Synthesis and characterization of cresol–benzaldehyde oligomers

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Cresol and benzaldehyde oligomers have been condensed in organic solvents with oxalic acid as catalyst. The influence of some reaction factors such as the mole ratio between initial monomers, reaction medium and duration of the polycondensation on the yield, softening temperature, content of free cresol and molecular weight characteristics of the cresol–benzaldehyde oligomers is described in the present paper. The products obtained were investigated by means of i.r. and n.m.r. spectroscopy. On the basis of the data obtained a mechanism for the interaction between cresol and benzaldehyde and a probable structure of the oligomers are proposed.

(**Keywords: polycondensation; 'Novolak' resins; cresol; benzaldehyde; phenolbenzaldehyde oligomers; properties; structure; i.r. spectroscopy; n.m.r. spectroscopy**)

INTRODUCTION

'Novolak' phenolformaldehyde oligomers are among the oldest synthetic polymeric products but nevertheless even now problems exist connected with their improvement. In order to improve the properties, many investigators[1–3] have suggested introducing either metal-containing groups, monomers with condensed aromatic rings or some other polymers. Information[4] as well as patent data[5] exist, related to the synthesis of cresol–benzaldehyde oligomers.

Our investigations aim to specify the influence of the basic conditions of the synthesis of cresol–benzaldehyde oligomers on their molecular weight distribution, structure and spectral characteristics.

EXPERIMENTAL

Materials

m-Cresol (Riedel de Haen) was purified by distilling prior to use. Benzaldehyde (Riedel de Haen), oxalic acid (Factory for Pure Reagents, Sofia, Vladaya), *o*-xylene (Fluka), methylisobutyl ketone (Fluka), ethyl acetate (POCH, Poland) and ethyl alcohol were used without further purification.

Methods

The polycondensation between *m*-cresol and benzaldehyde (BzA) was carried out in an organic solvent with oxalic acid as catalyst at a temperature below the boiling point of the solvent. Water was continuously taken from the reaction zone by azeotropic distillation with xylene, methyl isobutyl ketone or ethyl acetate. At the end of the polymerization the free monomers and the organic solvents were removed by vacuum distillation. The oligomer was separated from the obtained products by dissolution in ethanol and precipitation in water.

The weight average molecular weight ($\bar{M}_w$) and the polydispersity D, of the oligomers were determined by gel permeation chromatography on a 'Waters 244' apparatus with a WISP 710B automatic injector and a set of four ultra styragel columns with pore sizes 1000, 500, 100 and 100 Å, 'Waters R 401' differential refractometer and 'Waters M 440' u.v. detector. The analysis was carried out at 45°C. The eluent was tetrahydrofuran, the flow rate being 1.0 $cm^3 min^{-1}$. The molecular weight was calculated on the basis of polystyrene standards and the calibration curve was plotted using data from the u.v. detector. The free cresol (C) in the oligomer was determined photocolorimetrically[6] as well as by means of the 'bromide/bromate' method[7].

The softening temperature (T_s) was determined by means of the 'ball and ring' method[8].

The i.r. spectra of the cresol–benzaldehyde oligomers (CBzAO) were measured in KBr pellets and in $CHCl_3$ solution on a Specord M-80 i.r. spectrometer (Carl Zeiss, Jena, Germany). The n.m.r. spectra were recorded on a JNM PS 100 (JEOL) apparatus in a solution of hexadeutero acetone at room temperature. The peak shifts were measured relative to HMDSO. The condition of the field was external.

RESULTS AND DISCUSSION

Influence of reaction time

In order to produce higher molecular weight products, polycondensation of *m*-cresol with the less reactive

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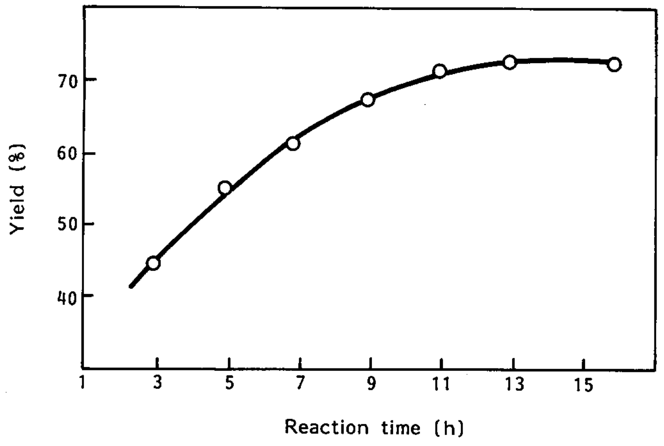


Figure 1 Dependence of the yield of CBzAO on reaction time (τ)

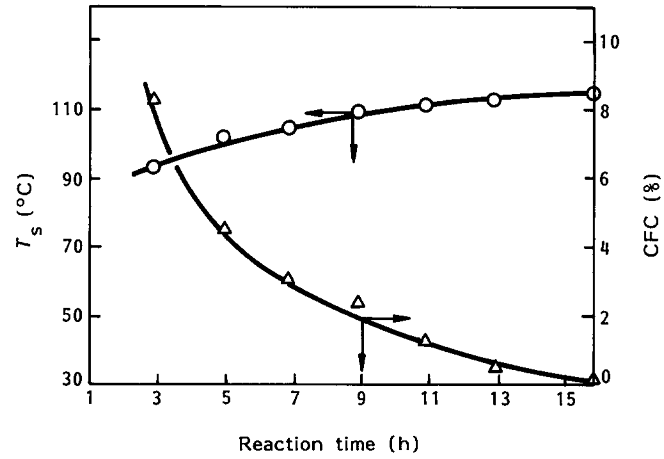


Figure 2 Dependence of the softening temperature (T_s) (○) and free cresol content (C) (△) in the cresol–benzaldehyde oligomers on reaction time

aromatic aldehydes was carried out at ratios close to equimolar[4]. In our experiments, the cresol/benzaldehyde ratio was 1 : 1, the reaction time (τ) from 3 to 16 h. Oxalic acid was used as the catalyst (0.22 mol mol^{-1} cresol).

The yield of CBzAO as a function of the reaction time is shown in *Figure 1*. It can be seen that the yield increases considerably up to 13 h and after that it remains practically unchanged. This is a result of the exponential conversion of the initial monomers to oligomeric products. The data in *Figure 2*, showing the dependence of the T_s values and the free cresol content in the oligomer products on the reaction time confirm this observation.

As expected, the content of free cresol in the oligomer decreases with the increase in reaction time and after 16 h it is only 0.1%. The softening temperature of the CBzAO is increased accordingly from 92°C after 3 h to 115°C after 16 h. A similar dependence has been observed for the system phenol–formaldehyde, by Knop and Scheib[9] and others[10].

The change of molecular weight and the polydispersity with the reaction time, given in *Figure 3*, is typical of the polycondensation process in the absence of exchange reactions. The weight average molecular weight ($\bar{M}_w$) and the polydispersity increase continuously with reaction time.

For the maximum reaction time of 16 h, the CBzAO obtained has an average degree of polycondensation of $n = 3$ and a softening temperature $T_s = 115$°C, while the cresol–formaldehyde oligomers (CFAO) have the same softening temperature[11] at $n = 12$. The higher T_s of CBzAO is due to the lower mobility of the bulky repeat units in the chain.

Influence of initial monomeric ratio

In order to establish the influence of the initial ratio of the monomers on the properties of CBzAO, BzA/C molar ratios from 0.8 to 1.2 were used. The reaction time was kept to 16 h, and catalyst concentration 0.22 mol mol^{-1} cresol.

Contrary to expectations, at monomer ratios close to the equimolar one, the yield and T_s of CBzAO decreased, see *Figure 4*. This can be attributed to the decrease of the catalyst concentration relative to that of benzaldehyde. A decrease of the weight average molecular weight and polydispersity with increase in the BzA/C ratio was also established, see *Figure 5*.

Influence of the reaction medium

The influence of four organic solvents with different polarity at constant concentration of 150 parts by volume per 100 parts by volume cresol was examined. The poly-

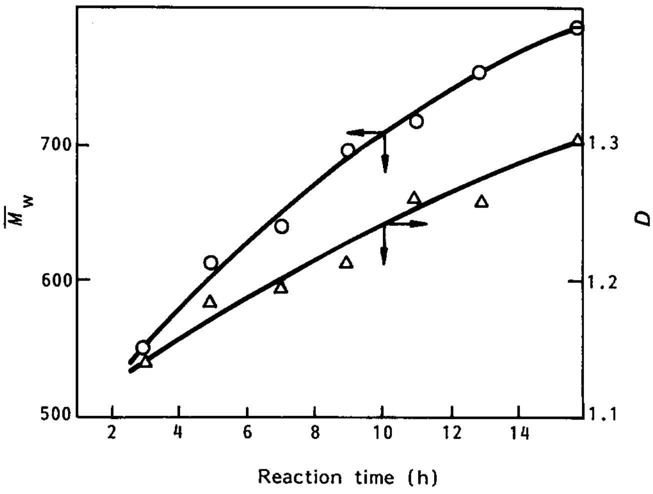


Figure 3 Dependence of the weight average molecular weights ($\bar{M}_w$) (○) and polydispersity (D) (△) of CBzAO on reaction time

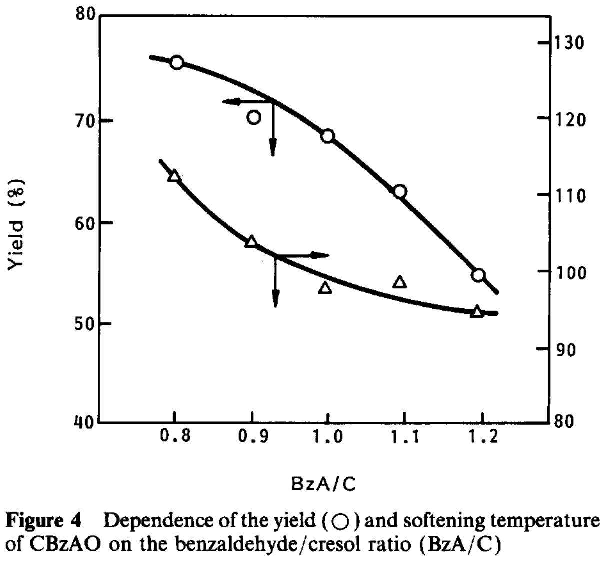


Figure 4 Dependence of the yield (○) and softening temperature (△) of CBzAO on the benzaldehyde/cresol ratio (BzA/C)

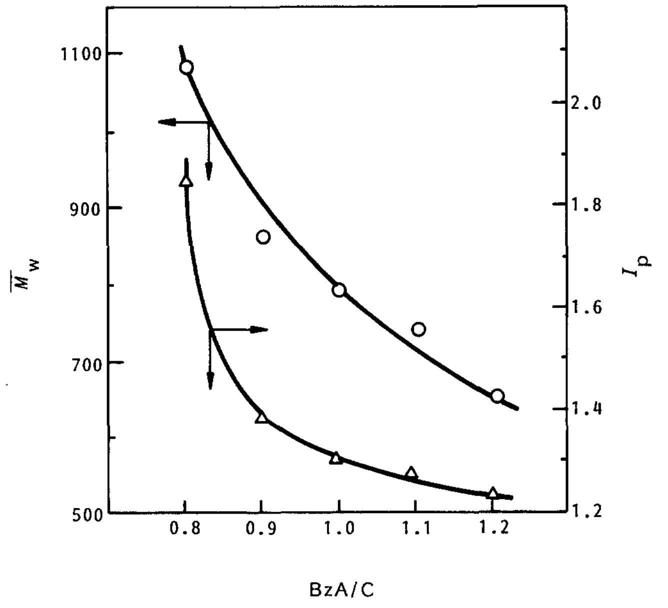


Figure 5 Dependence of the weight average molecular weight ($\bar{M}_w$) (○) and polydispersity (△) of CBzAO on benzaldehyde/cresol ratio (BzA/C)

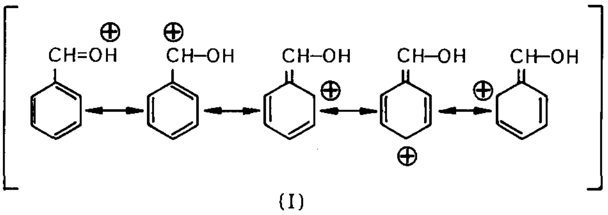
Table 1 Influence of solvent on the yield, softening temperature and molecular weight characteristics of cresol–benzaldehyde oligomers

Solvent	Yield (%)	T_s (°C)	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Ethyl acetate	47.7	83	640	1.24
Methyl isobutyl ketone	67.0	87	600	1.28
Dioxan	65.4	110	700	1.27
Xylene	74.6	114	1080	1.91

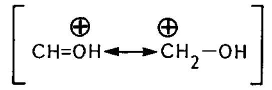
condensations were carried out at a BzA/C molar ratio of 1.0, concentration of the oxalic acid of 0.22 mol mol^{-1} cresol and reaction duration of 16 h. Data for the polymer produced is listed in *Table 1*.

Maximum yield of the polycondensation product is achieved using a non-polar solvent, attributed to the inactivation of the benzylol cation, and activation by solvation in polar solvent.

The lower activity of the benzylol cation (I) as compared to that of the methylol one (II) is due to the possibility of delocalization of the positive charge, according to structures (I) and (II).



(I)

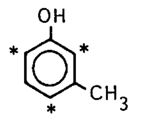


$$\left[CH{=}\overset{\oplus}{O}H \longleftrightarrow \overset{\oplus}{C}H_2{-}OH \right]$$

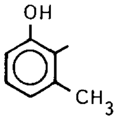
(II)

Structure and spectral characteristics of the cresol–benzaldehyde oligomer synthesized

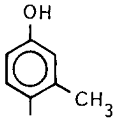
In order to explain the structure of CBzAO, it is important to determine the position of the CH bridges between the benzene rings. *m*-Cresol has three active positions, corresponding to the three protons in the molecule (III), marked with asterisks, for reaction with aldehydes. The presence of three reactive protons provides for the possibility of producing branched products[4]. From the g.p.c. chromatograms of the CBzAO it was established that the products were mixtures of seven homologues with a maximum degree of polymerization, $n = 6$ (*Figure 6*). In theory, the CBzAO contains five substituted cresol ring sites, four internal cresol rings and three end cresol rings. Three types of substitution are possible in the end aromatic rings (IV), (V), (VI).



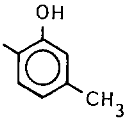
(III)



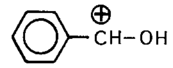
1,2,3-
(IV)



1,3,4-
(V)



1,3,6-
(VI)



(VII)

It is known that the polycondensation is carried out in the presence of the carbonium cation (VII). From steric considerations it can be supposed that the carbenium ion (VII) will attack and substitute a proton in the benzene ring either in the 4- or the 6-position (IV)–(VI), the 4-position being preferred since the electron density there is the highest.

The assumption made that the end benzene rings would have 1,3,4-substitution is confirmed by the i.r. spectra of CBzAO. Absorption bands in the range of the deformation vibrations, at 730, 810, 860 and 950 cm^{-1}, and such in the range of the overtone and combination frequencies characteristic of 1,3,4-substitution are observed (*Table 2* and *Figure 7*).

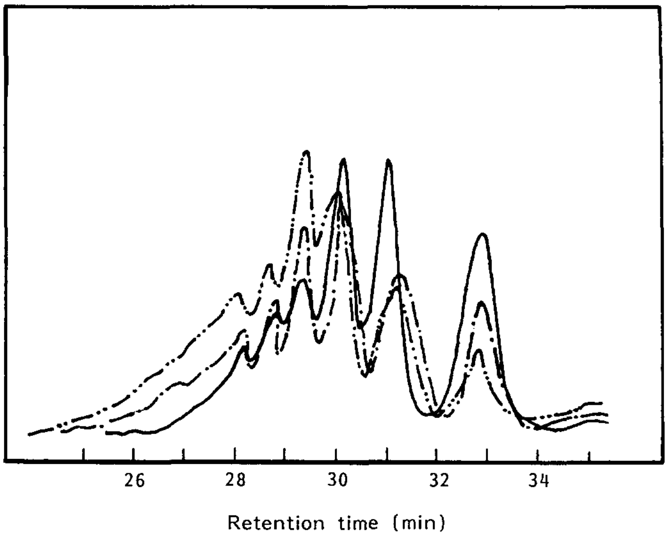


Figure 6 G.p.c. chromatograms of CBzAO with different molecular weights

Table 2 Ring substitution–i.r. absorption bands of CBzAO

1,2,3-substitution[12] ν (cm^{-1})		1,2,5-substitution[13] ν (cm^{-1})		1,3,4-substitution[13] ν (cm^{-1})	
a	b	a	b	a	b
1796	c	1740	c	1870–1880	Yes
1853	No	1840	No		
1917	c				

a—peaks required for the indicated type of substitution (cm^{-1})
b—presence or absence of the peaks in the spectrum
c—masking of the peak is possible

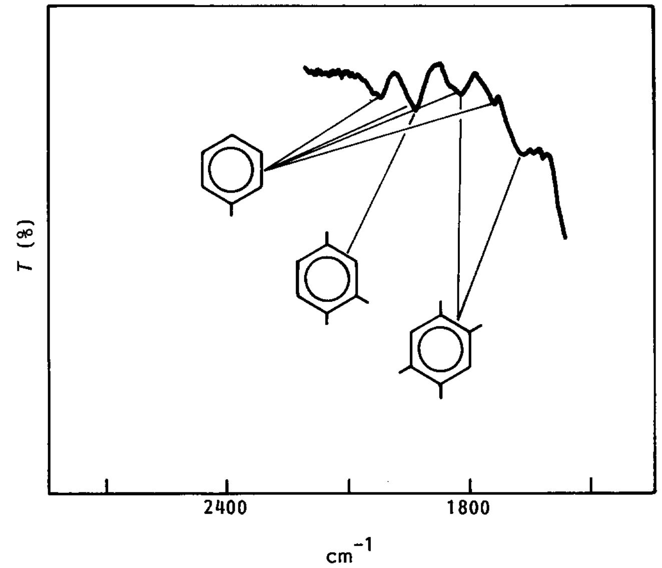
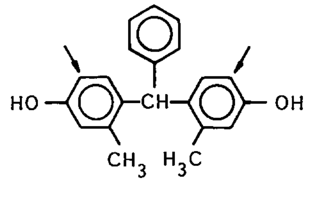


Figure 7 I.r. spectrum of CBzAO

Substitution of the end cresol rings only at the 4-position suggests that under the reaction conditions the first step of the growth of the CBzAO chain is the formation of a dimer with the structural formula (VIII).



(VIII)

The chain growth occurs as a result of the attack of the carbenium ion at the 6-6′-positions indicated (VIII). This results in products with a linear structure. The band at 860 cm^{-1} as well as those at 720 and 1805 cm^{-1} in the range of the overtone and combination frequencies suggest the presence of 1,3,4,6-substituted rings in the chain[14]. 1,2,3,4-substituted rings are either absent or their content is so small that the intensity of the absorption band at 1843 cm^{-1} is beyond the possibilities for registration by the apparatus (*Figure 7*).

The mono-substituted aromatic nucleus from the CH groups is registered in the i.r. spectrum of CBzAO with its characteristic absorption bands at 3020, 3055 and 3080 cm^{-1} (*Figure 8*) due to the vibrations of the valent CH aromatic bands as well as bands at 700 and 745 cm^{-1} caused by the deformation C–H vibrations. The absorption bands at 1955, 1871, 1825 and 1758 cm^{-1} characteristic of the mono-substituted aromatic ring in the range of the overtone and combination frequencies were recorded (*Figure 7*).

The symmetrical and asymmetrical vibrations of the methene CH-bonds produce absorption bands at 2860 and 2975 cm^{-1}, respectively, while the bands of the asymmetrical vibrations of the CH-bonds of methyl groups are at 2820 and 2955 cm^{-1} (*Figure 8*).

The shift of the peak of the OH groups to higher frequencies (3450 cm^{-1} compared with 3400 cm^{-1} for the hydroxy group of CFAO, *Figure 8*) can be explained by the appearance of the '*ortho*' effect. Obviously, the relatively bulky substituent in *o*-position to the hydroxy group hampers formation of hydrogen bonds. Absorption bands due to the unassociated groups are observed at 3590 cm^{-1} (*Figure 8*).

In the ^{1}H-n.m.r. spectra, the protons contained in CBzAO can be divided into four groups. The first group has methyl protons with a singlet at 2.02 ppm, and the second group methyne (CH) protons. The protons of $CH(C_6H_6)$ bonds give a complex multiplet in the range 5.60–6.00 ppm. The appearance of the peaks of these methyne protons in a relatively weak field is due to their higher descreening which is characteristic of methyne protons of compounds built up of or containing the so-called triphenyl methane structures[15]. The protons of OH groups give a peak in the range 7.40–8.10 ppm. The fourth group has aromatic protons. As mentioned

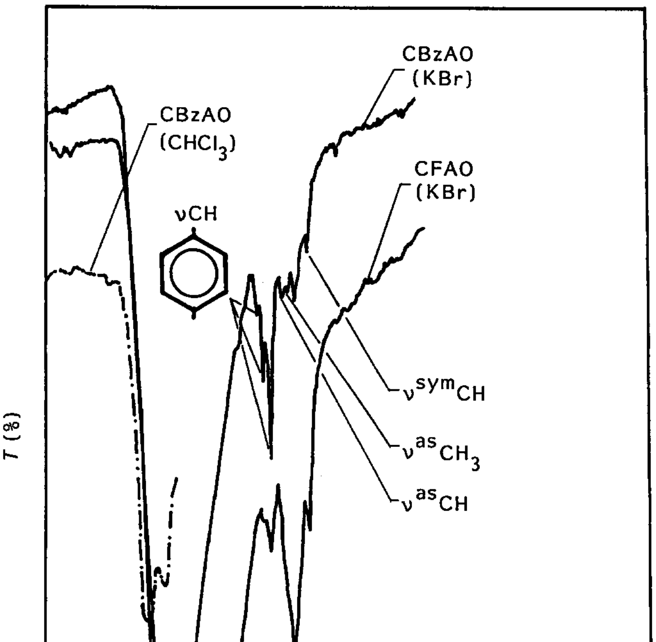


Figure 8 Absorption bands of $\nu_{O\text{-}H}$ and $\nu_{C\text{-}H}$ in the i.r.-spectra of CBzA and cresol–formaldehyde oligomers (CBzAO)

above, three types of aromatic rings differing in their degree of substitution are present in the chains of CBzAO. The signal of the protons of the mono-substituted aromatic rings is centred at 6.92 ppm. The protons from the end tri-substituted rings give a signal at 6.43 ppm, while the signal of the protons from 1,3,4,6-substituted rings is at 6.24 ppm.

CONCLUSIONS

The replacement of formaldehyde by benzaldehyde leads to the formation of polymeric products with higher softening temperatures.

Polycondensation in the presence of non-polar solvents results in more complete conversion of the initial monomers leading to oligomers with higher molecular weights.

The cresol–benzaldehyde oligomers synthesized are built up of benzene rings, connected with methyne groups in the 4- and 6-position.

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