

# Interfacial Polycondensation of Castor Oil Based Dimer Acid and Aromatic Diols

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**Abstract:** Direct Interfacial Polycondensation of various aromatic diols viz. Bisphenol-A (BPA), 1,5 Naphthalene diol (1,5 N), 2,7 – Naphthalene diol (2,7 N) and 4,4' – Dihydroxy biphenyl (4,4' B), Hydroquinone (1,4 – dihydroxy benzene) (Q), Resorcinol (1,3–dihydroxy benzene) (R), Phenolphthalein (P) with Dimer acid (DA) was carried out using phase transfer catalyst (PTC) : Cetyl Trimethyl Ammonium Bromide [CTAB]. Chloroform and water were used in immiscible phase system and acetone and water in miscible phase system. The byproduced water remained in the system in all the cases. The difference in the extent of polymerization of different aromatic diol may be due to the differences in the solubilities of the adduct with phenoxide in organic phase. A parallel study under same experimental condition was performed with Disodium salt of Dimer Acid [DSDA] to confirm the formation of Oligoester under these conditions which were confirmed by IR spectroscopy. The study of  $[\eta]$  intrinsic viscosity was reported to confirm polyesterification.

**Keywords:** Interfacial Polycondensation, Aromatic Diols, Phase Transfer Catalyst (CTAB), Dimer Acid.

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## I. INTRODUCTION

An unexplored alternative of commercial polyesterification involving melt condensation was studied by various scientists under interfacial polymerization involving heterogeneous media [1,2] so that the water produced forms in a hydrophobic phase. Transfer of the water to a hydrophilic phase can then reduce the net free energy to favourably shift the equilibrium towards polyesterification under micellar mechanism [1 – 3].

In the present work, synthesis of oligoesters of dimer acid (DA) with various aromatic diols viz.

- Bisphenol A (BPA),
- (1,5-Naphthalenediol) –[1, 5 N] –
- (2,7-Naphthalenediol) –[2, 7 N] –
- (4,4'-Dihydroxybiphenyl) –[4, 4' B] –
- Resorcinol [R], Hydroquinone [Q] Phenolphthalein [P]

catalyzed by cationic surfactant CTAB is reported.

## II. EXPERIMENTAL

### Materials:

Dimer acid [DA] 1010 (composition: dimer acid 98% + trimer acid 2%) was supplied by Jayant Oil Mills, Bombay, Bisphenol-A (BPA), Hydroquinone (Q), Resorcinol (R), Phenolphthalein (P) were obtained from Wilkinson Laboratories Bombay. 1,5- dihydroxy naphthalene (1,5 N), 2,7 dihydroxy naphthalene (2,7 N), 4,4' – dihydroxybiphenyl (4,4' B) were

supplied by Fluka chemicals. Cetyl trimethyl ammonium bromide (CTAB) supplied by E Merck India was used as received. Sodium hydroxide, hydrochloric acid and the solvents viz. Acetone, methanol, toluene, benzene, chloroform were from Qualigeous (Glaxo, India). All the chemicals used were of reagent grade and were used without further purification.

### Interfacial Polycondensation:

The interfacial polycondensation was performed as reported by Saam & Jong [ 4 - 6] taking 1 mM of DA dissolved in 20 mL chloroform / acetone, 0.002 g of CTAB and 1mM of various aromatic diols respectively which are dissolved in 2 N aqueous solution of NaOH were added in respective preparations. A haziness appeared instantaneously in every case which thickened rapidly and on stirring formed a frothy solid mass. StIrring was continued for 5 hours. The product formed was filtered under suction and washed thoroughly with acetone and dried in air oven at 80 °C for 3 hours (Table 1). For BPA other experiments were performed with variation in the reaction parameters such as solvents, temperature, time and proportion of the ingredients of reaction mixture (Table 2).

**Table 1. Interfacial Polycondensation of Various Aromatic Diols with Dimer Acid (DA)<sup>a</sup>**

Run No.	Compound Code	Organic Phase	Yield %	Intrinsic Viscosity [η]	$\nu_{COO^-}/\nu_{OH}$
1.	BPADA	CHCl <sub>3</sub>	80	0.4	2.0312
2.	BPADA-A	Acetone	89	0.24	0.7299
3.	BPADA-A <sup>b</sup>	Acetone	98	0.10	0.4019
4.	4,4' BDA	CHCl <sub>3</sub>	70	0.20	6.7970
5.	4,4' BDA-A	Acetone	90	0.18	2.5802
6.	1,5 NDA	CHCl <sub>3</sub>	60	0.25	7.6138
7.	1,5 NDA-A	Acetone	95	0.10	-
8.	2,7 NDA	CHCl <sub>3</sub>	66	0.16	7.4113
9.	2,7 NDA-A	Acetone	75	0.10	3.2063
10.	PDA	CHCl <sub>3</sub>	75	0.06	2.1420
11.	QDA	CHCl <sub>3</sub>	72	0.26	2.8899
12.	RDA	CHCl <sub>3</sub>	65	0.19	2.4997
13.	DSDA+P	-	-	-	1.2939
14.	DSDA	CHCl <sub>3</sub>	90	0.15	1.6771
15.	DSDA-A	Acetone	95	0.12	-

a:  $x \text{HOOC} - D - \text{COOH} (\text{DA}) + y \text{HO} - \text{Ar} - \text{OH} (\text{Diol})$

$\rightarrow \text{Na}^{+} - \text{O} - [-\text{OC} - D - \text{COO} - \text{Ar} - \text{O}-]_n - \text{Na}^{+} (\text{Oligoester})$

b: Reaction temperature was 27°C in every case except for run No. 3, where temperature was kept 50°C

**Table 2. Interfacial Polycondensation of Bisphenol-A (BPA) with dimer acid (DA)**

Run No.	Dimer Acid		Bisphenol-A		Organic Phase	Volume mL	Catalyst	Amount g	Temp °C	Time h
	g	mmol	g	mmol						
1	3.36	6	2.7393	12	Toluene	10	CTAB	1	80	0.25
2	3.36	6	2.7393	12	Toulene	10	CTAB	1	100	3
3	5.6	10	2.2828	10	CH <sub>2</sub> Cl <sub>2</sub> <sup>a</sup>	2	CTAB	0.0236	27	5
4	5.6	10	2.2828	10	Toulene	10	SLS <sup>b</sup>	0.750	27 <sup>c</sup>	48
5	5.6	10	2.2828	10	Toulene	15	SO <sup>b</sup>	0.456	100	5
6	5.6	10	2.2828	10	Toulene	10	PTSA <sup>b</sup>	0.004	100	25
7	5.6	10	2.2828	10	CH <sub>2</sub> Cl <sub>2</sub> Acetone	2 8	PTSA	0.004	27 <sup>d</sup>	15
8	5.6	10	2.2828	10	Pyridine DMF	5 15	TPP <sup>b</sup>	12.25	80	24

a- 8 mL of 1N aqueous solution of sodium carbonate

b- SLS – sodium lauryl sulphate, SO – sodium oleate, TPP – triphenyl phosphate

- c- Initially heated at 100 °C for 50 minutes to dissolve the monomers
- d- Initially heated at 50 °C for 1 hour.

**Remarks obtained for different Run No. :**

Run No.	Remarks
1	Monomers Incompletely Soluble
2	Thixotropic gel was obtained
3	Emulsion was obtained
4	Pale yellow colloidal emulsion obtained
5	Pale yellow colloidal emulsion obtained
6	Solution turned dark brown;
7	No solid product obtained
8	No solid product obtained

A blank run was performed by taking 1mM of DA dissolved in 20mL CHCl<sub>3</sub> under exactly the same conditions containing 0.002g of CTAB. To it was added 2N aqueous NaOH (excluding the diols). A white haziness appeared which thickened rapidly in this case, similar to one observed for aromatic diols, which thickened rapidly in this case too and on stirring it, formed a frothy solid mass. This product (DSDA) was washed and dried in exactly same procedure as with other oligoesters.

The extent of reaction in every case was determined gravimetrically in terms of percentage yield, evaluated is shown below:

$$\text{yield of the product (\%)} = \frac{\text{weight of the product}}{\text{weight of dimer acid} + \text{weight of diol}} \times 100$$

**Measurements:**

IR spectra were recorded on Perkin-Elmer spectrophotometer model 1403 and Shimadzu 8201 PC spectrophotometer in 4000-400 *cm*<sup>-1</sup> range using KBr as dispersant. The intrinsic viscosity was calculated by Ubbelohde viscometer.

### III. DISCUSSION

Direct interfacial polycondensation of various aromatic diols with DA was carried out using CTAB as phase transfer catalyst (PTC). Chloroform and water were used in immiscible phase system and acetone and water in miscible phase system. The results are presented in (Table1). The by produced water remained in the system in all the cases. The isolated yields represent the insoluble portion of polyesters poly (aryl dimerates) in aqueous NaOH solutions and reflect the losses incurred during work – up.

It is suggested that CTAB, a cationic surfactant forms mixed micelles with dimer acid. The aliphatic chains of dimer acid are soluble in CHCl<sub>3</sub> and the polar head groups (-COOH) from ion – pair with the positively charged head – group of CTAB. This speculation finds support from the observation that with the use of sodium oleate (SO) or sodium lauryl sulphate (SLS) which are an ionic surfactants, oligoester was not produced (Table2).

It was also found that formation of disodium dimerate (DSDA) was not possible under identical experimental conditions without using phase transfer catalyst (PTC), i.e. CTAB which otherwise needed a much higher concentration of NaOH for the formation of salt. Hence, it can be inferred that a micellar mechanism is operative for its formation. Interaction with the ArO<sup>-</sup> ion present in aqueous phase derived from the aromatic diol, probably occurs at the interface. The resulting ester group being less polar than -COOH is then drawn inside the micelles of CTAB. Possibilities of reverse reaction, i.e. hydrolysis of ester formed is ruled out even though 2N aqueous solution of NaOH has been employed.

**IR Spectral Analysis:**

All the products obtained were strongly hydrophilic in nature and formed colloidal solution in water. Strongly hydrophilic nature of these products introduced a doubt whether these are the disodium salt of dimer acid (DSDA). Due to very weak absorption band for *ν*<sub>CO</sub> characteristics of ester group at 1740 *cm*<sup>-1</sup>. Although the polyesterification was confirmed by observing the IR bands in fig.1.

The reaction DA was performed under identical conditions excluding the diols (run No, 14, 15 in Table 1). The IR spectrum of DSDA was compared with those of other products (fig. 2-4). The IR spectrum of an equimolar amount of (DSDA + P) was also recorded for comparison.

A comparison of IR spectra of mixture of (DSDA+P) and poly(phenolphthalein dimerate) (PDA) (Fig. 2 c ,d) makes it evident that a considerable reduction in intensity of  $\nu_{OH}$  of P has occurred on esterification Fig.2c. Similarly, the  $\nu_{COO^-}$  and  $\nu_{CO}$  of lactone ring of P are overlapping in IR spectrum of mixture whereas for the polyester these peaks are well separated. Further more, when the intensities of carbonyl stretching is compared taking  $\nu_{as}CH_2$  as the standard using literature method [7], it is observed that the intensity of  $\nu_{CO}$  is slightly greater in case of the polyester in comparison to (DSDA + P) mixture (Table 1). The stretching vibration of hydroxyl groups and carboxylate anions were compared using antisymmetric stretching frequencies of  $CH_2$  group as a reference (Table 1).

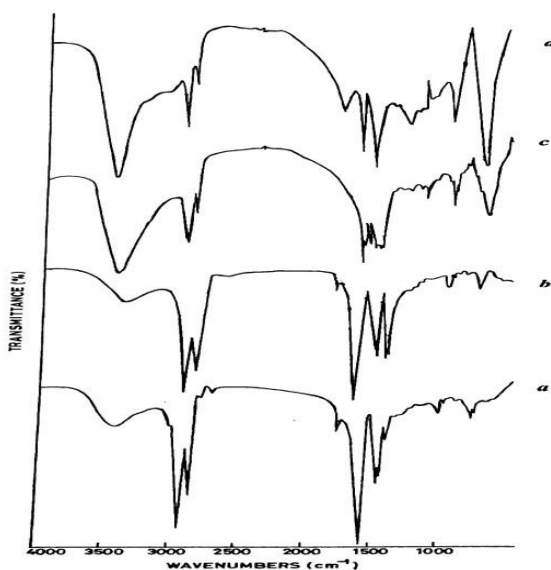


Fig. 1

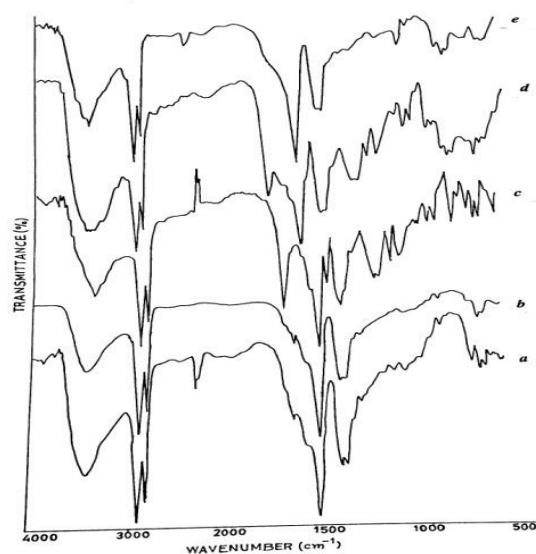


Fig. 2

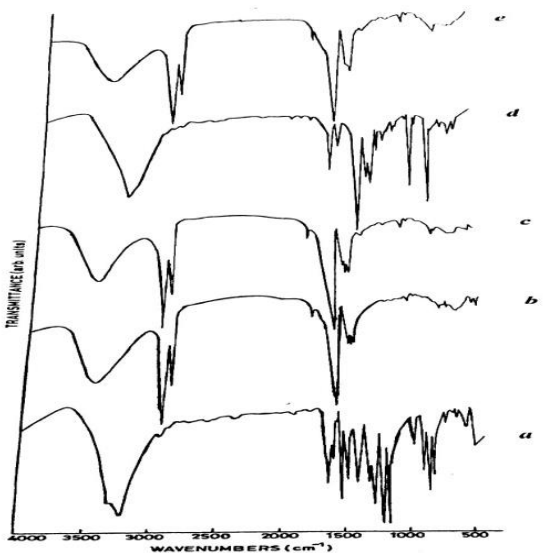


Fig. 3

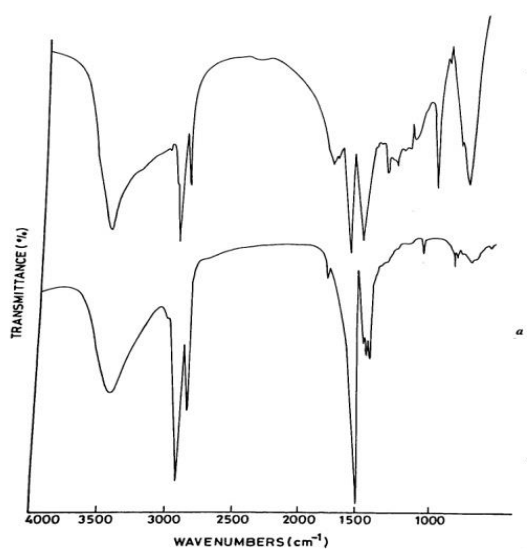


Fig. 4

Fig. 1 IR spectra of (a) BPADA (b) BPADA-Melt condensed at 160 °C (c) BPADA-A (d) BPADA (50°C)

Fig. 2 IR spectra of (a) RDA (b) QDA (c) PDA (d) DSDA+P (e) DSDA

Fig. 3 IR spectra of (a) 2,7-N (b) 2,7 NDA-A (c) 2,7 NDA (d) 1,5-N (e) 1,5-NDA

Fig. 4 IR spectra of (a) 4,4'-BDA (b) 4,4'=BDA-A

It is observed that a higher ratio of  $\nu_{COO^-} / \nu_{OH}$  is obtained in case of products obtained in  $CHCl_3$  than in the case of the products obtained in acetone, which is indicative of greater absorption intensity due to water molecules in latter. The IR spectra of the products in acetone further evince the presence of water molecules by the appearance of broad bands near 3400, 1600 and  $650\text{ cm}^{-1}$  due to stretching, banding and rocking vibrations of OH groups from absorbed water molecules [8].

A perusal of Table 1 shows that yields are higher when acetone was the organic phase than for  $CHCl_3$  in all the cases, and was highest for BPADA which can also be taken for increasing order of reactivity due to basic strength of diol. Yield Strength is reported as : 1,5 NDA < RDA < 2,7 NDA < 4,4' BDA < QDA < PDA < BPADA. The intrinsic viscosity  $[\eta]$  may be taken as the extent of polymerization follows the order as: PDA < 2,7 NDA < RDA < 4,4' BDA < 1,5 NDA < QDA < BPADA, highlighting contribution of structural units. Therefore, for studies BPADA was used as a model diol for oligoester formation. It is evident from Table 1, the oligoester obtained in the run No. 1, 6 and 11, the highest intrinsic value were obtained as 0.4, 0.25 and 0.26 respectively. Higher degree of polymerization is obtained in chloroform which may be regarded as a better solvent for the polymer in comparison to acetone. The benefit for employing a polymer solvent is presumed to result from the mobility of the polymerising mixture and the continuation of contact of dimer acid with aromatic phenoxide ion near the interface. Solubility of the oligomers in the solvent is also expected to promote degree of polymerization as a result of increased contacts with the complementary intermediates near the interface. The cation of the additive is presumed to be the effective agent to form an adduct with phenoxide ion which is more soluble in the organic phase than the phenoxide itself. Thus, contact with monomer is promoted and the polymerization rate is increased. The by-produced salt is then extracted by the aqueous phase and cation is free to follow the cycle again.

The variation in solvents and catalyst (Table 2) shows that the oligoester was not formed. With CTAB and PTC in toluene, at room temperature monomers were insoluble and even on increasing the temperature oligoester could not be obtained. The non-surface active catalyst p-toluene sulphonic acid (pTSA) could not produce the oligoester as observed by Jong and Saam for other anionic / cationic surfactants [4,9]

#### IV. CONCLUSION

The interfacial polycondensation as types of nucleophilic displacements are carried out with phase transfer catalyst [10,11,12]. Generally, small symmetric quaternary cations [13,14] are used as PTC. It has been suggested that the function of both surfactant and PTC aid in transfer of monomer between phases. Cationic emulsifiers have been extensively used for the synthesis of polymers [15 – 19]. The reported work is significantly supporting the preparation of oligoesters of renewable origin, requiring lesser hazardous techniques for polyesterification, hydrophilic nature of the product can be explored for its high performance criteria and is eco friendly.

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