Dielectric Relaxation in Poly(1,4-phenylene Terephthalamide)

U. M. S. MURTHY, SRIRAMAN SRINIVASAN, and J. SOBHANADRI,*

Department of Physics, Indian Institute of Technology, Madras-600 036, India

Synopsis

The dielectric behavior of poly(1,4-phenylene terephthalamide) is reported in this paper as a function of frequency (400 Hz–100 kHz), temperature (30–290°C), and the degree of polymerization (134–228). The general behavior of all the samples of different degrees of polymerization is the same except for the occurrence of the peaks at different positions on the frequency and temperature scales. This difference in behavior could be because of the combined effect of the difference in molecular weights and packing of molecules. The data are completely analyzed for the sample with degree of polymerization $n = 210$. Two distinct processes are observed, one being observed in the entire temperature range, another originating in the vicinity of glass transition temperature. The former is analyzed in terms of Cole–Cole distribution and the latter is conformed with a nonexponential decay function. Activation energies are calculated from plots of I/T vs. ln τ.

INTRODUCTION

The electrical properties of polymers are usually interpreted in terms of the molecular motions, which are very complex. The dielectric technique is very sensitive and powerful in studying the molecular motions in polar compounds. Many solid polymers have their significant dielectric dispersions in the low frequency range only.

In general, polymers show more than one type of loss peak, and it is customary to refer to them as α, β, and γ etc.[1] The γ-loss peak is also referred to as $\alpha\beta$-peak since it has been found to be the superposition of α- and β-loss peaks.[2] The β-relaxation occurs at lower temperatures and is observed in both amorphous and crystalline regions.[3] The general observation is that the β-relaxation process is very complicated to interpret in terms of molecular motions; nevertheless, this process is attributed to the reorientation of the dipoles attached to the main chain. The α-process is caused by the motion of segments which is possible only around and above the glass transition temperature.[4] α-Peaks are found to be very sensitive to temperature and pressure which move faster towards high frequency side, with increasing temperature, and merge with β-peaks, giving rise to the $\alpha\beta$-relaxation process. The general features of these losses indicate that the α-peaks are more nearly symmetric and narrower than the lower temperature ones.[5] The characteristic features of these processes in crystalline polymers is well discussed and reviewed by Williams.[6] These loss processes can be interpreted by considering distribution of relaxation times[7,8] or nonexponential decay functions or both.[9]

* To whom all correspondence should be addressed.

In the present paper the dielectric properties of poly(1,4-phenylene tere-phthalamide) in the audio frequency range (400 Hz–100 kHz) and over a temperature range of 30–290°C are presented. The polymer chosen for the present study is a completely aromatic polyamide. This material is of special interest because of the greater strength of the interchain forces and the importance of such structures in proteins, synthetic textiles, and their use in space technology.[10] The complete aromatic nature of this polymer will enhance melting temperature, stiffness, and dimensional stability compared to the aliphatic amides. There are several reports on the dielectric studies of polyamides,[11–13] which are aliphatic in nature but there are relatively very few reports on the aromatic polyamides. The dependence of dielectric behavior on the degree of polymerization is also examined by extending these studies on four polymers with different degrees of polymerization.

MATERIALS

The polymer is prepared at Polymers and Special Chemicals Division, Chemical and Materials Group, Vikram Sarabhai Space Center, Trivandrum, India, by the polycondensation of aromatic diamines with aromatic diacid chlorides. The molecular weights are found, by viscosity measurements. The glass transition temperature of this kind of polymers is indicated to be around or above 260°C.[10] The material obtained is in the form of powder and is light yellow in color.

EXPERIMENTAL

Dielectric study was performed on powders compressed into the form of circular pellets. The measurements were carried out in an apparatus previously described.[14] The dissipation factor and capacitance were measured using a GR 1620 Capacitance Bridge. The sample is kept at 70°C for few hours under a pressure of 10^{-2} torr to eliminate the effect of water sorbed on the products and further experiments were also carried out in vacuum. The experiment was repeated for various thicknesses of the pellets. The temperature was measured with a plastomatic Phillips temperature controller, with an accuracy of ±1°C with the use of an Iron-constantan thermocouple.

RESULTS

The dielectric constant and loss for the polymer with different degrees of polymerization are measured. Table I shows molecular weights and degrees of

TABLE I
Samples with Different Molecular Weights and Corresponding Degree of Polymerization

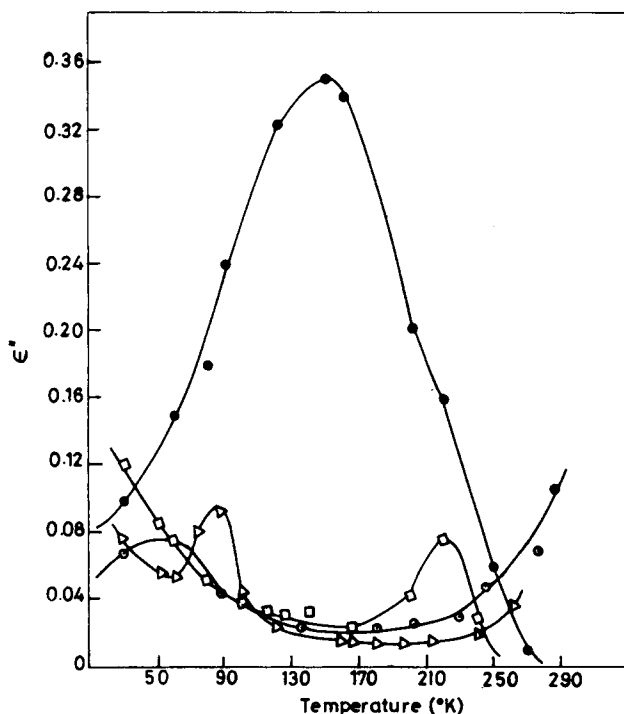| Sample	Molecular weight	Degree of polymerization
PA 183	32,000	134
PA 179	45,000	190
PA 188	50,000	210
PA 182	54,000	228

Fig. 1. Variation of ϵ'' with temperature at 6 kHz of samples of different degrees of polymerizations: (⊙) PA183, A; (▱) PA179, B; (●) PA188, C; (△) PA182, D.

polymerizations of the samples. The general trend shows no difference in the significant dispersions. But there is a difference in the relative intensities and relative positions of the occurrence of loss peaks on the temperature and frequency scales. These features are depicted in the Figure 1. The electron microscope pictures of these samples, which are in powder form, have shown that all samples except PA 188 (Table I) have some agglomerations and nuclei for crystallization. So this could be one of the reasons for the difference in the behavior. Another reason could be the difference in molecular weights, which can cause a change in glass transition temperature. The dispersions in the ranges of frequency and temperature, chosen in this study, occur completely for PA 188. So we have resorted to the analysis of data on PA 188.

The variation of dielectric constant and loss with temperature and frequency is shown in the Figures 2–4. In Figure 4 there is only one loss peak which occurs at higher temperatures for higher frequencies. Figures 3(a) and 3(b) show the variation of ϵ'' with frequency at different temperatures. In Figure 3(a) there is only one peak which moves towards high frequency side with increasing temperature. In Figure 3(b) another loss peak originates at low frequency side, indicating the presence of another loss mechanism.

ANALYSIS

The molecular motions which are responsible for the dielectric dispersion have characteristic relaxation times, and these are very sensitive to temperature. Also
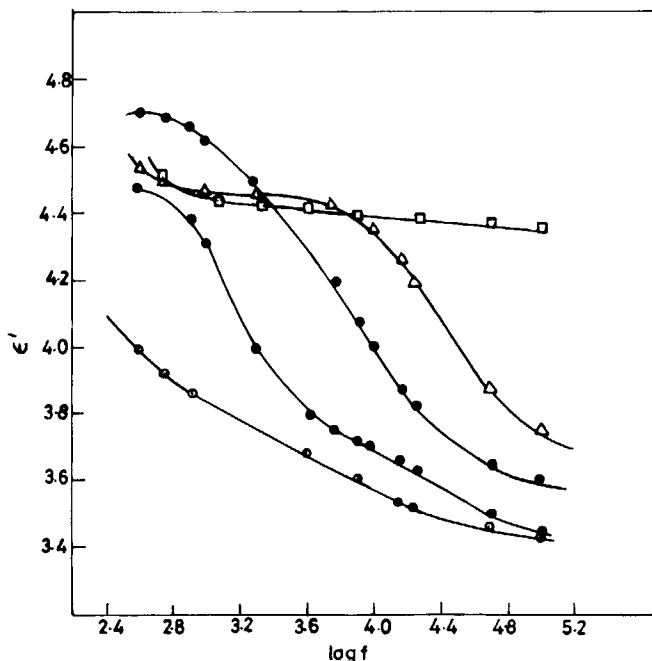
Fig. 2. Variation of dielectric constant with frequency at different temperatures (°C): (⊙) 30; (⊗) 80; (●) 140; (△) 220; (□) 270.

these molecular motions exhibit differences in activation energies below and above the transition temperatures such as melting points, which are characteristic of crystalline regions as well as the glass transition temperature and lower temperature transitions and relaxations. The α-process in polymers occurs around and above the glass transition temperature, where the segmental motion is
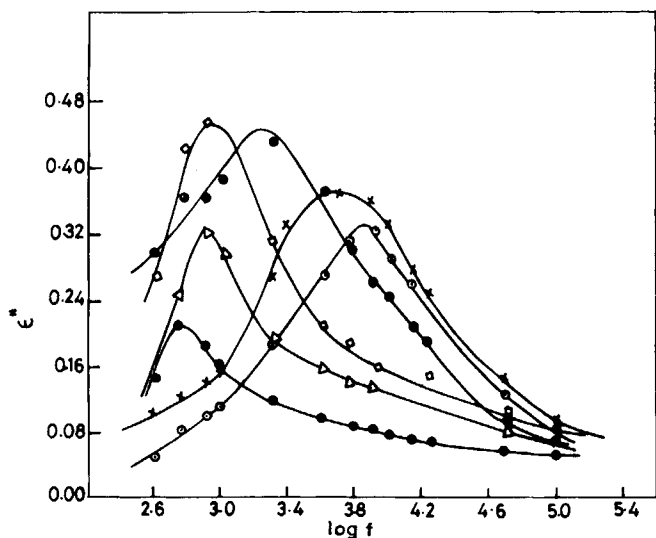

Fig. 3(a). Variation of ϵ'' with frequency at different temperatures in the range 30–180°C: (●) 30; (△) 60; (□) 80; (⊗) 100; (×) 140; (⊙) 180.
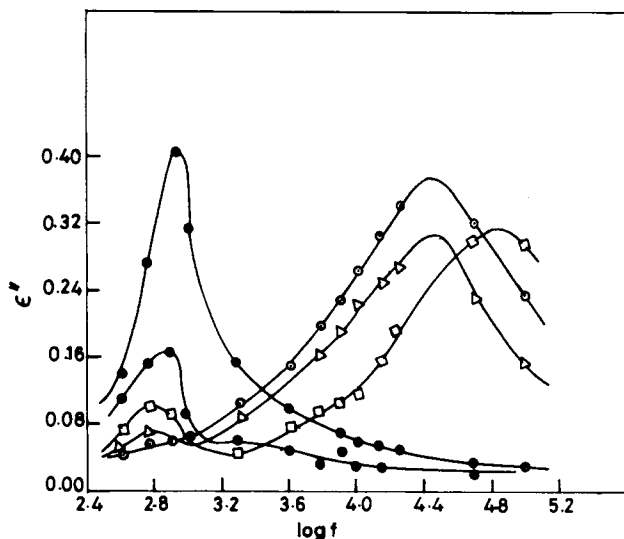
Fig. 3(b). Variation of E'' with frequency at different temperatures in the range 200–290°C: (⊙) 200; (△) 220; (□) 250; (●) 270; (⊗) 290.

possible even in alternating fields of high frequency. The dielectric data on polymers is usually represented by either Cole–Cole[15] or Cole–Davidson[16] or Havriliak–Negami[17] equations. Of late, Williams et al. presented an empirical form of the decay function responsible for the α-process and proved its validity in the case of several polymers.[18,19]

In the present study there are two distinct loss processes, one of which occurs over a wide temperature range from 30°C to 250°C and moves towards higher frequency side. Another loss process comes into picture at 220°C, and the peaks shift towards higher frequency side. The loss peak which originated at 220°C is attributed due to the α-loss process. Our observations on this loss process, in the present study, are consistent with the general characteristics of an α-process, such as the occurrence near glass transition temperature and the relaxation time and slight asymmetry about the maximum value. So we have re-
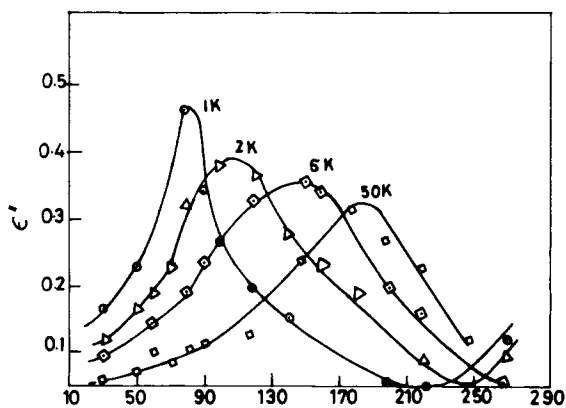

Fig. 4. Variation of ϵ'' with temperature at different frequencies.
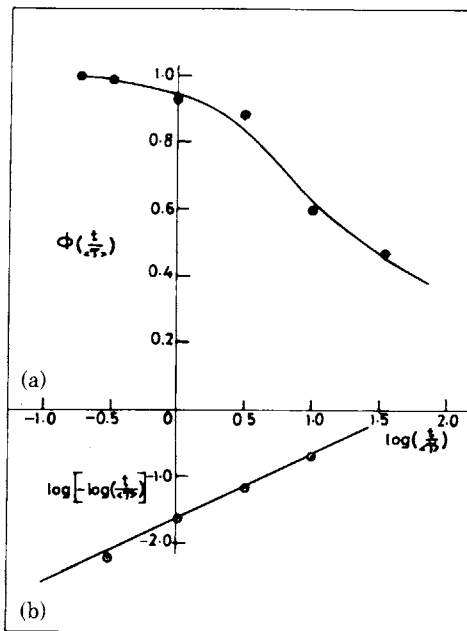
Fig. 5. (a) Decay function $\phi_\alpha(t/\langle\tau\rangle)$ vs. $\log(t/\langle\tau\rangle)$ at 270°C; (b) $\log[-\log(t/\langle\tau\rangle)]$ vs. $\log(t/\langle\tau\rangle)$.

sorted to the analysis of this process in terms of the emperical decay function suggested by Williams et al.[18,19] Figure 5 shows the decay function $\phi_\alpha(t/\langle\tau\rangle)$, which is calculated from the following relation and from the normalized plot of ϵ'' and frequency at 270°C:

$$\phi\left(\frac{t}{\langle\tau\rangle}\right) = \frac{\left[\int_{-\infty}^{\infty} (\epsilon''/\epsilon''_{max}) \cos(\omega/\omega_{max})(t/\langle\tau\rangle)\, d\log(\omega/\omega_{max})\right]_\alpha}{\left[\int_{-\infty}^{\infty} (\epsilon''/\epsilon''_{max})\, d\log(\omega/\omega_{max})\right]_\alpha}$$

where $\omega_{max}\langle\tau\rangle = 1$.

For the present data we note that $\phi_\alpha(t/\langle\tau\rangle)$ conforms with the emperical relation $\phi(t) = \exp[-(t/\tau_0)^\beta]$, $0 < \beta \le 1$, where τ_0 is some effective relaxation time. The plot of $\log[-\log \phi_\alpha(t/\langle\tau\rangle)]$ vs. $\log(t/\langle\tau\rangle)$ is found to be linear, in the present case; the β value estimated from this is 0.95, and $\log(\langle\tau\rangle/\tau_0)$ is found to be 1.62.

The decay function calculated for the α-process drops rapidly for $\log(t/\langle\tau\rangle)$ > 0. The molecular origin for this process is attributed to the gross micro-Brownian motions of chain segments of the polymer. The activation energy for this process is calculated from the plot of frequencies at which ϵ'' is maximum vs. absolute temperatures $1/T$. This plot (Fig. 6) is linear, and the activation energy $E_\alpha = 7.16$ kcal/mol.

The loss mechanism which took place in the range 30–250°C is analyzed in terms of Cole–Cole function. Up to 80°C the data do not fit into Cole–Cole or
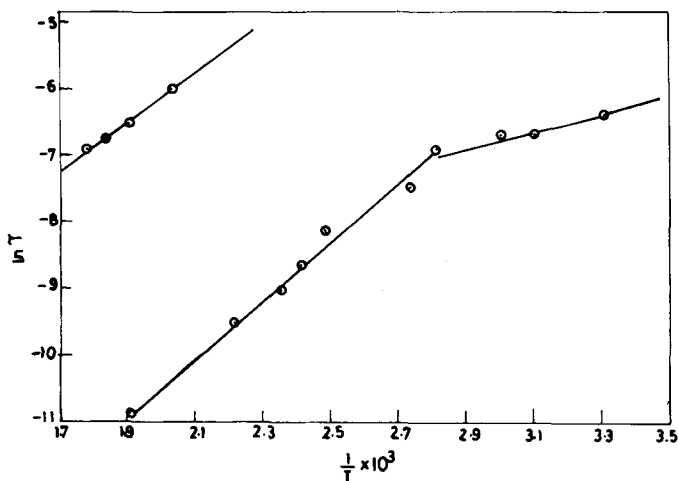
Fig. 6. ln τ vs. $1/T$.

Cole–Davidson functions, but it nearly approximately goes into Havriliak–Negami function. At 100°C and at subsequent temperatures, a single Cole–Cole plot is observed. The width of the dispersion $(\epsilon_0 - \epsilon_\infty) = \Delta\epsilon$ has shown a decreasing trend with increasing temperature above 100°C (cf. Table II).

The plot of relaxation times vs. $1/T$ shows a sharp change in the slope at 90°C (Fig. 6), which results in a change in the activation energy. We have attributed this entire loss mechanism to the β-process observed in polymers. There are two kinds of dipoles rigidly attached to main chain of the polymer, chosen in the present case. The reorientation of these dipoles in the alternating field accounts for the β-process in the present case. Also the possibility of independent and coupled rotation will account for the difference of behavior shown below and above 100°C. The decrease in $\Delta\epsilon_\beta$ with increasing temperature is due to the increase of symmetry of distribution of relaxation times.

CONCLUSIONS

Two distinct relaxation processes are observed: One is attributed to the segmental motion which is possible only around glass transition temperature. This process is described in terms of a nonexponential decay function. The other

TABLE II
Variation of $\Delta\epsilon$ with Temperature

Temperature (°C)	$\Delta\epsilon$
100	1.54
120	1.23
140	1.15
160	1.12
180	0.95
220	0.80
250	0.75
270	0.305

process is a relatively complicated one which may be due to the independent and combined motions of the two rigidly attached dipoles which are $C{=}O$ and $N{-}H$ in the polymer. The representation in terms of the Cole–Cole plots indicates that there is a distribution of relaxation times, and the increase of symmetry of this distribution with temperature is evidenced by the decrease of $\Delta\epsilon$ with increasing temperature.

References

1. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.

2. G. Williams, *Faraday Soc. Trans.*, **62**, 2091 (1966).

3. Y. Ishida, K. Yamafuji, H. Ito, and M. Takayanagi, *Kolloids*, **184**, 97 (1962).

4. E. Riande, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1–11 (1978).

5. A. K. Jonscher, *Colloid Polym. Sci.*, **253**, 231–250 (1975).

6. Graham Williams, *Advances in Polymer Science*, Springer-Verlag, New York, 1979, Vol. 33, p. 59.

7. C. P. Smyth, *Dielectric Behaviour and Structure*, McGraw-Hill, New York, 1955.

8. N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, *Dielectric Properties and Molecular Behaviour*, Van Nostrand Reinhold, London, 1969.

9. G. Williams and D. C. Watts, in *Dielectric Properties of Polymers*, F. E. Karasz, Ed., Plenum, New York, 1971, p. 17.

10. G. Govindan, *J. Sci. Ind. Res.*, **40**(Mar.), 173–180 (1981).

11. D. W. McCall and E. W. Anderson, *J. Chem. Phys.*, **32**, 237 (1960).

12. W. O. Baker and W. A. Yager, *J. Am. Chem. Soc.*, **64**, 2171 (1942).

13. R. H. Boyd, *J. Chem. Phys.*, **30**, 1276 (1959).

14. J. Gowri Krishna, O. S. Josyulu, J. Sobhanadri, and R. Subrahmanian, *J. Phys. D: Appl. Phys.*, **15**, 2315–2324 (1982).

15. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

16. R. H. Cole, *J. Phys. Chem.*, **23**, 493 (1955).

17. S. Havriliak and S. Negami, *J. Polym. Sci. Part C*, **14**, 99–117 (1966).

18. G. Williams and D. C. Watts, *Trans. Faraday Soc.*, **66**, 80 (1970).

19. M. Cook, D. C. Watts, and G. Williams, *Trans. Faraday Soc.* **66**, 2503 (1970).