

Organic Reactions Utilizing Cyclic Carbonate

I. Polymerization of monochloroethylenecarbonate with phenols

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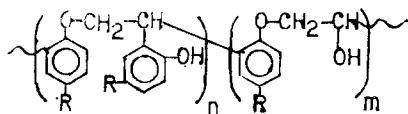
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Abstract □ The polymerization of title compound (MCEC, I) with phenols led to give corresponding resole type polymer. Phenol and p-methoxyphenol polymer had a relative higher molecular weight and a property of elastomer, but p-chloro- and p-nitrophenol polymer had a lower ones. Also, phenol and p-methoxyphenol gave to crosslinking polymer by elongation of reaction period and raising of temperature.

Keywords □ Resole type polymer, Number-average molecular weight, Resin, Crosslinked polymer, Re-precipitation, Elastomer, Aryloxyacetaldehyde.

Because of their important applications commercially, the reaction sequences and structures of resins when phenols react with formaldehyde have been studied extensively¹⁾. This title compound has been shown to give glycoaldehyde in the treatment of alkaline solution²⁾ and by heating alone to give chloroacetaldehyde³⁾. With 7-hydroxycoumarine, it was converted to psoralen and angelicin that are benzofuran analogs⁴⁾. This paper describes the polymerization of MCEC with phenols:



Resole type (1a-d)

The yield of polymer increased as following order; p-nitro-(pKa=7.15), p-chloro-(pKa=9.37), phenol (pKa=9.99) and p-methoxyphenol (pKa=10.21). It means that higher pKa phenols were more reactive than lower ones. In spite of 8.48 pKa value, o-chlorophenol did not react.

Title compound was readily polymerized itself in the presence of catalytical amounts of sulfuric acid. Only p-chlorophenol polymer had a melting range of 190-5°C and phenol polymer exhibited softening phenomenon at 240°C, the others did not melt until 350°C. Result of reactions was summarized in Table I.

Table I: Polymerization of MCEC with phenols.

run	R	temp (°C)	time (hrs)	yield (g)	Cl*	M _n
1a	H	170-5	2	8	no	7630
1b	p-OCH ₃	170-5	2	10.2	no	12070
1c	p-Cl	175-80	6	5.8	yes	755
1d	p-NO ₂	175-80	6	5	no	790
2a	H	180-5	2.5	9.7	no	
2b	p-OCH ₃	180-5	3	11	no	
3	o-Cl	175-80	6	20mg	yes	
4	@	170-5	15min	4	yes	

*Cl : chlorine was checked by Beilstein test.

M_n is number-average molecular weight.

@ : MCEC+H₂SO₄(0.2ml). run 2a, 2b and 4 were insoluble in DMF, DMS and others.

In order to find the anticipative phenoxyacetaldehyde intermediate and by-product, benzofuran, the benzene washing layer of 1a was checked by gc-mass analysis. None of them could be detected, but degradable products of MCEC were identified.

The structural assignment of these polymers was established on the basis of ir and pmr spectral data. IR spectra indicated that di- and trisubstituted aromatics occurred in the region between 740 and 940cm⁻¹ and hydrogen bonded hydro-

xyl appeared in the range of 3,000~3,400 cm^{-1} .

It agrees with the facts that signals corresponding to para and ortho methine appears as 4.1 and 4.6 ppm., respectively⁵⁾, and the ratio of phenolic hydroxyl resonance at 7.9 ppm. increases significantly. In 1b, the signal at 5

ppm is assigned to the ortho methine proton owing to an ortho orientation is possible uniquely. Oxymethylene and methoxy proton are in the same position. Judging from the ratio of signals listed in Table II, the presented sequences are considered to be correct.

Table II: The estimated sequences and pmr data of 1a and 1b.

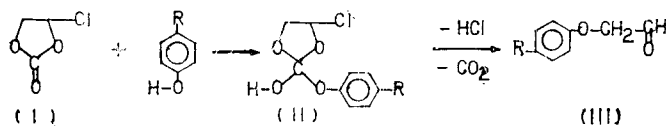
Sequence	signal	OCH ₂	p-CH	o-CH	C ₆ H ₄	OH
	ppm(d)	3	4.1	4.6	6.7	7.9
	intg.	18	4.5	4.5	53	18
	ratio	4	1	1	12	4(H ₂ O)
	proton	4	1	1	12	2
	signal	OCH ₂ & OCH ₃	o-CH	C ₆ H ₃	OH	
	ppm(d)	3.6	5	6.6	7.7	
	intg.	36	5	26	7.5	
	ratio	7.2	1	5.2	1.5(H ₂ O)	
	proton	29	4	21	4	

The intramolecular hydrogen bonding was confirmed by D₂O exchange technique, and the hydrogen bonding with external water was also verified by measurement of the decrement of the

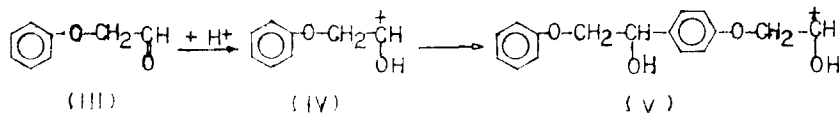
ratio at 7.9 ppm. in dried acetone; it was 0.4.

The plausible mechanism for the formation of these polymers was suggested:

1. Intermediated aryloxyacetaldehyde (III),

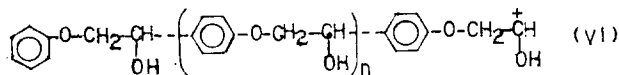


2. Initiation (in the case of 1a), (III) + (IV) \longrightarrow (V) o,p,

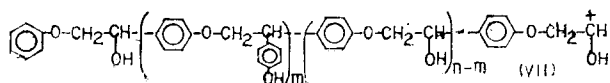


3. Propagation, alternating of addition and condensation.

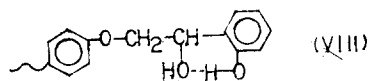
a, addition; (V) + n (III) \longrightarrow (VI) o,p,



b, condensation; (VI) + m phenol $\xrightarrow{+H^+}$ m H₂O + (VII) o,p,



4. Termination, (VII) + phenol \longrightarrow (VIII) o,p,



Scheme I: Mechanism of polymer formation.

This reaction would be resulted in the formation of aryloxyacetaldehyde(III), via a transitional state of the cyclic ortho-acetal (II) in the initial step. It suggests that o-chlorophenol do not react with MCEC because of the expecting rotational hindrance due to ortho chlorine.

Although benzofuran was expected to form through an intramolecular electrophilic attack of the hydroxymethine ion (IV) and followed by dehydration *in situ*, it was not so. Consequently, all the produced ion (IV) would be converted to the initial species (V) at once as shown in Scheme I.

The propagation process would be proceeded to form the polymer chain (VII) being balanced between addition and condensation according to their hydrogen bonding force and polar effect of phenols. 1a consisted of the same number of condensated and noncondensated sequences, and

much more condensated sequences were contained in 1b. But 1c and 1d had a very short chain.

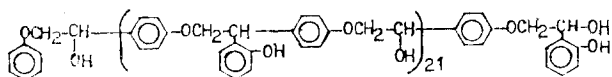
It seems that so the grown polymer chain (VII) was terminated by the formation of a cyclic six-membered hydrogen bond with phenol.

The crosslinked polymer arising from intermolecular coupling of (VII) randomly⁶⁾ will be reported in next opportunity.

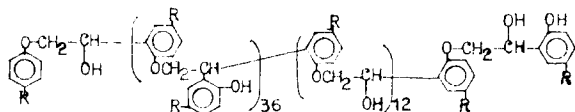
The number-averaged structures of these polymers (1a-d) being assumed from sequences and mechanism of polymer formation were presented in Scheme II.

It was conclusively demonstrated that 1) these new polymers would be formed through an aryloxyacetaldehyde intermediate. 2) in comparison with resole resins⁷⁾, these had a higher molecular weight and melting range. 3) also had a regularity of the ratio of addition versus condensation.

1. Phenol polymer(1a) mol. wt., cal; 7674 obs; 7630

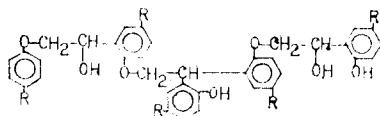


2. p-Methoxyphenol polymer (1b, R=OCH₃) cal; 12240 obs; 12070



3. p-Chlorophenol polymer (1c, R=Cl) cal; 756.5 obs; 755

4. p-Nitrophenol polymer (1d, R=NO₂) cal; 803 obs; 790



Scheme II: The number-averaged structures of polymers.

EXPERIMENTAL METHODS

The ir spectra was determined in KBr disk on a Perkin-Elmer Model 281B. The pmr spectral determinations performed by using of a Varian FT 80A. And determinations of spectra with Hewlett-Packard HP 5985B gc-mass instrument was performed by Mr. Jeoung-il Park, National Products Reseach Institute. Melting range of polymers were determined on a Reichert Thermovar Kofler. The number-average molecular weight determination was performed by using of a Knauer Vapor Pressure Osmometer with benzophenone as a reference material.

Ethylenecarbonate and phenols were commercially purchased.

General method of polymerization.

This reaction will serve as an example for the polymerization of all the phenols listed in Table I, since each of these polymers was prepared in the same manner as phenol.

A solution of 9.4g (0.1mol) of phenol and 12.25g (0.1mol) of MCEC⁸⁾ was allowed to heat for 2 hours *in vacuo* with an aspirator until the reaction mixture became to be viscous. The reaction mass was reprecipitated with acetone-benzene solvent system to remove unreacted materials. And the well dried sample which was dried *in vacuo* and on irradiation with ir lamp was offered to determine physical properties and instrumental analysis.

phenol polymer: yield; 8g., ir; 3400(hydroxyl), 1600(aromatic) and 1250 cm^{-1} ($-\text{OCH}_2-$), pmr(in acetone- D_6); described in the discussion part., mol. wt.(in acetone); 7630.

p-methoxyphenol polymer: yield; 10.2g., ir; 3400(hydroxyl), 1600(aromatic) and 1200 cm^{-1} (methoxy and $-\text{OCH}_2-$), pmr(in acetone- D_6); same as above., reprecipitation; acetone-benzene

system., mol. wt. (in acetone); 12070.

p-chlorophenol polymer; yield; 5.8g., ir; 3350 (hydroxyl), 1600(aromatic) and 1240 cm^{-1} ($-\text{OCH}_2-$), pmr(in acetone- D_6); d. 8.7(4H, $-\text{OH}$), 7.2(16H, aromatic), 4.75(3H, ortho-methine) and 3(6H, $-\text{OCH}_2-$), reprecipitation: acetone-cyclohexane system., mol. wt. (in acetone); 755.

p-nitrophenol polymer: yield; 5g., ir; 3050 (hydroxyl), 1600(aromatic) and 1230 cm^{-1} ($-\text{OCH}_2-$), pmr(in DMSO- D_6); d. 8.0(4H, $-\text{OH}$), 6.7(16H, aromatic) 4.5(3H, ortho-methine) and 3.3(6H, $-\text{OCH}_2-$), reprecipitation; DMF-acetone system., mol. wt. (in DMSO); 790.

Preparation of crosslinked polymer (2a and b).

A solution of 0.1 mole of MCEC and phenol was heated to solidify the reaction mixture under the listed condition. The solid mass refluxed with 100ml acetone to remove la and unreacted monomers. After filtering, the residue was reprecipitated with DMSO-acetone system, and dried as above la.

GC-Mass analysis of the benzene washing layer.

The six fractions being detected were as follows: a-hydroxy-b-chloropropanal ($\text{ClCH}_2-\text{CH}(\text{OH})-\text{CHO}$), chloropyruvic acid ($\text{ClCH}_2-\text{CO}-\text{COOH}$), a-chloro-a'-hydroxyacetone ($\text{ClCH}_2-\text{CO}-\text{CH}_2\text{OH}$), chloroformylepoxyde ($\text{C}_6\text{H}_4-\text{OCOC}_2\text{H}_4$), phenol and MCEC.

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