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Catalysis by Heteropolyacid. I. Polymerization Reaction of Benzyl Alcohols

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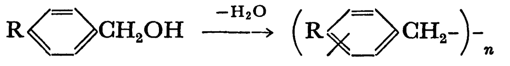
Synopsis. Benzyl alcohol and its derivatives catalyzed by heteropolymolybdic acids such as $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ have been found to polymerize, leading to the formation of polyaromatics. The properties of the polymers obtained and the function of catalysts have been studied.

Heteropolyacid has high oxidation activity and strong acidic property.[1] From its structure it can be regarded as a polynuclear metal complex and also as a molecular model for solid catalyst.[2] Recently we found a new type of polymerization reaction of benzyl alcohol and its derivatives catalyzed by 12-heteropolymolybdic acids leading to aromatic polymers. The typical stoichiometry is as follows.



Heteropolyacids, $H_4SiM_{12}O_{40}$ and $H_3PM_{12}O_{40}$ (M= Mo, W), were examined as catalyst. These catalysts promote the reaction, but neither the tetraalkylammonium salts of their acids nor the mononuclear acids (H_2MoO_4 and H_2WO_4) show catalytic activity. In this paper the Mo system is discussed.

In all catalytic reactions, the catalyst undergoes the color change yellow→green→blue, corresponding to the various reduced states of molybdenum ions.[3] However, the reduction of catalyst, as indicated by the color change, would not be substantial in the coupling reaction since initial activity of catalyst, selectivity and yields of products were not influenced by the addition of an excess amount of reactants to the reduced blue acid obtained. Since the tetrabutylammonium salts of both the unreduced yellow anion and the reduced blue anion provide no catalytic activity, remarkably strong acidity of catalyst would be important. The reduction mechanism from yellow to blue has not been clarified as yet.

Characteristics of the reaction are as follows: (a) The amorphous polymer obtained has a low molecular weight. (b) No solvent is employed. (c) The reaction is carried out by merely passing a gas (oxygen, nitrogen *etc.*) through a benzyl alcohol solution of heteropolyacids at ambient temperature. (d) The reaction does not proceed in a sealed tube. (e) The temperature of the reaction depends on the flow rate of a passing gas, *e.g.*, under atmospheric oxygen the temperature is 195 °C, whereas with increase in flow rate it is lowered to 110 °C. (f) The reaction time for obtaining the polymer in 100% yield is a few minutes. (g) The catalyst is very stable, not being decomposed during the course of polymerization.

In (c) the role of the passing gas may be only to remove the water produced and keep the reaction mixture anhydrous; oxygen and inert gas fulfill this purpose. The refluxing of benzyl alcohol in the presence of a solvent such as benzene, toluene, or anisole also gives the same polybenzyl as that obtained in a solvent-free system. However, the yield is lowered because of the simultaneously promoted side-reaction such as alkylation and condensation-etherization.

In a typical experiment, 12.4 ml of benzyl alcohol (0.12 mol) and 73.0 mg of $H_4SiMo_{12}O_{40}$ (0.4 mmol) were added to a 100 ml wide-mounted Erlenmeryer flask equipped with a gas inlet tube and a thermometer on a hot-plate at 110 °C. The gas was passed (150 ml/min) through the vigorously stirred solution. The color of the reaction mixture changed from yellow to green, and finally to blue. While the reaction mixture turned green, it began to bubble slightly, the bubbling becoming drastic as soon as the color turned blue. Within a few seconds the vigorous bubbling ceased, the system becoming highly viscous. With fall of temperature the mixture began to solidify. On cooling, a resinous and brittle substance was obtained. It was found that the reduced blue catalyst is homogeneously dissolved in the system, above 40 °C, the polymer becoming stringy. The resionoid is soluble in chloroform and the catalyst contained can be readily removed by shaking the chloroform solution with water. The pure polymer was isolated by dissolving the reaction mixture in 50 ml DMF containing LiCl (1%) and adding the solution dropwise to 150 ml methanol. The precipitate was purified by reprecipitation. The almost colorless polymer obtained was dried *in vacuo* for *ca.* 30 h. The yield was 9.7 g (75%) of pure polymer having intrinsic viscosity $[\eta]=0.19$ dl/g (in *N,N*-dimethylacetamide containing 1% LiCl at 25 °C). Thermogravimetric analysis shows that the polymer is thermally stable up to 525 °C; in air it begins to lose weight at 375 °C.

The derivatives of benzyl alcohol as monomer reactant; 4-chlorobenzyl alcohol, 4-methylbenzyl alcohol, and 2,4,6-trimethylbenzyl alcohol gave the corresponding polyaromatics. However, no corresponding polymers were obtained from triphenylmethanol and 1- and 2-phenylethanols.

The IR spectra of polymers obtained show the disappearance of the original alcoholic OH group. ^{1}H-NMR intensities of benzene moieties, methyl substituents and benzyl methylenes in the polymers indicate that the polycondensation takes place on the elimination of one H of the benzene moiety of one reactant and one OH group of another reactant. Thus the highly branched species are not dominant. Analytical data, intrinsic viscosities, melting points and decomposition temperatures of the polymers are given in Table 1 and ^{1}H-NMR data in Table 2. Viscosities and melting points indicate that the polymers have low molecular

Table 1. Analytical data, intrinsic viscosities, melting points, and decomposition temperatures of polymers

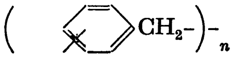
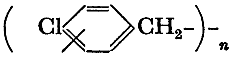
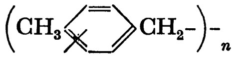
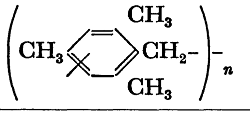
Reactant	Polymer				Elemental analyses (%) C	H	Cl	[η] dl/g	Mp °C	Dec temp °C
Benzyl alcohol		**1**	C_7H_6	Calcd	93.33	6.67		0.194	51—81	525
				Found	93.21	6.65				
4-Chlorobenzyl alcohol		**2**	C_7H_5Cl	Calcd	67.47	4.02	28.51	0.055	86—119	478
				Found	67.61	4.05	28.51			
4-Methylbenzyl alcohol		**3**	C_8H_8	Calcd	92.31	7.69		0.079	84—114	512
				Found	91.45	7.59				
2,4,6-Trimethylbenzyl alcohol		**4**	$C_{10}H_{12}$	Calcd	90.91	9.09		0.100	152—189	537
				Found	90.48	9.13				

Table 2. ^{1}H-NMR data for the polymers

Polymer	Chemical shift ppm from TMS Phenyl	Methylene	Methyl	Observed intensity ratio
1	7.02	3.81		4 : 2
2	7.07 6.90	3.90		3 : 2
3	6.83	3.75	2.25 2.12	3 : 2 : 3
4	6.68	3.93	2.19 1.99 1.80	1 : 2 : 9

weight.

The electronic and MCD spectra in the 240—300 nm region of the polymer were measured in comparison with those of the corresponding monomer. The characteristic vibronic structure of the monomer is largely diminished, the whole spectral shape broadening. The maximum absorption of polymer shifted to the longer wavelength region by *ca.* 10 nm. This is also the case in the MCD spectra. In both the polymer and its monomer, the sign of MCD is negative, except in the case of poly(2,4,6-trimethyl-1,3-phenylenemethylene) and 2,4,6-trimethylbenzyl alcohol, in which the positive MCD of monomer turns to the negative MCD of polymer.

In the first run of the experiment, the reduced blue compound, converted from the initial yellow catalyst, is isolated as a tetraethylammonium salt having the formula $[Et_4N]_4[SiMo_{12}O_{40}H_n]$ (n=2—4). This was determined on the basis of the observed value of elemental analysis; C, 16.43; H, 3.30; N, 2.32%.

During the course of the reaction, no evidence was obtained of the direct coordination of arene ring of reactant to the molybdenum ion in the blue catalyst. The type of polymerization might be a carbonium ion mechanism brought about by the remarkably strong Brønsted acidity of catalyst.

The heteropolyacids also give the same polybenzyl from benzyl chloride by dehydrohalogenation as that obtained from benzyl alcohol in relatively high yields. Thus the acids appear to possess an analogous function to that of $Mo(CO)_6$ and arene–$Mo(CO)_3$ as "Friedel-Crafts" like catalyst.[4,5] However, particular advantages of the reduced blue heteropolyacid over $Mo(CO)_6$ and $ArMo(CO)_3$ have been observed in the undiminished activity for repeated use of the same catalyst with no decomposition. This remarkable stability of the reduced acid would be related to the fact that it does not dissociate into sexivalent molybdenum as in the case of unreduced form of the complex because of its resonant state in the molecule as a whole making each molybdenum have a mean valency less than +6.[3]

In this reaction, the heteroatoms Si and P of heteropolymolybdic acids would play no direct important role; rather they would contribute to the maintenance of Keggin-structure of catalyst and the complete valency saturation leading to the strong Brønsted acidity.

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