

Synthesis and characterization of phenolic oligomers

D J DESAI, K C PATEL*, R G PATEL and V S PATEL

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, India

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Abstract. Phenolic oligomers were prepared by Friedel-Craft polymerization from different phenols with dichloro methane and 1,2-dichloroethane. The samples were characterized by IR spectra, viscosity measurement and thermal analysis by differential scanning calorimeter (DSC). The number average molecular weight (\bar{M}_n) was determined by vapour pressure osmometry (VPO) and by conductometric titration.

Keywords. Phenolic oligomers; *p*-cresol; differential scanning calorimeter (DSC); limiting viscosity number (LVN); vapour pressure osmometer (VPO).

1. Introduction

Friedel-Craft's (FC) reaction of benzene or substituted benzene with dichloromethane (DCM) and 1,2-dichloroethane (DCE) gives oligomers in which benzene nuclei are linked through methylene (Patel and Patel 1979) as well as ethylene bridges (Shinkle 1935; Towne 1937). Oligomers having methylene (Patel and Patel 1979) bridges and oligomers with ethylene (Patel *et al* 1979; Patel *et al* 1980) bridges, made from 8-hydroxy quinolines, salicylic acid and salicyldehyde under FC conditions have been reported. This paper reports the synthesis and characterization of different phenolic oligomers.

2. Experimental

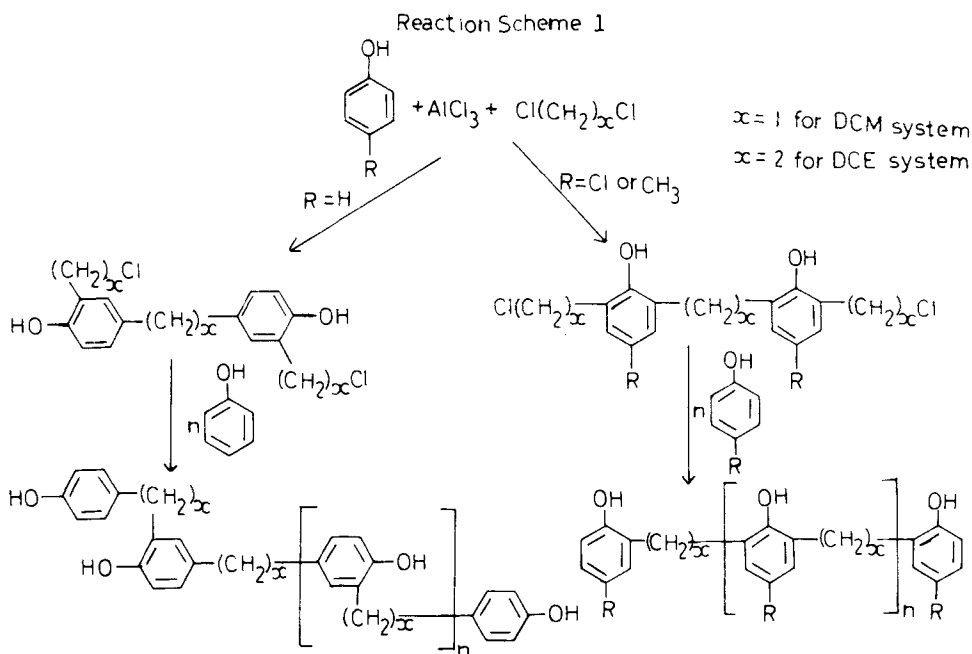
2.1 Friedel-Craft polymerisation

The chemicals used were of analytical grade. To phenolic compound (table 1) (0.20 mol) in a three-neck flask anhydrous aluminium chloride (1.00 mol for the DCM and 0.40 mol for the DCE oligomer) was added in powdered form. A condenser was fitted to the flask and ice cold water was circulated in the case of reaction with DCM. The entire assembly was placed in ice cold water. From the top of the condenser an aliquot of DCM (1.00 mol) or DCE (0.60 mol) was added. After the reactants were uniformly mixed, the temperature of the water bath was gradually increased upto 75°C for the reaction with DCM and 90°C for that with DCE. After the reaction was over, the temperature was maintained constant for 1.5 hours. The reaction mixture was kept overnight at room temperature. It was placed in ice bath and hydrochloric acid (50%) was added to the reaction product which was then filtered. It was washed with distilled water till free of the acid. The resin was further purified by dissolving in alkali (10% NaOH) and precipitated with acid (50% HCl). The resin was filtered, washed with distilled water till free of acid, and then dried. The general reaction is shown in reaction scheme 1.

* To whom all correspondence should be addressed.

Table 1. Heat of fusion, molecular weight and limiting viscosity number of phenolic oligomers.

Oligomers	Heat of fusion (ΔH_f) cal/mg by DSC	Molecular weight			Limiting viscosity number	
		\bar{M}_n calculated	\bar{M}_n VPO	\bar{M}_n conductometry	dlg ⁻¹ in methyl- ethylketone at 35°C	dlg ⁻¹ in pyridine at 35°C
phenol-DCM	—	318	—	307	0.04	0.04
<i>p</i> -chlorophenol-DCM	10.81	843	802	786	—	0.08
2,4-dichlorophenol-DCM	0.80	352	383	332	—	0.06
<i>p</i> -cresol-DCM	2.67	360	399	397	0.05	0.08
α -naphthol-DCM	—	312	302	317	0.02	0.03
β -naphthol-DCM	—	312	369	343	0.03	0.04
phenol-DCE	—	360	342	399	0.02	0.07
<i>p</i> -chlorophenol-DCE	16.6	463	455	478	0.06	—
2,4-dichlorophenol-DCE	5.99	380	390	383	0.03	0.08
<i>p</i> -cresol-DCE	6.10	402	441	415	0.04	0.10
α -naphthol-DCE	—	342	—	361	—	0.04
β -naphthol-DCE	—	342	314	324	—	0.04



2.2 Characterization

The IR absorption spectra of phenolic oligomers dispersed in KBr and in the form of pellets were scanned in the range 650 to 5000 cm^{-1} . The number average molecular weight (\bar{M}_n) of the resin samples in methylethyl ketone (MEK) were determined using a vapour pressure osmometer. \bar{M}_n was also determined by conductometric titration

estimating -OH groups in a chain. The limiting viscosity number measurements were carried out in MEK and pyridine solvents using an Ubbelohde suspended level type viscometer. A thermal study was also carried out. The heat of fusion, ΔH_f , was determined using a differential scanning calorimeter.

3. Results and discussion

All the oligomers were in powdered form and of dark-brown or reddish-brown colour. Most of them were soluble in common organic solvents. The IR spectra of the oligomers showed absorption bands in the region ascribed to C-H stretching vibration due to $-\text{CH}_2-$ ($2825-3000\text{ cm}^{-1}$) and $-\text{CH}_2-\text{CH}_2-$ ($2875-2950$) bridges. The bands due to $-\text{CH}_2-\text{CH}_2-$ are strong or medium as compared to $-\text{CH}_2-$ bridge. The distinct absorption bands at $1438, 1460, 1440, 1430\text{ cm}^{-1}$ represent methylene bending and scissoring modes which offer clear evidence for the existence of $-\text{CH}_2-$ and $-\text{CH}_2-\text{CH}_2-$ groups in these resins. This is further evident by the bands appearing in the region $1285-1355\text{ cm}^{-1}$ due to methylene bending (wagging and twisting) modes. The rocking of methylene groups in the polymer chain is exhibited in the region $750-850\text{ cm}^{-1}$. Absorption around 1300 cm^{-1} and 1250 cm^{-1} can be assigned to -OH deformation and C-O stretching vibrations respectively (Kozyrava and Malayu 1968). The bands observed at $1065, 1073, 1070, 1100\text{ cm}^{-1}$ etc. are assigned to ortho and orthopara substitution (Richard and Thompson 1947). A broad band between $3400-3260\text{ cm}^{-1}$ can be assigned to polymerically associated -OH group of phenolic oligomers.

The number average molecular weight (\bar{M}_n) of the phenolic oligomers obtained by vpo (James *et al* 1968) and conductometric titration (Chetterjee 1969) helps in the estimation of the degree of polymerization (DP) which was obtained by dividing the total amount of base added at short interval to neutralize all the -OH groups in the chain (Chetterjee 1970). For instance DP for *p*-chlorophenol-1,2-dichloro-ethane oligomers would be $652/210 = 3.1$. The product of the average degree of polymerization and repeating formula weight gave the \bar{M}_n (3.1×154.5) = 479. The comparative study of vpo and conductometry data revealed (table 1) that \bar{M}_n of the oligomers determined by both the techniques for both DCM- and DCE-systems agree fairly well.

In general it is revealed that limiting viscosity number (η), of the oligomers increased with increasing molecular mass. It is noted that the limiting viscosity number of the same oligomer sample was higher in pyridine than those in MEK (table 1). This indicates that pyridine is a good solvent. Industrially, viscosity measurement is useful in controlling (Marshall 1953; Dienes 1949) the flow of the polymer melt in polymer processing.

The data revealed that the heat of fusion, ΔH_f of DCM-oligomer was lower than that of corresponding DCE-oligomer. It is concluded that the methylene bridge has lowering effect on ΔH_f than the corresponding ethylene-bridge in the oligomers. Predominant endothermic peak is also observed in some cases. In such cases oligomers are softened below 350°C .

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