Studies on Linear Polymers from p-Substituted Phenol. II

Y. F. Khobragade[a]; M. C. Gupta[a]

[a] Chemistry Department, Nagpur University, Nagpur, India

PLEASE SCROLL DOWN FOR ARTICLE

STUDIES ON LINEAR POLYMERS FROM
p-SUBSTITUTED PHENOL. II

Y.F. Khobragade & M.C. Gupta*
Chemistry Department, Nagpur University
Nagpur-440 010, India

INTRODUCTION

In our previous communication[1], the characterisation, physical characteristic, and the crystal structure of the linear polymers with methylene bridge derived from p-substituted phenol were reported. In this communication, we report ^{13}C NMR, UV-visible spectra, transport properties of these linear polymers with methylene bridge.

METHOD

^{13}C NMR

^{13}C- solution nmr spectral determination were run at 100 MHz Bruker WM-400 spectrometer at RSIC, Lucknow. The polymer was dissolved in DMSO - d_6 which provided an internal lock signal for ^{13}C - nmr.

U.V. - visible spectra

U.V. - visible spectra of polymer were recorded in D.M.F. solution using UV-240 shimadzu Automatic recording double beam spectrophotometer at room temperature in the range 190-700 nm.

Dielectric & electrical conductivity measurements

Polymer sample pellets were prepared by pressing the powder in a steel die by a hydrolic press under 5 metric ton/cm^2 pressure.

_____

*To whom all correspondence to be addressed.

These pellets were used for dielectric & electrical conductivity measurements using a systronics Direct Reading LCR Bridge Model 926 as a function of temperature at a heating rate 1 °C min^{-1}. Measured capacitance and resistance at 1 KHz was converted as dielectric constant, dielectric loss and conductance using cell dimensions.

FTIR Spectra

FTIR spectra of poly (bisphenol A-methylene-4' -aminobenzoic acid) was recorded on Perkin Elmer 1800 (FTIR) spectrometer at RSIC, Lucknow in the range 500-4000 cm^{-1}.

RESULTS & DISCUSSION

Main peaks in the ^{13}C-NMR spectrum along with assignment are listed in Table 1. It can be seen that all ^{13}C-NMR spectra show Ar-C-OH, Ar-C-CH$_2$-, -CH$_2$- and carbonyl carbon.

The carbonyl carbon peak area is small compared to the phenolic carbon. Poly (4-hydroxy acetophenone-methylene -4' aminobenzoic acid and nitro benzoic acid) shows an additional peak at 142 and 135 ppm which may be due to Ar-NH$_2$ group in the polymer. In case of polymer derived from bisphenol-A, H$_3$C-C-CH$_3$ peak appears at 30 ppm; the FTIR, spectra of this polymer shows C=O peak at 1702 cm^{-1}, -CH$_2$-bending 1456; Ar-C=O at 1233, 1184 cm^{-1}. The data on ^{13}C-NMR and FTIR on the polymer of Bisphenol-A, pertain to the structure of polymers as given below :
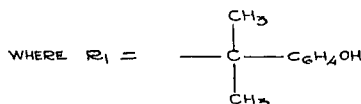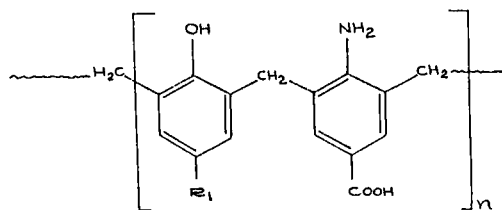
UV Spectra

The UV-visible spectra of polymer is given in Fig. 1 and 2 and bands are summarised in Table 1. All polymers show an intense band between 270-283 nm due to $\pi - \pi *$ transition. The shift can be correlated to the substitute groups in the monomer unit. Polymers derived from

TABLE 1

| Name of polymer	σ (T) $cm^{-1} ohm^{-1}$	Activation energy(e.v.)	Optical Absorption maxima in D.M.F. (nm) (e.v.)		^{13}C NMR spectral peak (ppm)	
A) Poly(4-hydroxy acetophenone-methylene-4'-chlorobenzoic acid)	9.05×10^{-8}	0.037	270	4.60	$-CH_2$ $-CH_3$ $Ar-Cl$ $-C=O$	40 32 160-165 200
B) Poly(4-Hydroxy acetophenone-methylene-4'-nitrobenzoic acid)	2.42×10^{-9}	0.03	275	4.28	$-CH_2$ $Ar-NO_2$ $Ar-OH$ $-C=O$	40 130-135 150 200
C) Poly (4-Hydroxy chlorobenzene-methylene-4'-chlorobennzoic acid)	2.55×10^{-8}	0.077	278	4.46	$-CH_2$ $Ar-OH$ $Ar-COOH$ $Ar-Cl$	40 135-140 165-170 125-130
D) Poly (4-Hydroxy acetophenone-methylene-4'-aminobenzoic acid)	1.82×10^{-7}	0.20	283	4.39	$-CH_2$ $-CH_3$ $Ar-OH$ $-C=O$	40 25-30 150-155 200
E) Poly (Bisphenol A-methylene-4'-aminobenzoic acid)	2.62×10^{-7}	0.12	278	4.46	$-CH_2$ $Ar-HN_2$ $Ar-COOH$ $-C(CH_3)_2$	40 140 170 30
F) Poly (4-Hydroxy chlorobenzene-methylene-4'-nitrobenzoic acid)	3.80×10^{-9}	0.039	280	4.43	$-CH_2$ $Ar-OH$ $Ar-NO_2$ C_6H_5-	40 150 135-140 130

Fig- I
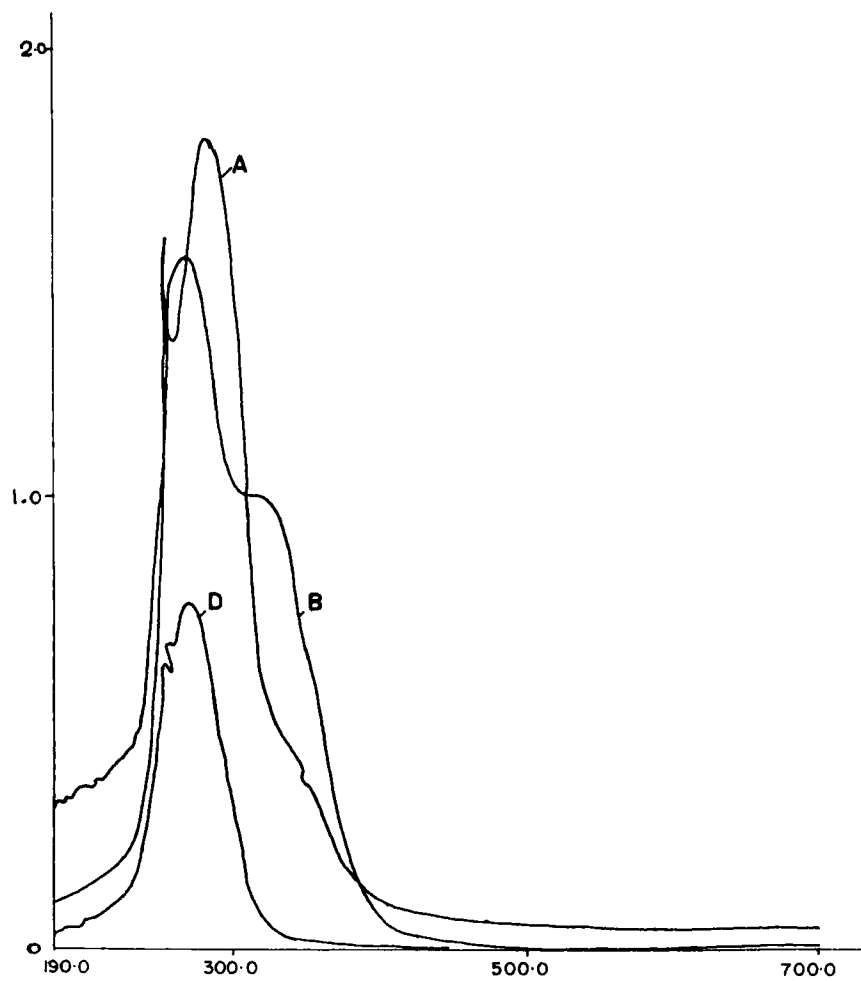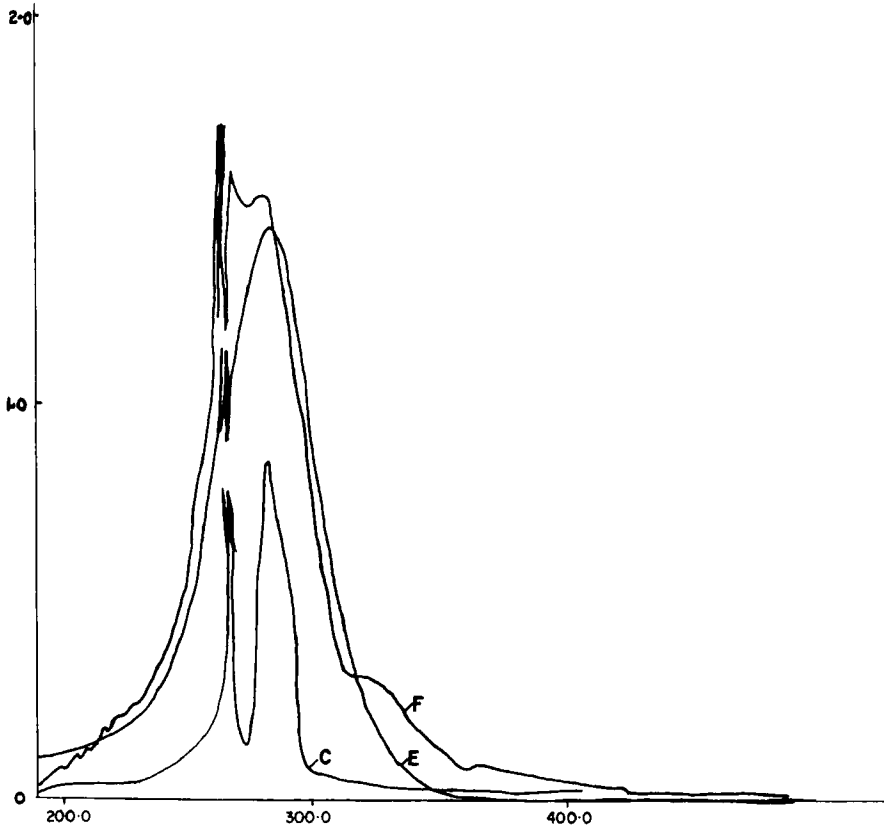
Fig-2

nitrobenzoic acid show absorption maxima at larger wave length as compared to that of chlorobenzoic acid.

Dielectric properties

The dielectric constant, dielectric loss were computed from the capacitance measurement, the dimension of the sample and the D-loss factor. The dielectric onstant (ϵ') and dielectric loss (ϵ'') are plotted as a function of temperature as in Fig. 3 and 4. From Fig. 3, it is observed that for amino acid substituted derivative ϵ' is
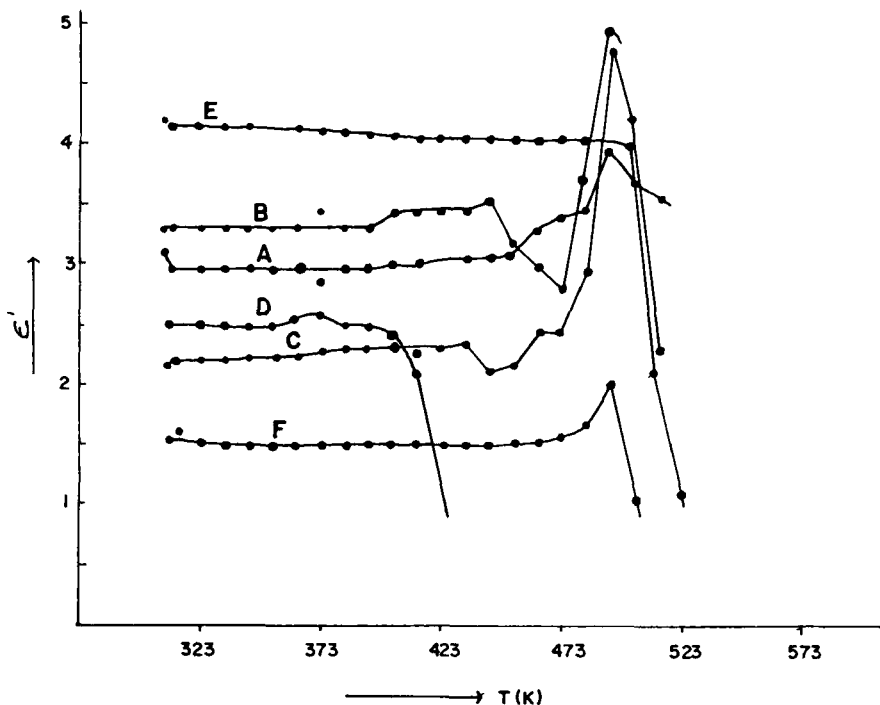
Fig-3

initially constant but decreases at higher temperature. While for others, it increases at higher temperature. Fig. 4 shows that the dipole segmental loss maxima shifts to higher temperature in the order chloro, nitro, amino groups in the p-substituted benzoic acid. Whereas it shifts to lower temperature, when more polar group is substituted at p-position in the phenol. This may be due to the dipole segmental motion of the substituents in the opposite direction.

Conductivity

All polymers exhibit low conductivity and the temperature dependence of the electrical conductivity is hown in Fig. 5. The activation energy of conductivity and σ_O (T) value obtained
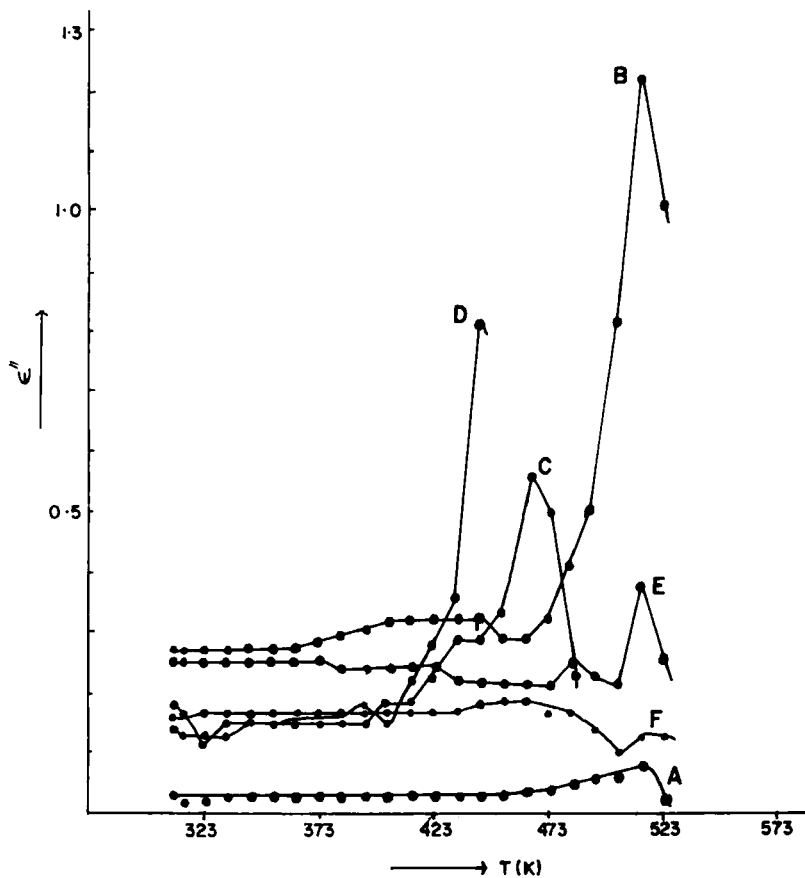
Fig-4

from Fig. 5(a) are recorded in Table 1. It can be noted from
table 1,that when the substitutent groups are chloro or nitro
(electron withdrawing groups), the conductivity & the activation
energy of conduction less by a factor of about 10 as compared to
electron donating groups such as amino group present in the chain
To understand the mechanism of conduction in these polymers through
grain   barrier   conduction;   hopping   conduction   and   tunneling
conduction were considered,accordingly[2-5].
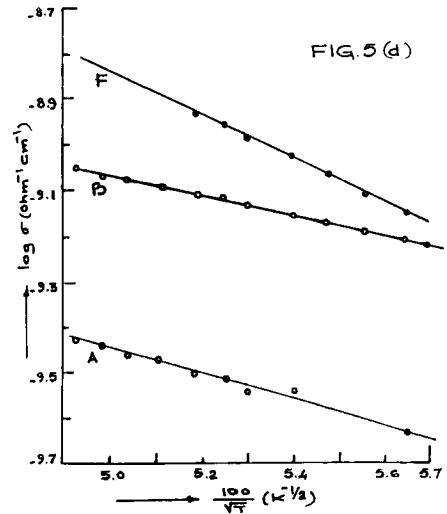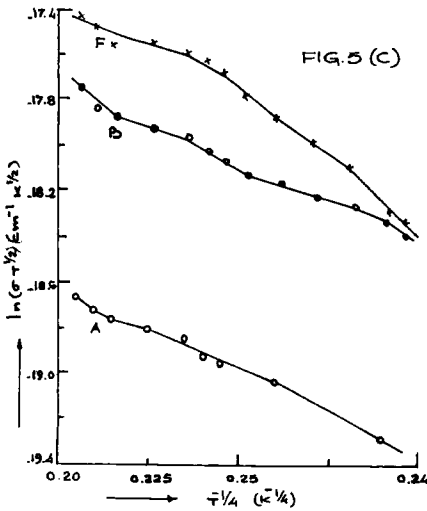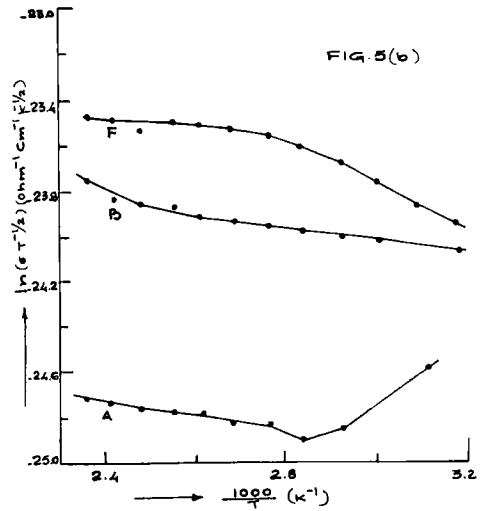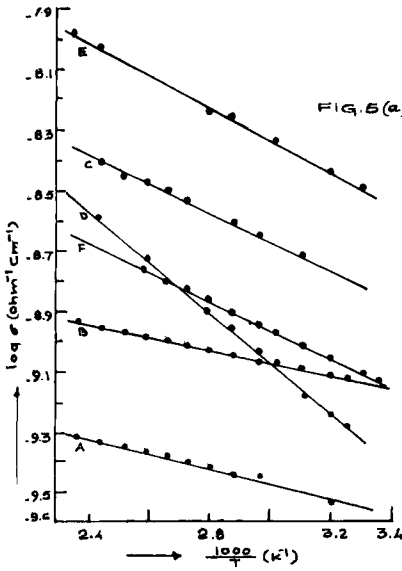
FIG.5(a),(b),(c),(d):- THE TEMPERATURE DEPENDENCE OF CONDUCTIVITY (G)
FOR (A), (B), (C), (D),(E), (F) POLYMERS.
ACCORDING TO (a) THE BAND THEORY.
(b) GRAIN BARRIER CONDUCTION.
(c) HOPPING CONDUCTION.
(d) TUNNELING CONDUCTION.

$$\ln \ (\sigma/T^{\frac{1}{2}}) \quad \mathrm{Vs} \quad \frac{1000}{T} \qquad .. \quad .. \quad .. \quad (1)$$

$$\ln \ (\sigma T^{\frac{1}{2}}) \quad \mathrm{Vs} \quad T^{-\frac{1}{4}} \qquad .. \quad .. \quad .. \quad (2)$$

$$\mathrm{and} \ \log \sigma \quad \mathrm{Vs} \quad \frac{100}{T^{\frac{1}{2}}} \qquad .. \quad .. \quad .. \quad (3)$$

were ploted. Linear plots are obtained as shown in Fig.5(d) for tunneling mechanism.   Thus the conduction in these polymers may be predominant by a tunneling of electron mechanism. The presence of   electron   withdrawing   group   in   the   chain   decreases   the probability of tunneling of electron.

REFERENCES

1. Khobragade Y F and Gupta M C ; Macromolecular Reports (1993).

2. Choi K M, Kin K H , Choi J A ; J Phys Chem Solids   (1988) 50; 283.

3. Matare M F ; J Appl Phys ; (1984) 56 ; 2605.

4. Mott N F ; J Appl Phys ; (1980) 1 ; 1.

5. Zeller H R ; J Phys Rev Lett ; (1972) 28 ; 1452.