction patterns were affected by the humidity content systematically. As samples are being dried, definite diffraction patterns evolve. Studies on the morphology on N-oxide polymers (see ref. 10) pointed out structure modifications by humidity loss observed in the X-ray data.

Water content was quantitatively estimated by t.g.a., as in the case of the carboxylic polymer. Sample weight loss after 20 min at 40°C was 18% with negligible loss for longer times (0.84% after 60 min). Humidity content affects conductivity measurements by acting as ion source or plastifier, diminishing potential barriers to conduction.

It is important to mention that these polymers do not form continuous films. The films were brittle and cannot be handled for conductivity measurements. Instead, the samples were prepared in powder form and pressed to form disc-shaped specimens for the tests.

Conductivity measurements

The a.c. spectroscopy technique was used to measure the dielectric properties of the polymers, as described elsewhere[11]. The polymers were moulded at room temperature under vacuum for 20 min without cooling, using an Instron 1125 machine, to render disc-shaped samples of 12 mm diameter and 1–2 mm thickness. The compacting pressure varied within 2.6×10^8–8.7×10^8 Pa. In addition, the N-oxide polymer with different amounts of sodium was pressed at 6.07×10^8 Pa which actually corresponds to the pressure of the maximum in conductivity (see Figure 2 in ref. 1). Measurements were taken in a temperature-controlled dielectric cell under vacuum, as described elsewhere[11].

A Hewlett–Packard impedance analyzer (HP-4192-A) controlled by a HP-85 microcomputer was used. Voltage was fixed at 0.5 V and measurements were taken from 19°C up to 300°C, covering a frequency range from 5 Hz to 13 MHz. Data were taken every 25 min to allow temperature equilibration. Further details of the experimental device and technique used can also be found elsewhere[1,11].

RESULTS

Carboxybetaine polymer

Experimental data were processed to obtain the impedance plots from which the resistance values are worked out. *Figure 2* shows the corresponding Cole–Cole plots of this polymer at several temperatures. A compacting pressure of 4.34×10^8 Pa is used to conform the samples. The presentation of data is made through complex impedance curves. Information

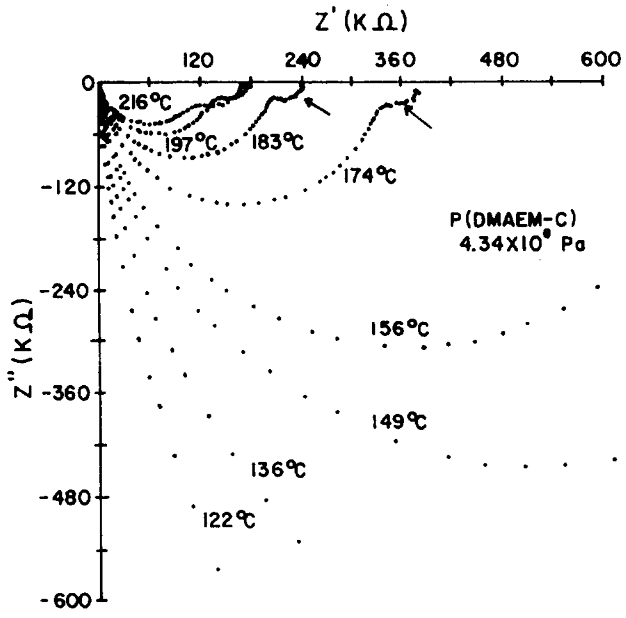


Figure 2 Cole–Cole plots of the real and imaginary parts of the complex impedance for several temperatures at a compacting pressure of 4.34×10^8 Pa. Carboxybetaine polymer. Arrows indicate semicircles corresponding to grain boundaries contributions

obtained from this form of presentation allows us to examine how strongly electrode polarization contributes to the complex dielectric function[13]. It is known that electrode polarization causes deviations on the low frequency side of the semicircle[14] which appear as minima followed by a further increase for lower frequencies. It also allows us to examine the response from grain boundaries in powder samples.

In general, it is observed that the plot comprises two semicircles: one corresponding to the response of the bulk polymer sample and the other one, whose capacitance (C) and resistance (R) values show the presence of a potential barrier which impedes the free transfer of charge carriers similarly as the grain boundaries in polycrystalline ceramic systems. (For example, in *Figure 2*, arrows show the small semicircles corresponding to the grain boundaries contribution at two temperatures.) The capacitance values of the second semicircle (low frequency) are substantially dependent on temperature, as found in *Table 3*. Capacitances of the bulk polymer, on the other hand, do not change with temperature. It was found that the second semicircle depends strongly on the method of preparation and homogeneity of the sample. To investigate this aspect further, two types of experiments were carried out. In the first case, the sample was compacted from a polymer which presented a grainy appearance and big agglomerates, similar to samples of microcrystalline ceramics. The dielectric response of such a system showed two semicircles in the impedance plane. In the second case, the polymer was processed in powder form and upon moulding the sample the pellet so formed showed an homogeneous appearance. The resulting dielectric response in this case corresponded to a single semicircle.

Data of the bulk sample show an increase in conductivity as temperature increases. Values of conductivity calculated through the product of the geometrical factor (width of sample divided by its area) times the reciprocal resistance are presented in *Table 2* for several temperatures. Further information provided by the impedance curves is the value of the capacitance associated with the curves minima, calculated according to the relation

$$C = \frac{1}{2\pi\omega_{\min}R} \qquad (1)$$

where $\omega_{\min}$ is the frequency at the minimum of each curve and R is the resistance. Equation (1) considers that the electric response of the sample is described by a parallel R–C circuit, where R is associated to a conduction path and C is related to polarization processes in the bulk. As

Table 2 Measurements of resistance and conductivity at several temperatures for the carboxylic polymer. Compacting pressure: 4.34×10^8 Pa. Geometrical factor: 0.15 cm^{-1}

Temperature T (°C)	Resistance R (ohms) $\times 10^{-6}$	Conductivity σ (S) $\times 10^8$
98	11.40	1.32
110	7.80	1.92
122	3.98	3.77
136	1.97	7.61
149	1.08	1.39
156	0.74	2.01
174	0.33	4.42
183	0.20	7.50

Table 3 Carboxylic polymer. Capacitances obtained for the bulk polymer (C_1) and grain boundaries (C_2). Compacting pressure: 4.34×10^8 Pa

Temperature T (°C)	Capacitance $C_1 \times 10^{11}$ (F)	Capacitance $C_2 \times 10^9$ (F)
149	2.04	—
156	1.94	—
174	2.04	—
183	1.99	15.3
197	1.97	9.1
216	2.02	2.51
231	2.02	1.31
240	2.91	75.0

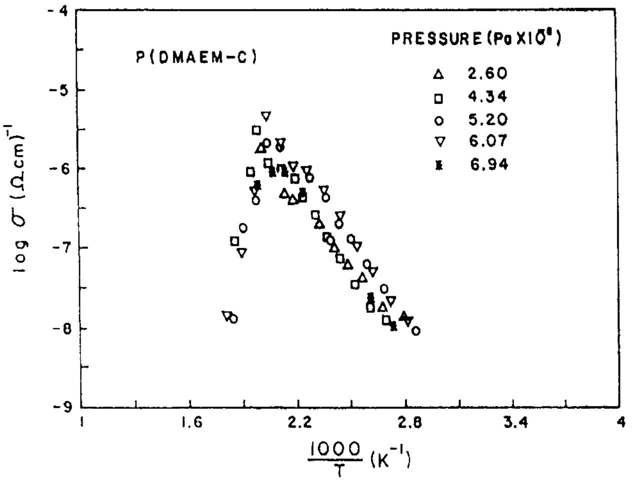


Figure 3 Arrhenius plot of ionic conductivity as a function of reciprocal temperature for several values of the compacting pressure. Carboxybetaine polymer

Table 4 Carboxylic polymer. Variation of the activation energy (E_a) and decomposition temperature (DT) with compacting pressure

$P \times 10^8$ Pa	E_a (eV)	DT (°C)
2.6	0.5359	222
4.34	0.6624	222
5.64	0.5635	204
6.07	0.7383	215
6.5	0.5589	226
6.94	0.7038	201

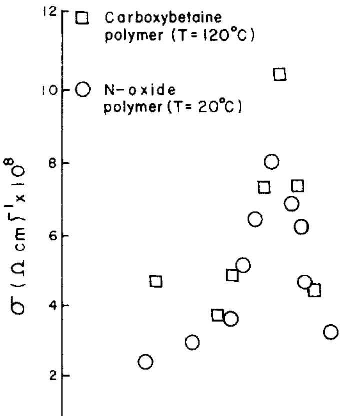


Figure 4 Variation of ionic conductivity with compacting pressure for both polymers

observed in *Table 3*, values associated with the bulk polymer are of the order of pF, whereas those of the grain edges lie within the nF range. These results reveal that the dielectric response within the pF range indeed comes from the bulk polymer, and that the variation of the relaxation times with temperature is attributed to changes in the resistance. This behaviour is quite common to other systems such as ceramics and dielectric solids.

In *Figure 3*, Arrhenius plots depict the variation of conductivity with inverse temperature for various values of the compacting pressure. An almost linear relation is obtained up to temperatures around 200–225°C, where conductivity drops for higher temperatures. This sudden decrease is closely associated with the onset of sample decomposition, corroborated by thermogravimetric analysis (*Figure 1*). In general, decomposition temperatures vary with compacting pressure, as observed in *Table 4*, where the variation of activation energies with pressure is also illustrated.

Besides temperature, *Figure 3* shows that conductivity is also a strong function of compacting pressure, as in the case of N-oxide polymers[1]. *Figure 4* clearly illustrates the variation of conductivity with pressure at constant temperature (120°C). A region of monotonic increase is followed by a steep drop with a maximum located at approximately 6.0×10^8 Pa. This value is surprisingly similar to that found in N-oxide samples[1]. To better illustrate this comparison, *Figure 4* also depicts simultaneously results from the carboxybetaine and N-oxide samples (the latter were taken from ref. 1). Present results of conductivity are higher than those found in the N-oxide sample at the indicated temperatures. The fact that both polymers present the same critical pressure is certainly due to the contribution of the macromolecular backbone. Both polymers have different lateral pendant groups: N-oxide and carboxylic, but with the same structure of the amorphous main chain. The critical pressure is associated with a specific arrangement of the structure which optimized the ionic transport, inducing a maximum in the conductivity, which, as shown later, is very dependent on the available free volume for molecular rearrangements. The magnitude of the maximum, however, depends on the crystalline content that induces different degrees of segmental mobility at a given temperature.

It is well known that relaxation times of polymers increase as the 'hydrostatic pressure' rises[3–7]. In general, an increase in the hydrostatic pressure is related to a decrease in the fractional free volume of the polymer, and a smaller free volume is accompanied by lower segmental mobility, restricting molecular motions and thus increasing the relaxation times[7]. An opposite effect is produced by an increase in temperature, which is also accompanied by the melting of crystalline domains inducing a higher molecular mobility, and promoting conductivity[12]. The compacting pressure, on the other hand, produces modifications in the morphology and microstructure of the polymer (see ref. 10) which may induce larger mobility with increasing pressure.

It has been found in ref. 11 that zwitterionic polymers with inorganic salts behave as ionic conductors where a non-localized or long-range diffusion process occurs[15]. In this case, the dielectric response may be represented by a parallel R–C circuit where the product RC gives the conductivity relaxation time. A perfect semicircle appears in the complex impedance plane rather than in the dielectric permittivity plane[16]. Ideal conduction can be treated as an extremely strong Debye relaxation with a very large Debye relaxation time. In fact, the imaginary part of the dielectric function has no maxima at any frequency value.

The Debye relaxation can also be represented in terms of the complex impedance. It has been demonstrated[16] that the larger the relaxation ratio (ratio of the static and optical dielectric constants), the smaller the deviation from the semicircular arc in the impedance plane. As this is the case in the zwitterionic polymers treated here, the complex impedance can be represented by an R–C circuit (see equation (2) with exponent equal to one).

Figure 5 shows the variation of the real and imaginary parts of the complex impedance with frequency for several temperatures at fixed compacting pressure (2.6×10^8 Pa). There is a shift in the frequency of the maxima from 100 kHz at 226°C down to 10 kHz at 156°C. These values are little different to the typical ionomer case, and reflect the differences in morphology and microstructure existing between zwitterionic polymers and ionomers. These differences have been analysed in previous studies[10]. Data in *Figure 5* show an apparent deviation from the single relaxation time behaviour (half width of 1.14 decades in the loss peak). Quantifying this deviation at several temperatures and for various compacting pressures, the smaller departures correspond to compacting pressures close to those of the peak conductivity. To better quantify the departure from a single relaxation time behaviour, we calculate the value of the parameter β following the empirical expression for the impedance,

$$Z^* = \frac{R}{1 + (i\omega RC)^\beta} \tag{2}$$

which corresponds to a superposition of a group of single-time relaxation processes with a range of relaxation time symmetrically distributed about the main relaxation time, $\tau = RC$. At $P = 2.6 \times 10^8$ Pa and within the mentioned temperature range, the average β value is 0.886.

The above-mentioned non-localized conduction process generally dominates at low frequencies[15]. In the absence of interfacial effects, the non-localized

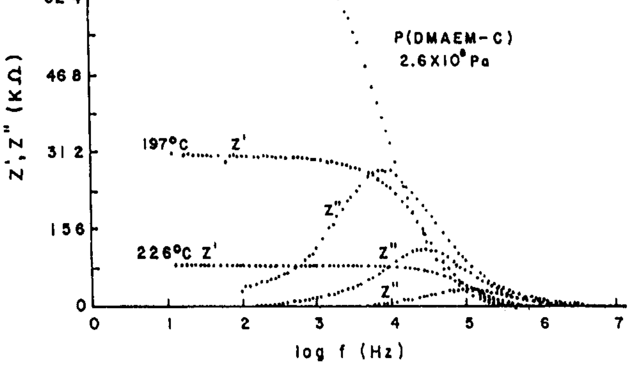


Figure 5 Variation of the real and imaginary parts of the complex impedance with frequency for several temperatures at a fixed compacting pressure. Carboxybetaine polymer

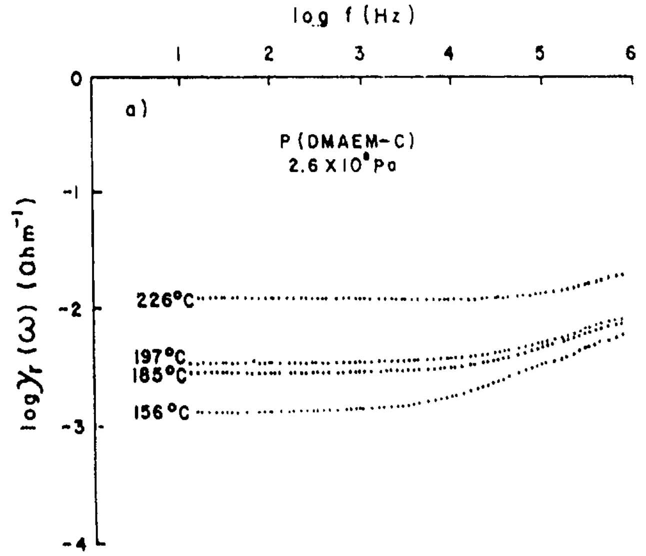


Figure 6 Variation of the conductivity with frequency for several temperatures at a compacting pressure of 2.6×10^8 Pa. Carboxybetaine polymer

conductivity is known as the d.c. conductivity. Determinations of d.c. conductivity can be made from the real part of the admittance (Y_r)-frequency plots. *Figure 6* exhibits the variation of conductivity covering five decades of frequency for various temperatures where the samples were moulded at 2.6×10^8 Pa. At low frequencies, a frequency independent value (d.c. conductivity) is apparent.

Data reduction is obtained by using the time-temperature superposition principle. *Figure 7* shows the reduced real and imaginary parts of the complex impedance plotted with reduced frequency at 150°C and for several pressures. The factor a_T is the ratio of the relaxation times to that evaluated at 150°C

$$a_T = \frac{\tau_T}{\tau_{150}} \tag{3}$$

It is particularly interesting that data from several temperatures and compacting pressures superpose following time–temperature reduction. To illustrate these results better, *Figure 8* shows the variation of a_T with temperature for several pressures. For temperatures lower than 170°C, data collapse into a single curve. The larger deviations occur for temperatures close to those of sample decomposition (shown in *Table 4*).

It is well known that within the region $T_g + 10\,\mathrm{K} < T < T_g + 100\,\mathrm{K}$, where T_g is the glass transition temperature, the applicability of the WLF equation to describe the temperature dependence of the dynamic response of a system is generally accepted[17]. Data in *Figure 8* may be predicted by the WLF equation which follows the expression

$$\ln a_T = \frac{C_1(T - T_0)}{C_2 + (T - T_0)} \tag{4}$$

In this case, the fitting of the experimental results was accomplished using $C_1 = 3.0$ and $C_2 = 150$°C. These values are similar to those found in the literature[8] for methyl methacrylate polymers with flexible lateral groups and for flexible polymers such as polybutadiene derivatives. The constants C_1 and C_2 may be expressed in terms of the free volume through the relations

$$C_1 = B/f_0 \tag{5}$$

$$C_2 = f_0/\alpha_f \tag{6}$$

From the values of C_1 and C_2 we obtain 0.145 and $9.66 \times 10^{-4}\,\mathrm{deg}^{-1}$, for the fractional free volume and thermal expansion coefficient, respectively.

Figure 7 also shows that the master curves for each pressure depict small variations in the relaxation times (related with the frequency of the maxima in Z''). However, the pressure does change the value of Z' at low frequencies, and these values are directly connected with the bulk conductivity of the sample. In other terms, this is a process where large changes in conductivity are observed without substantial changes in the relaxation times, whose trend is predicted by the WLF equation

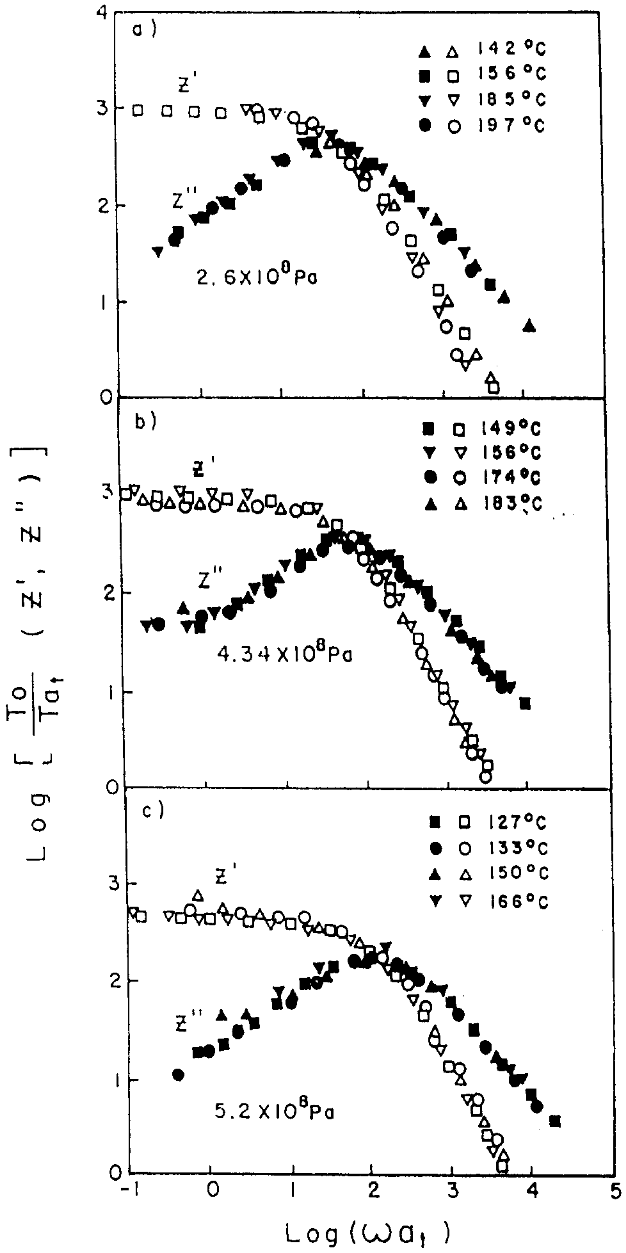


Figure 7 Reduced real and imaginary parts of the complex impedance *versus* reduced frequency for several temperatures and compacting pressures: (a) 2.6×10^8 Pa, (b) 4.34×10^8, (c) 5.2×10^8 Pa. Carboxybetaine polymer

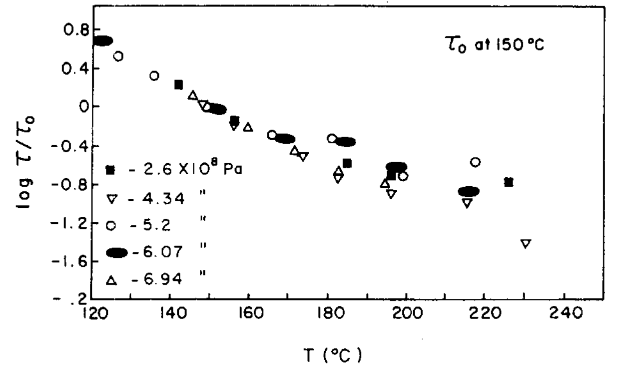


Figure 8 Shift factor a_T as a function of temperature for several compacting pressures. Carboxybetaine polymer

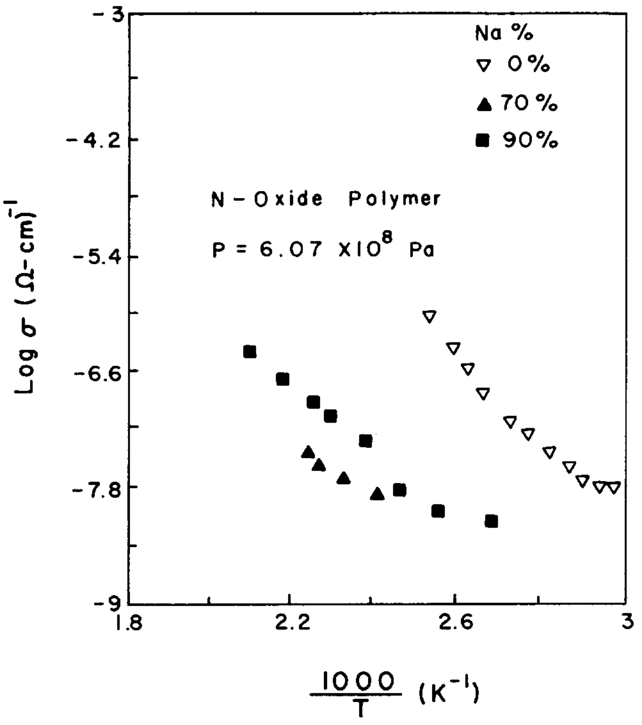


Figure 9 Arrhenius plot of ionic conductivity vs inverse temperature for the N-oxide polymer with several neutralization degrees. Sample with 0% corresponds to the amorphous polymer. $P = 6.07 \times 10^8$ Pa

without the pressure contribution to the shift factor. Consequently, the fractional free volume referred to that at 150°C is not substantially affected with increasing pressure and only changes with temperature.

Figure 8 illustrates that the effect of the compacting pressure may be eliminated in the data analysis of this sample simply by making use of time–temperature reduction at several temperatures. Nevertheless, it points out the importance of generating enough data at several temperatures if an appropriate interpretation of the phenomenon is sought. When the sample is highly crystalline, however, it is not possible to perform such reduction as is shown later in the paper.

N-Oxide polymer

Figure 9 shows the Arrhenius plots of conductivity vs inverse temperature for N-oxide polymers with various neutralization degrees. To interpret the data, it is necessary to consider the mechanisms present: the mobility of charges and the concentration of mobile ions. Mobility is enhanced in samples with low glass transition temperature, and the increase in sodium concentration may raise the mobile ion concentration. In addition, crystallinity is large in samples with high sodium concentration, and it is well known that crystals act as potential barriers to conductivity.

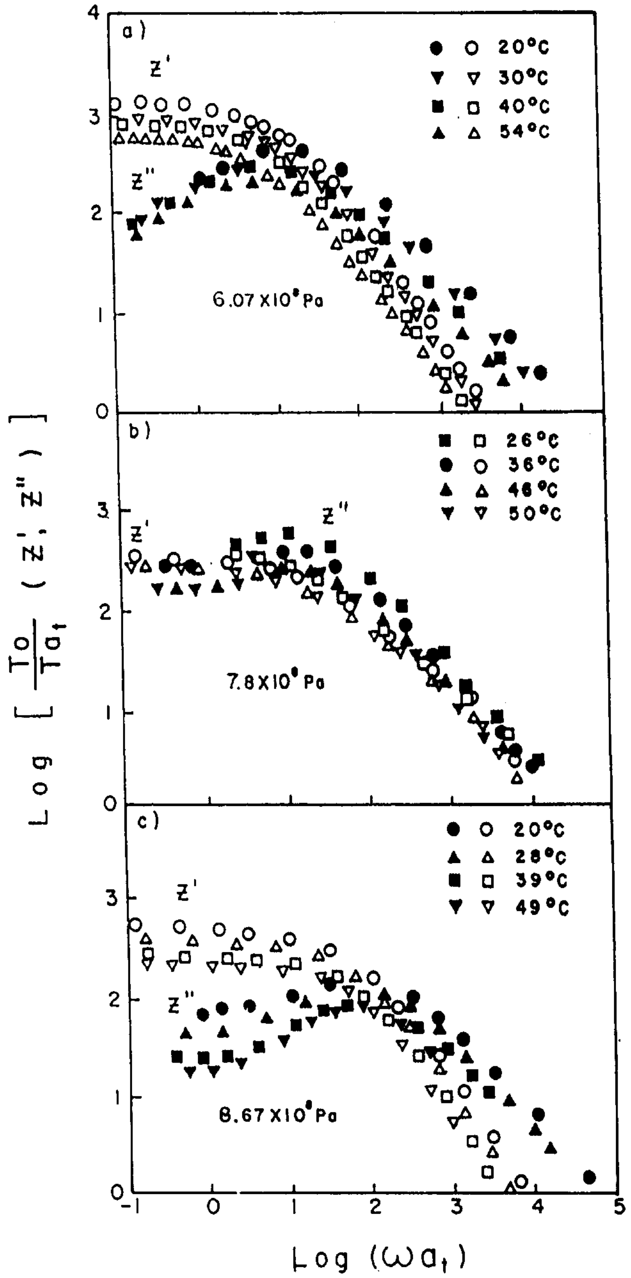


Figure 10 Reduced real and imaginary parts of the complex impedance vs reduced frequency for several temperatures and compacting pressures: (a) 6.07×10^8 Pa, (b) 7.8×10^8 Pa, (c) 8.67×10^8 Pa. N-oxide polymer

Applying time–temperature superposition to the sample with 100% sodium content, data reduction is not as good as that obtained in the carboxylic sample (see *Figure 10*). *Figure 11* shows the variation of a_T with temperature. As in the carboxylic sample, in this case a single curve is obtained except at the highest pressure, where large deviations take place for temperatures higher than 20°C.

As is well known, the method of reduced variables is inapplicable when the sample presents high crystallinity, due to the marked changes in the internal structure with

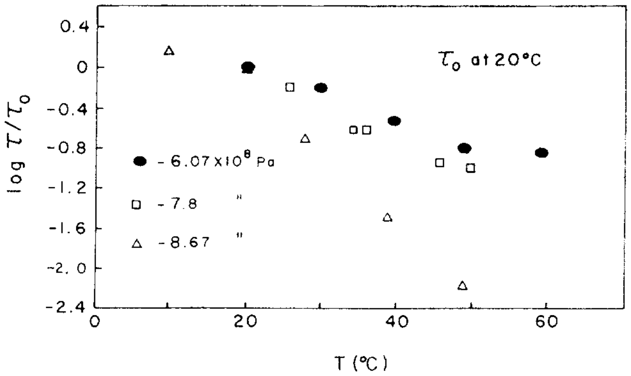


Figure 11 Variation of the shift factor a_T with temperature for several compacting pressures. N-oxide polymer

changing temperature. Empirically, rather large vertical shifts combined with horizontal shifts might achieve a single composite curve in *Figure 10*, but this procedure lacks a theoretical basis. This situation is also present in polymers with side groups long enough to crystallize, where large deviations appear[19].

In a previous work[1], it was pointed out that the large changes observed in the conductivity indicates that the compacting pressure may modify the amorphous regions between crystalline domains extensively. The deformations induced on the amorphous regions and the presence of uncoordinated motions within the crystal lattice may lead to different mechanisms and temperature dependences, which are expected to be highly anisotropic[20]. These are some reasons of the inapplicability of the time–temperature superposition in these samples.

Calculations of the fractional free volume and thermal expansion coefficient give values of 0.097 and 6.44×10^{-4} deg^{-1}, respectively. These values are lower than those of the amorphous carboxylic sample, reflecting the effect of the crystalline content of the N-oxide polymer.

As observed in *Figure 11*, the curve at high pressures shows large deviations from the WLF equation. In this case, we believe, the decrease in the relaxation times observed in this figure and in *Figure 10* (where the peak value of Z'' is shifted to higher frequencies) takes place due to an increase in the free volume brought about by morphological changes in the microstructure, as discussed in the following section.

DISCUSSION AND CONCLUDING REMARKS

One of the results of this work illustrates that the compacting pressure has a small effect on the relaxation times with the exception of the highly crystalline sample at high pressures. On the other hand, the conductivity is largely modified, presenting a maximum at a critical moulding pressure. Since there is structural modification of the morphology due to pressure (see ref. 1), it is tempting to relate these changes to variations of the available free volume.

As is well known[21], the relaxation times obtained from the different loss peaks which occur in polymers above the glass transition temperature usually follow the Vogel–Fulcher equation which leads to the WLF equation. There is an extensive literature which relates this equation to models for free volume or configurational entropy.

One of the most interesting results presented so far shows that the position of the maximum in conductivity as a function of the compacting pressure coincides for both polymers. To investigate this result further, we will intend to relate the mobility that both polymers have at the temperature where the peak in conductivity is observed (120 and 20°C, respectively). An equal level of mobility should be found when the fractional free volume becomes similar in both polymers. The variation of the reduced relaxation times (shift factor) with reduced temperature (T/T_0) is similar for both polymers, and with the exception of the contribution from the curve at high pressures in the N-oxide polymer, it shows the fact that an increase in temperature produces the same decrease in the relaxation times and hence, the same increase in the fractional free volume in the carboxylic and N-oxide polymers.

In *Figure 4*, estimations of the reduced temperatures referred to the temperature of the onset point for conductivity of both samples (356 and 270 K), we obtain 1.103 and 1.085 for the carboxylic and N-oxide polymers, respectively. These values give similar estimates of a_T, which means that at the temperatures of the experiments (393 and 293 K), both polymers have similar fractional free volumes and hence similar chain mobility.

This simple argument explains why the position of the maximum coincides for both polymers and that similar changes in the fractional free volume of both samples take place in the amorphous regions. However, the fact that the maximum is present at a specific critical pressure is due to modifications of the original polarization state induced by morphological changes in the microstructure of these polymers (as illustrated in refs 1 and 10 for the N–O polymer). Indeed, morphological studies made on these polymers reveal the presence of aggregates and clusters. As pressure is applied to mould the samples, the amorphous regions are modified and hence the spatial distribution of ionic sites. A specific state of deformation of the system will optimize the ionic transport and ionic interactions, producing an onset of the conductivity associated with a critical pressure. In the N-oxide sample, this is further corroborated by evidence of morphological changes in the crystalline domains, showing the modifications in the shape of crystalline domains can be induced if those domains gather in a tight-packing structure, as the presence of clusters shows. Changes in the amorphous regions are thought to be larger, leading to substantial modifications in the dipole–dipole interactions of the ionic groups. We believe these are the main reasons for the observed conductivity behaviour.

As a conclusion, although the compacting pressure does not change substantially the relaxation times in these systems (with the exception of the highly crystalline sample at high pressures), ionic conductivity is greatly affected. In this regard, these results have also illustrated the importance of the preparation methods for conductivity studies.

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