Thermal and dielectric properties of linear p-substituted phenol with Methylene Bridge  

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Abstract. A novel method is used for the preparation of new linear polymer from p-substituted phenol with Methylene Bridge like –Cl, -COOH, -NO₂ etc. and these polymers have been characterized by IR, NMR and TGA method. We have studied the thermal analysis from TG thermogram to obtain the activation energy, structural analysis and effect of p-substituted groups on dielectric constant/loss.  

1. Introduction  

The polymers were derived from hydroxy aromatic compounds, are most interesting class of polymeric compound such as quinine polymers, which behave as oxidation-reduction system with respect to their properties [1-2]. From phenol-formaldehydes are used to synthesis phenolic resin, which is an effective conducting polymers [3-4] Synthesis of linear high molecular weight polymers were very difficult like polyquinones [5], which are similar to phenolic resin. The reaction of hydroquinone with trioxane was investigated in the studies [6]. The polymeric material was a cross linked, insoluble poly (bimethylene hydroquinone) a ladder polymer with high intrinsic viscosity the reaction is written as,  

Likewise, the related polyesters, those derived from p-hydroxybenzoic acid have application in engineering plastics. However, study on polyesters of p-hydroxybenzoic acid (PHBA) has revealed that it does not melt up to 300°C. Survey by Economy [7] on PHBA indicates that product has been commercialized in the form of ‘Ekonol’ and has numerous industrial applications. Some workers have reported the liquid crystal character of aromatic polyesters [8] studies by Zachariades and Economy [9] have demonstrated better mechanical properties of the products made from these polyesters. The studies of the reaction of phenol with formaldehyde yields a linear low molecular products known as resols [10] and the acidolysis of esters and amides has been conducted [11-12] The influence of HCHO, PhOH mole ratio and conversion on the comparison of the novalac is discussed. Phenolic resin is most useful for industrial applications as adhesive and impregnating resins and also plastics. Phenol formaldehyde resin gives excellent properties like mechanical, thermal and weather stability.
The required higher curing rate temperature are lower as compared to other thermosetting adhesive, which gives limited application of PF resins used as impregnating resins or adhesives [14-15]

2. Experimental

2.1. Preparation of Polymer [16]

0.01 mole of p-substituted phenol (Bisphenol –A, p-hydroxy acetophenone and p-chloro phenol) was dissolved in 10.0 mol NaOH solution and 0.02 mol of formaldehyde (37% solution) was added while stirring. To this homogenous mixture, 0.01 mol of p-substituted benzoic acid (p-chloro, P-amino, and p-nitro) was added and deareated by passing N₂ gas. The mixture was refluxed at 120°C - 150°C for 6-12 Hours. On acidification a solid mass was obtained and dried. This dried colored was used in studies.

3. Result and Discussion

The infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer using KBr pellet technique at CDRI, Lucknow, India. In the present investigation, Infrared spectra of a polymers prepared from p-chloro substituted phenol and p-substituted aromatic carboxylic acids with methylene bridge showed characteristic bonds of C-Cl stretching vibration at 680 cm⁻¹ and carboxylate anion stretching vibration at 1100 cm⁻¹ respectively. The other characteristic absorption beak due to –COCH₃ at 1690 cm⁻¹, methylene bridge due to C-H bending of –CH₂ – bridge. The characteristic peaks at 1670 cm⁻¹ due to N-H stretching vibration of p-substituted –NH₂ group, broad peak due to O-H stretching vibration at 3200-3400 cm⁻¹ in polymeric associated phenolic – OH groups as shown in Figure1.

![Figure 1. IR Spectra of Poly ((4 – hydroxy acetophenone – methylene – 4′- chlorobenzoic acid)](image-url)

Proton and ¹³C-NMR studies of non-aqueous solution with recommended reference compound as tetramethyl silane [(CH₃)₄ Si], where it is magnetically and isotropic, chemically reasonably inert. It is
also non-associating with any common compound. Carbon resonances of organic compounds are found around 230 ppm as compared to proton nuclei at 12 ppm with modern instrumental method. The narrower lines in CMR obtain than in PMR. $^{13}$C-NMR gives peak of Ar-C-OH at 150-155 ppm and other peak at 129-130 ppm for Ar-C-CH$_3$, peak at 40 ppm for -CH$_2$ and carbonyl carbon at the peak at 142 and 135 ppm which may be due to Ar-NH$_2$ group in the polymer. The NMR and $^{13}$C – NMR Spectral data valid with a linear monomeric unit structure.

**Figure 2.** NMR Spectrum of Poly (4 – hydroxy acetophenone – methylene – 4’- aminobenzoic acid) in DMSO$_4$ Solvent

The ionic mechanism of polycondensation can be exemplified by interaction of phenol with aldehydes in the presence of alkaline crystals as shown figure 3.

**Figure 3.** Mechanism of Polymerisation

Table 1. Decomposition pattern and activation energy of p–substituted aromatic hydroxy compounds with methylene bridge in inert atmosphere
| Polymers   | Temp. Range (°C) | Degradation Temperature | Observed mass loss (%) |
|-----------|------------------|--------------------------|------------------------|
| Ea (KJ/mole) | T | T_d |                  |
| a) PHAMCBA | 268 | 120 | 2.07               |
|           |     | 400 | 35.12             |
|           |     | 37.50 |                |
| b) PHAMABA | 328 | 120 | 4.16               |
|           |     | 400 | 55.70             |
|           |     | 20.32 |               |
|           |     | 900 | 47.36             |

Organic polymers are generally insulators. There are no mobile charges in them to support conduction. However, appropriate charge carriers may generated in them by partial oxidation (removal of electron from filled valence band) or partial reduction (addition of electrons to conduction band) with appropriate oxidant or reductant this in p-substituted phenol with methylene bridge oxidation gives a positive character as a result electron assumes a polaron state (radical cation), and polymer exhibit diamagnetism. However, such reduction mechanism is influenced by factors at dopant level. The presence electrons with drawing group in the chain decrease the tunneling of electron. When the substituent groups are-chloro (electron with drawing groups), the conductivity and 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 polymer.

Thermo gravimetric analysis is seen that the stability of the polymer depends on the p-substituted group on phenol, from Table 1. TG curves are indicates that the thermal stability of strained chain polymers is less than flat or linear chain polymers such as different high polymensation temperature. TG thermogram of poly (4–hydroxy acetophenone–methylene–4′–aminobenzoic acid) in nitrogen atmosphere is shown in figure 4(A) From these figures it is noted that in nitrogen atmosphere, the sample which refluxed at 150 °C for 12 hours is more thermally stable than the sample prepared at 120 °C for 6 hours. During product formation the moisture will be trapped. Do to this water molecules the mass loss occurs at around 120-130 °C temperature. The degradation temperature is noted in Table 1. After loss of water molecules, the continuous degradation of the pure sample. The most important step is post curing and oxidation degradation in temperature range 250-400 °C, the mass loss due to products formed like CH₂O, CO₂ and above the 400 °C temperature, the thermal fragmentation is formed in which the mass loss occurs due to the phenol molecules. On the above temperature range i.e. 600 °C, the carbon char formation occurs and lastly the product remains called residue. The residue remains are 12.5% and 1.39% on the basis of TGA data, the molecular formula of the above polymer monomer is [C₁₇H₁₅O₄N]·½[H₂O]
Figure 4. Thermogram of (A) (4-hydroxy acetophenone – methylene – 4’-aminobenzoic acid) (B) (4-hydroxy acetophenone – methylene – 4’-chlorobenzoic acid)

Figure 5. Dielectric constant as a function of Temperature for (i) (4-hydroxy acetophenone – methylene – 4’-chlorobenzoic acid) (a) 120°C for 6 hours (b) 150°C for 12 hours (ii) (4-hydroxy acetophenone – methylene – 4’-aminobenzoic acid) (c) 120°C for 6 hours (d) 150°C for 12 hours

From figure 4(B) TG thermogram of poly (4-hydroxy acetophenone – methylene – 4’- Chlorobenzoic acid) in nitrogen atmosphere from these figures, it is noted that, in nitrogen atmosphere, the sample which refluxed at 150 °C for 12 hours is more thermally stable that the sample prepared at 120 °C for 6 hours. During product formation, the moisture will be trapped. Due to these water molecules the mass loss occurs at around the 110-140 °C temperature. The degradation temperature is noted in Table 1. After the loss of water molecules, the continuous degradation of the pure sample. The most important degradation in temperature range 180-300 °C, the mass loss due to product formed like CH₂O, CO₂ and above the 300 °C temperature the thermal fragmentation is formed in which the mass loss occurs due to phenol molecules. On the above 600 °C temperature range, the carbon char formation occurs and lastly the product remain is called residue. The residue remains are 1.39% and 6.25%. On the basis of TGA data, the molecular formula of the above polymer as monomer is
Dielectric constant, dielectric losses were computed from the capacitance measurement, the dimension of the sample and the D-loss factor. From figure 5(C), Dielectric constant for amino acid substituted derivatives initially remains constant but decreases at higher temperature while for other it increases at higher temperature. Whereas, dielectric loss with different temperatures shows that dipole segmental loss maxima shifts at higher temperature for amino group substituted derivatives and for chloro group on p-substituted phenol polymers, dielectric loss increases at higher temperatures. The dielectric constant in p-substituted phenol chains increases at higher temperature in the order chloro, followed by amino groups due to more polar groups. The dielectric loss maxima shift to lower temperature for dipole segmental motion due to overlation in opposite direction. The magnetic properties of all the polymers have diamagnetic nature.

4. Conclusion
TGA studies in inert atmosphere shows the initial mass loss due to water molecules, while at high temperature most of polymers show more thermal stability as they do not decompose completely even up to 900 °C. The intermediate mass loss in the temperature range above 180 °C have been found due to the loss of low molecular mass hydrocarbons in nitrogen gas during pyrolysis and the residues corresponds to carbon char residue. Electron withdrawing groups present on the chain may affect the conductivity of the polymers which may also decrease/increase the dielectric constant. However, true value of the linear polymers like poly(p-hydroxy acetophenone – 4'- methylene - chlorophenol ) and aminophenol are such that they are non-flammable, partially insoluble, inert to both acid and alkali, light weight and strong. The method for making linear polymer with an alkaline catalyst has been obtained.

5. References
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