Castor Oil Based Polyester by Melt Condensation Process

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Abstract: **Aliphatic – Aromatic Oligomeric polyester namely, poly (2,2'-isopropylidene-diphenylene, 4,4'-dimerate) [BPADA] was synthesized from Bisphenol-A[BPA] and Dimer acid [DA] derived from Castor oil by melt condensation under various atmospheric condition and its degree of polymerization $\overline{DP}$ and acid number were studied in order to report the affect of atmospheric conditions on its molecular weight. The Oligoester formation was characterized by IR spectroscopy.**

Keywords: **Aliphatic – Aromatic Oligomeric Polyester, Dimer Acid, Bisphenol-A, Acid Number, Degree of Polymerization.**

I.   INTRODUCTION

The Dimer acid based polyester are mainly the condensation products of di – or poly functional hydroxy compounds of dimer acid. The dimer acid based polyesters originated back in the 1940 [1-3]. Among the polyesters based on dimer acids versatile compositions are those used to achieve high performance speciality polyesters. Efforts are made only to increase molecular weight, little efforts has been made to prepare polyesters of low molecular weight useful as plasticizers. A couple of references [4,5] describes the preparation of plasticizers comprising glycidyl esters of dimer acid and epoxy resin compositions containing them. The kinetics of the polyesterifications of dimer acid with different polyhydroxy compounds was studied by Bajpai et al [6-8].

The commercial polyesterification typically includes melt processes where a viscous polymerizing mass of carboxylic acid and glycols is held at temperatures as high as $250^0 C$ to drive the polymerization and remove the byproduced water. The troublesome consequences are side reactions that can include etherification of hydroxyl groups, ene or Diels-Alder additions, decarboxylation, chain cleavage by ester pyrolysis, acidolysis, alchoholysis and ester redistributions [9-11]. This leads to broadened molecular weight distributions [12], sporadic gelation and loss of functionality. Thus, while adequate for many materials, the process is however unsuitable for preparing polyesters with ordered or temperature sensitive structures due to the extreme process conditions. In the present work polysterification by melt condensation technique has been explored under variable atmospheric condition and analysis of molecular weight and prevailing drawbacks has been explored to find a better alternative.

II.   EXPERIMENTAL

Dimer acid [DA] 1010 (composition: dimer acid 98% + trimer acid 2%) was supplied by Jayant oil mills, Bombay, Bisphenol-A [BPA] was obtained from Wilkinson Laboratories, p-toluene sulphonic acid [pTSA] supplied by E. Merck Bombay, were used as received. All other chemicals used were of reagent grade and were used without further purification.

Polyesterification by Melt Condensation Technique:

Polycondensation reaction of dimer acid with aromatic diol under melt condensation technique was carried out under different atmospheric conditions and with variation in temperature in the respective experiments. In a standard

experiment, a 250 ml three necked round bottomed flask equipped with a thermometer, a condenser and an inlet tube for nitrogen was charged with 5.6 g (0.01 M) [DA], 2.2828 g (0.01M) of [BPA] and 0.05 g% of pTSA. The oxygen free dry nitrogen gas was passed through the reaction mixture initially at a fast rate to remove dissolved oxygen in the reaction mixture and then at the rate of one bubble per second. Aliquots ($\sim$ 0.2 g each) of hot resin were withdrawn from the reaction mixture initially and at fixed time intervals, dissolved in 10mL acetone and titrated with standard alcoholic KOH solution. Finally, in every case the viscous brown resinous product was obtained which was transferred to a beaker and cooled to room temperature in a desiccator. It was then washed thoroughly with acetone to remove the unreacted monomers and catalyst. The intrinsic viscosity, [η] in acetone solution was found to be 0.1 and acid number of the product was determined by dissolving $\sim$ 0.2 g of the product in 10mL acetone and titrated against 0.1 N alcoholic KOH and was found to be 112. Mn was calculated to be 1455.4.

Determination of Acid Number:

The acid number is expressed as the number of milligrams of potassium hydroxide required to neutralize the carboxyl group in 1g of the acid/material under investigation. The carboxyl group is readily determined by alkalimetric titrations, the end points being determined with visual indicators or potentiometrically [13,14]. For the determination of the acid number, 0.2g of the sample was withdrawn from the reaction mixture initially and dissolved in 10mL of acetone. It was titrated rapidly with 0.1N alcoholic KOH in the presence of phenolphthalein as an indicator. The appearance of pink colour was taken as the end point. The alkali consumption of the solvent was determined in a blank run. The acid number gives the amount of KOH consumed per gram of sample and is calculated from the formula:

$$Acid\ Number = \frac{56.1 \times N_1 \times (A-B)}{x} \qquad \text{....... (1)}$$

Where

N_1 - Normality of alcoholic KOH

A – Consumption of KOH by the sample (in mL)

B – Consumption of KOH by the solvent (in mL)

x - Weight of the sample in gram

Since an excess of hydroxy compound over dimer acid is used, the course of polysterification reaction may easily be followed by the estimation of – COOH groups.

Degree of Polymerization $\overline{DP}$:

The degree of polymerization of a given polymer molecule is the number of structural units which it contains. The symbols $\overline{X_n}$, P and $\overline{DP}$ are commonly employed to symbolise number average degree of polymerization. A molecule with degree of polymerization of x is called x-mer. The definition may be used for branched as well as linear polymers. The dependence of the degree of polymerization on yield and stoichiometry can be very elegantly described in terms of the extent of reaction.

The extent of reaction or the progress of poly condensation reaction can be followed in a simple manner by qualitative analysis of the unreacted functional groups. According to the concept of the equal reactivity of functional groups, if the reactive groups are present in equimolar quantities, as is generally desired, the analysis of one of the two groups suffices for example, analysis of the carboxyl groups in polyesterification. If N_o is the amount of carboxylic groups initially present (acid number) and N is their quantity after a given time t, the extent of polycondensation p, is given by the fraction of those functional groups that have already reacted at that time.

$$p = \frac{(N_o - N\ )}{N_O} \qquad \text{....... (2)}$$

Multiplying p by 100 gives the conversion in percentage. In terms of extent of reaction p, a value for the number – average degree of polymerization $\overline{DP}$ can be obtained. This is clearly equal to the ratio of the initial number of monomer molecules N_o, to the amount of molecules present N, at the respective stage of the reaction.

$$\overline{X_n}\ or\ \overline{DP} = \frac{N_o}{N} = \frac{1}{(1-p)} \qquad \text{..... (3)}$$

This equation relating the degree of polymerization to the extent of reaction was originally set forth by Carothers [15] and is sometimes referred to as the Carothers equation.

The number – average molecular weight $\overline{M_n}$, defined as the total weight of a polymer sample divided by the total number of moles in it as:

$$\overline{M_n} = \frac{W}{\sum N_x} = \frac{\sum N_x M_x}{\sum N_x} \qquad \text{....... (4)}$$

Where the summations are over all the different sizes of polymer molecules from x=1 to x= ∞ and N_x is the number of moles whose weight is M_x can also be written as :

$$\overline{M_n} = \sum N_x M_x \qquad \text{...... (5)}$$

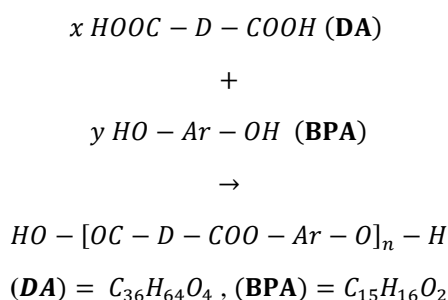Where N_x is the mole fraction (or the number - fraction) of molecules of size M_x is given by

$$\overline{M_n} = M_o \overline{X_n} + M_{eg} = \frac{M_o}{(1-p)} + M_{eg} \text{ .... (6)}$$

Where M_o is the mean of the molecular weights of the two structural units, and M_{eg} is the molecular weight of the end groups.

III. SPECTRAL ANALYSIS

IR spectra was recorded on Perkin – Elmer spectrophotometer model 1403 and Shimadzu 8201 PC spectrophotometer in $4000 – 400\ cm^{-1}$ range using KBr as dispersant.

A general reaction scheme of polyesterification is presented as

$$x\ HOOC - D - COOH\ (\textbf{DA})$$

$$+$$

$$y\ HO - Ar - OH\ \ (\textbf{BPA})$$

$$\rightarrow$$

$$HO - [OC - D - COO - Ar - O]_n - H$$

$$(\textbf{DA}) = C_{36}H_{64}O_4\ ,\ (\textbf{BPA}) = C_{15}H_{16}O_2$$

Melt Condensation:

Polyesterification by melt condensation yielded a dark brown resinous material, however, needle shaped crystals of bisphenol – A gradually deposited on the neck of the flask (this observation was even more pronounced in case of 1,5 – Nephthalene diol, 2,7 – Naphthalene diol and 4,4' – Dihydroxy – biphenyl). As the volatility of diols is quite apparent at the reaction temperature used and failure to consider the effect of small losses of volatile components, it may seem unreasonable to derive information from this system, still the plot of 1/(1-p) where p is extent of reaction against time is a straight line suggesting the second order kinetics quite appropriate for the catalyzed polyesterification reaction. The increase in molecular weight in melt condensation during the course of polyesterification reaction has been studied by end group analysis [16].

The molecular weight of polymer is calculated by multiplying the molecular weight of the monomer by the degree of polymerization $\overline{DP}$. The degree of the polymerization of the product for polyesterification may be represented by the equation (7) [17,18]:

$$\overline{DP} = \frac{(1+r)}{[2r\,(1-p)+\,(1-r)]} \qquad \text{.... (7)}$$

If this polymer in general is represented as an A-A-B-B type, then r is the ratio of A-A to B-B molecules and p is the extent of reaction or the fraction of end groups that has already reacted at that particular time, given by equation (2).

For complete conversion of reaction groups (i.e. when p=1) eq. (7) reduces to eq. (8).

$$\overline{DP} = \frac{(1+r)}{(1-r)} \qquad \text{....... (8)}$$

Thus an excess of either diol or dicarboxylic acid regulates the molecular weight of the resulting polymer and the nature of the end groups. The polycondensation reaction of dimer acid and Bisphenol – A was carried out in air, in flow of dry nitrogen gas and under vacuum respectively. The plots of extent of reaction $1/(1-p)$ against time for all the three cases are depicted in Fig. 1.
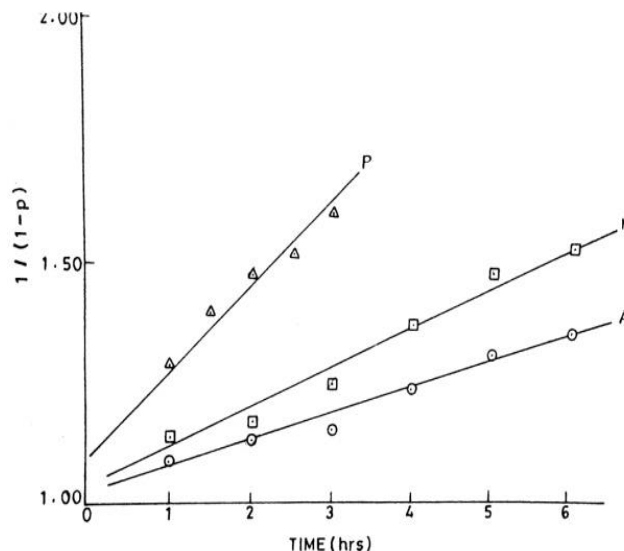
Fig 1: Plot of 1/(1-p) Vs. time for catalyzed Melt Condensation of (DA) and (BPA);

A- In air, N- Nitrogen atmosphere,

P- Reduced pressure

The straight line graph suggest second order reaction kinetics which is quite consistent with the condensation reaction. The reaction rate was found to be greatest under reduced pressure which can be attributed to the facile removal of water molecules from the reaction atmosphere. The decrease in acid number as shown in fig. 2 for all the cases.
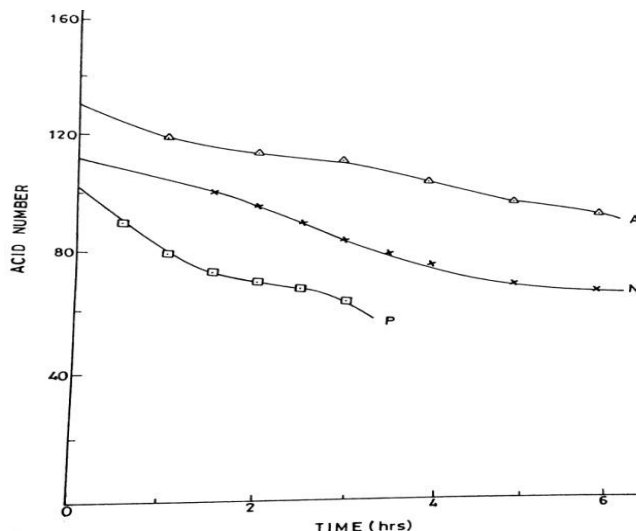
Fig 2: Curves of Acid Number for catalyzed Melt Condensation DA and BPA;

A- In air, N- Nitrogen atmosphere,

P- Reduced pressure

 It was found that for the same duration of reaction, highest value for $\overline{M_n}$ is obtained under reduced pressure as 1214 for reaction under nitrogen $\overline{M_n}$ = 943 and in air $\overline{M_n}$ = 868. In case of inert atmosphere, the reaction was followed upto 20 h and the maximum value of $\overline{M_n}$ was found to be 2700 with $\overline{DP}$ = 3.597.

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The most efficient removal of moisture under reduced pressure may be the driving factor to bring about an increase in the rate of reaction. However, Flory [19] has shown in an experiment with diethylene glycol and adipic acid that reaction velocity is not necessarily affected by the reduction in pressure and consequent escape of moisture, the rate must be controlled by factors inherent in the mechanism of reaction. Probably with the present case due to hydrophobic nature of monomer (as opposed to hydrophilic monomer studied by Flory) reduction in pressure is an efficient means of expulsion of moisture from the reaction moisture, hence the observed increase in $\overline{M_n}$.

IR Spectral Analysis:

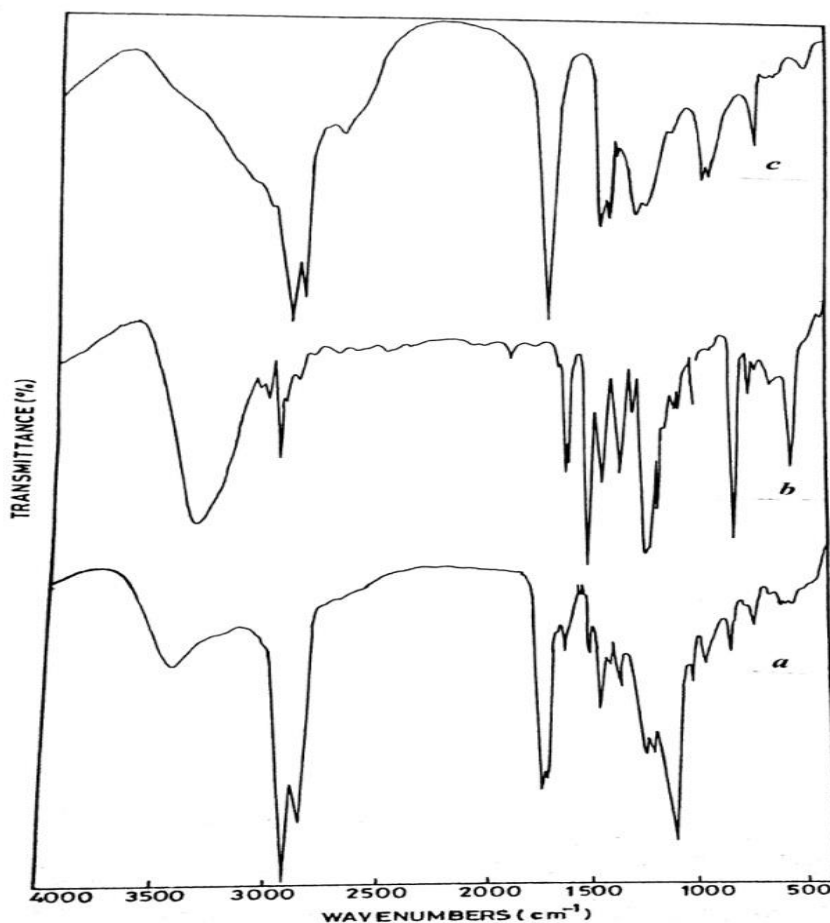The IR spectra of DA, BPA and polyester (BPADA) are depicted in fig. 3.

Fig 3: IR Spectra of (a) BPADA by melt condensation (b) BPA (c) DA

A perusal of these spectra gave evidence for polyesterification. In the IR spectrum of DA broad wings of υOH from –COOH group appears on either side of narrow υCH bands (υ_{as}CH$_2$ at 2925.69 cm^{-1} and υ_sCH$_2$ at 2854.9 cm^{-1}) [20]. These wings disappears in the spectrum of polyester and only the narrow peaks of υCH$_2$ are visible. Further a very strong and broad band in BPA due to the H- bonded phenolic OH groups appear with significantly reduced intensity in the polyester at 3427.4 cm^{-1}. On the basis of reduction in intensity it is inferred that number of hydroxyl groups decreased on polyesterification and the band shifted to higher wave number due to decreased H- bonding interactions. Polyesterification is strongly evidenced by the appearance of a very strong peak due to $\upsilon_{c=o}$ of the ester group at 1742.6 cm^{-1}. A very intense band appears at 1110.8 cm^{-1} in the polyester which is broad by super imposition of other absorption bands due to skeletal vibrations associated with the species derived from the dimer acid and BPA [21].

IV. CONCLUSION

The dimer acid based polyesters by melt condensation has gained enough commercial importance because of their fine properties. However the drawbacks associated in melt condensation technique can be avoided by adopting interfacial polycondensation in heterogeneous media.

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