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Dielectric Properties of Polyacrylamide Polymer Films.

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Summary. — Polyacrylamide polymer films of thickness 4.15 μm were prepared by isothermal immersion technique. The dielectric capacitance and dielectric loss of the films were studied as functions of frequency and temperature in the range 100 Hz ÷ 10 MHz and (300 ÷ 450) K, respectively. Two dielectric loss peaks were observed in the dielectric loss spectra and were identified as β and α peaks. The β peak was attributed to the reorientation of dipoles and the α-peak was attributed to the deformations accompanied by large changes in the directions or locations of the dipoles.

PACS 77.55 - Dielectric thin films.

1. - Introduction.

The dielectric behaviour of polymer films is of considerable interest due to their applications for insulation, isolation and in microelectronics. The dielectric constant and the loss factors are the crucial quantities required in the design of devices. Furthermore, these studies as functions of temperature and frequency reveal the nature of chemical and physical state of the polymer and its molecular structure.

Hence an attempt has been made to study the dielectric measurements on pure and doped polyacrylamide films to have an insight into the molecular structure of the polymer.

2. - Experimental.

Polyacrylamide used in the present investigations was obtained from Chempure company Pvt. Ltd., Calcutta (India). Polymer films of thickness 4.15 μm were formed by isothermal immersion technique [1]. The polyacrylamide polymer was dissolved in a solvent like triple distilled water. The solution was stirred continuously by means of a magnetic stirrer to obtain a homogeneous solution.

Glass substrates with vacuum-evaporated bottom aluminium electrodes were isothermally immersed in the solution. After withdrawal from the solution the substrates were dried in a hot air oven for 24 hours at a constant temperature of 75 °C. Top aluminium electrode was then vacuum evaporated so as to sandwich the experimental film between the crossed electrodes. The electrical connections from these electrodes are taken by soldering silver wires using silver paste. The effective area of the films used in the present study is $0.0847 \cdot 10^{-4}$ m^2. The thickness of the film was measured by means of a mechanical stylus arrangement. The capacitance and dielectric loss were measured using Hewlett-Packard Impedance analyser HP 4992 in the frequency range from 100 Hz to 10 MHz. Before actual measurements were made, the films were annealed by keeping the films at a temperature of 450 °C for 2 hours and cooling down slowly to room temperature. All the measurements were made in a vacuum of 10^{-3} Torr.

3. – Results and discussion.

3·1. *Effect of annealing on dielectric properties.* – Figure 1 shows the variation of capacitance *vs.* frequency measured at room temperature (303 K) for unannealed (*a*)) and annealed (*b*)) samples. Figure 2 also shows the tg δ *vs.* frequency at room temperature for unannealed (*a*)) and annealed (*b*)) samples. It is clear that annealing leads to significant decrease in capacitance and tg δ. Samples studied in the thickness range of 0.8 μm to 11 μm showed a similar type of behaviour. The change in dielectric properties due to annealing could be due to rearrangement for polymer chains which results in improvement of crystallinity of the film after temperature treatment. Such a type of decrease in dielectric loss and capacitance on thermal heating was reported by several workers [2, 3].

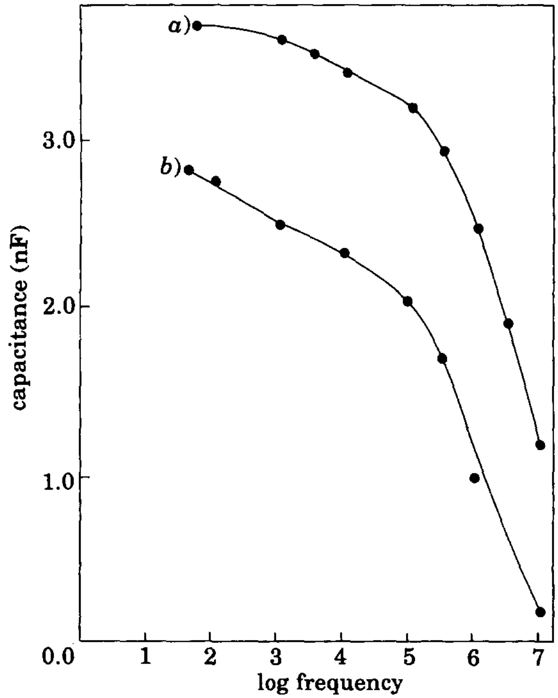

Fig. 1.

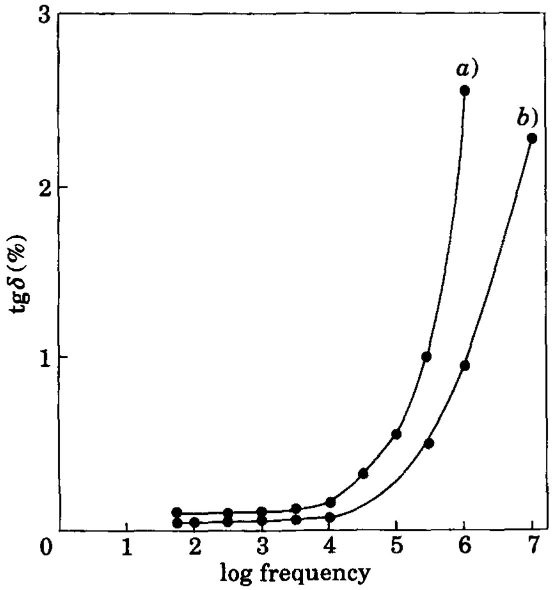

Fig. 2.

3'2. *Capacitance vs. frequency*. – In the present investigations the capacitance was found to be decreasing with increasing frequency at all temperatures of study as seen from fig. 3. The decrease in capacitance with increasing frequency indicates the polar nature of dielectric. A similar type of behaviour was reported in a number of polymers like polyvinylchloride [4], polyvinylalcohol [5], polyvinyl fluoride [2] and polymethylmethacrylate [6].

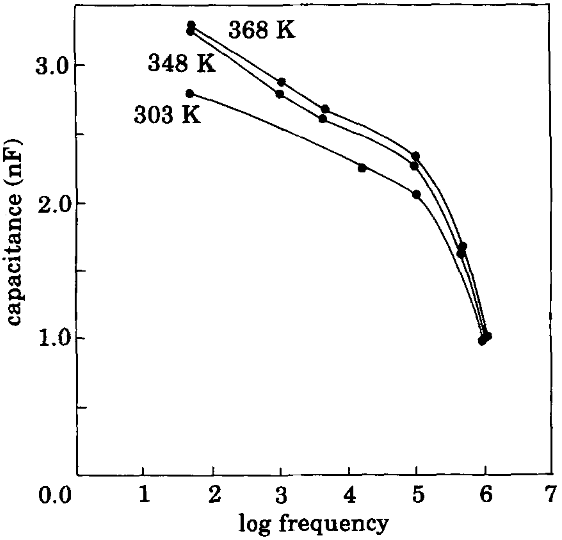

Fig. 3.

3'3. *Capacitance vs. temperature*. – Figure 4 shows the capacitance as a function of temperature at various frequencies. The capacitance was found to increase as the

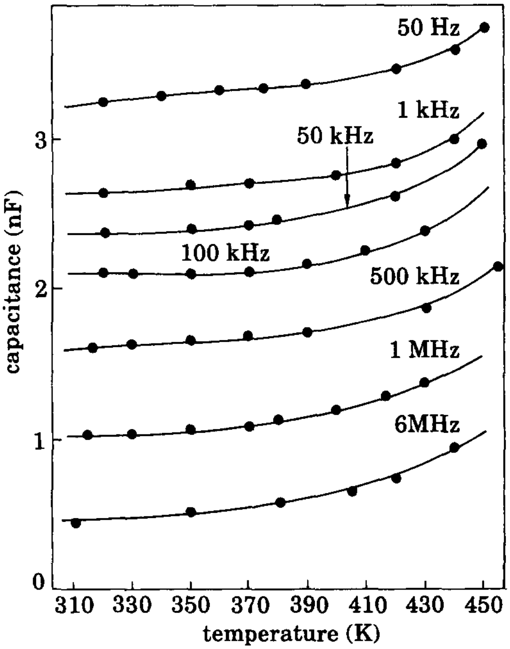

Fig. 4.

temperature increases from 303 K to 450 K at all the frequencies. Such a type of increase in permittivity was observed by Pillai [6] *et al.* in polymethylmethacrylate films which is a polar material. The molecular alignment of chains may cause the observed increase in the capacitance with temperature in the polyacrylamide films.

3'4. Tg δ *vs. frequency.* – Jonscher [7] suggested that a complete characterization of the dielectric response is obtained by taking either the temperature dependence at constant frequency or the frequency dependence at constant temperature in the case of Debye processes. The former procedure is very commonly employed for rapid assessment of materials, since it is generally much simpler experimentally. However, in cases where the behaviour departs seriously from the Debye response, which corresponds to the majority of materials, temperature dependence ceases to be a reliable guide to the frequency response and it becomes essential to measure the complete dependence of tg δ $(\omega \cdot T)$ as a function of two independent variables. It often happens that temperature dependence shows well-defined loss peaks while frequency response remains substantially flat, *i.e.* non-Debye. So, if the dependence of tg δ of a dielectic material on frequency is considered, it is possible to observe either an increase or a decrease at a higher frequency or transition through the maximum or even through several maxima suggesting relaxation processes.

Figure 5 shows the typical behaviour of tg δ measured as a function of frequency at different temperatures. It is observed from fig. 5 that the tg δ was found to be independent of frequency up to 10 kHz and thereafter found to increase with frequency at all temperatures of study. Several workers [2, 8-10] observed different relaxation peaks in tg δ *vs.* frequency plots, suggesting the relaxation process operating in the polymer. In the present case no such peaks were observed up to 10 MHz. But the increasing trend in tg δ with frequency suggests that a relaxation peak

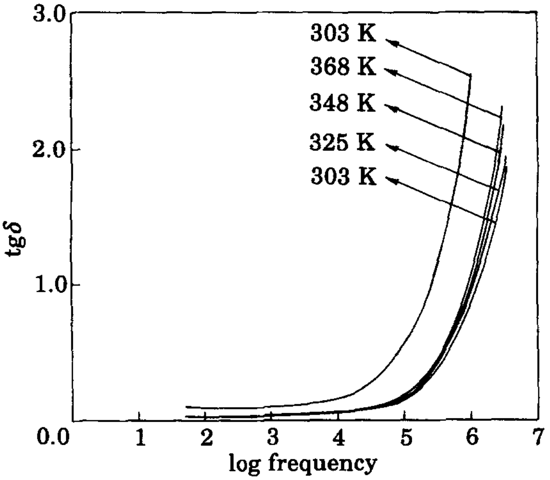

Fig. 5.

may be beyond the frequency range of the present study. The rise in tg δ with frequency is due to the relaxation in the frequency range above 10^6 Hz. Amrhein [11] observed a similar variation in ε [11] with frequency.

3'5. Tg δ *vs. temperature.* - Figure 6 shows the plots of tg δ *vs.* temperature at different frequencies in the temperature range of (300 ÷ 450) K. The plot depicts two maxima around 335 K and the other around 355 K. With the increasing frequency of measurements, it is observed that the loss peaks shifts to lower temperatures,

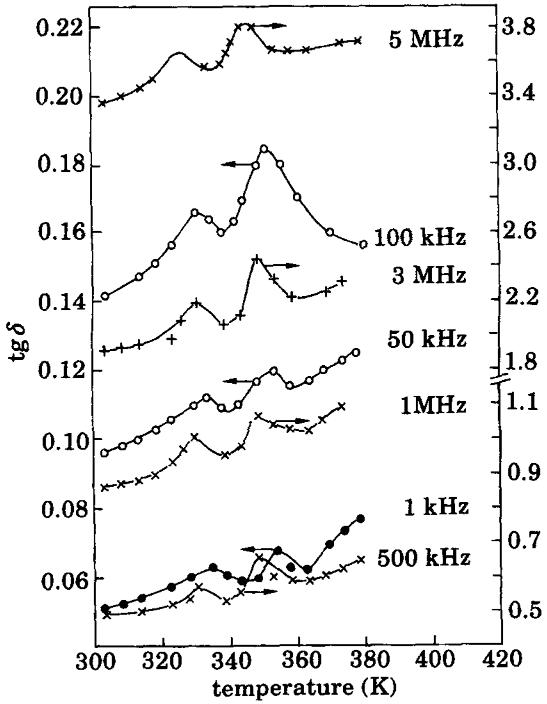

Fig. 6.

indicating that these dielectric loss peaks are of a relaxation in nature [8]. The shift in the loss peaks with frequencies was observed by several authors [2, 4, 8, 9, 12].

In the present investigations, the high-temperature peak (355 K) was below the T_g of the polymer. According to the usual convention the high-temperature peak may be designated as α-peak, whereas the low-temperature (355 K) peak may be designated as β-peak.

The β-processes which occur at low temperatures are generally associated with low activation energies [9].

The microscopic structure of polyacrylamide films provides some information to understand the physical nature of loss due to the β-process. In the present investigations, the X-ray diffraction studies suggest that the polyacrylamide films are semi-crystalline in nature. In semicrystalline polymers, some amount of amorphous regions exists separating the crystalline regions [13]. In amorphous regions the chains are irregular and entangled whereas on the crystalline regions the chains are regularly folded or orderly arranged. Since the arrangement of the molecules in the amorphous state is not regular, the Van der Waals forces between the molecules vary from place to place. It is therefore easy to conform or move the molecular chains in the amorphous state. The molecular packing in the amorphous regions is loose and so the density is smaller than that of crystalline regions. Thus, the chains in the amorphous phase are more flexible and are capable of orienting themselves relatively more easily and rapidly. In crystalline regions, the forces which hold the structural units together are of a homopolar chemical binding nature and are much stronger than the Van der Waals forces.

The dipole ($C = O$) associated with the side chain of polyacrylamide main chain will orient with a certain frequency governed by the elastic restoring force which binds the dipoles to their equilibrium positions and the rotational frictional forces exerted by neighbouring dipoles. Moreover, the dipolar molecules in the crystalline phase will have discontinuous jumps from one equilibrium position to another and hence contribute to the absorption at the same temperature or frequency whereas, in the amorphous phase, dipolar molecules should be able to orient from one equilibrium position to another relatively more easily and will contribute to absorption over a wide frequency or temperature range. In view of the above observations, the loss peak β may be due to the orientation of the dipolar group, in the direction of local electric field.

In the present investigations, the activation energies associated with the loss peaks could not be evaluated due to incomplete nature of loss peaks over the frequency range studied. However, some rough idea may be obtained about the activation energies associated with peaks from TSDC results, since TSDC studies relate to relaxation mechanisms. In the literature [2, 14, 15] it has been observed that the correlation may be obtained between the two types of studies, since the two studies correspond to different frequency ranges [8]. In the present investigations, the peaks obtained in dielectric studies are in the same temperature as that of TSDC.

	Dielectric	TSDC
β	335	327
α	355	360

Hence the β peaks may be associated with an activation energy of $\simeq 0.8$ eV, whereas the α-peak may be associated with an activation energy of $\simeq 0.95$ eV. In most of the amorphous polymers, the activation energies associated with movement of dipoles from one equilibrium to the order of $\simeq 0.5$ eV [8, 16, 17]. The high value of activation energy associated with β-peak in the present investigations may be due to the dipolar orientation in crystalline matrix, which requires high activation energies [9]. Hence the observed β-relaxation process may be due to the reorientation of dipoles from one equilibrium position to another.

Generally the α-peaks were around or just above T_g [8, 18]; but there are evidences where peaks appeared well below the glass transition temperature.

Bahri [4] attributed the α-peak appeared at 90 °C ($T_g = 65$ °C) in PVC films to the unfreezing of segmental mobility within the noncrystalline clusters. Similarly in the case of polystyrene [18] the α-peak was attributed to the free volume theory put forward by Fox and Flory [19, 20].

The α-peak in the polycarbonate [8] was found to be due to the deformations accompanied with large-scale segmental motion or translation of the main chain with comparatively high activation energies.

Rastogi and Chopra [9] attributed the high-temperature α-peak (330 K) in polyvinylchloride ($T_g = 356$) to the local segmental motion of the backbone.

It may be observed from the literature that the high-temperature loss peak is generally attributed to the deformation caused by the molecular motion involving the main chain motion or the large segments of the main chain. Higher activation energies and the large magnitude in loss are some of the salient features of this peak as observed in most of the polymeric materials [7]. So, the high-temperature α-peak might be due to the deformations accompanied by large changes in the directions or locations of the dipoles, which involve rather high activation energy. In the deformation process, the dipole orientations will change to segmental motion or translation of the main chain. The increase in relaxation time with lowering temperature is a characteristic of dipole motion and hence the α-relaxation becomes hardly observable at low temperatures.

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