Polymers from Benzaldehyde. A Copolymer with Dihydropyran and the Cyclic Trimer

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ABSTRACT: A copolymer of benzaldehyde and dihydropyran was prepared by low-temperature cationic polymerization. The cyclic trimer of benzaldehyde was obtained by the catalytic dehydrogenation of the corresponding oligomer of tetrahydrobenzaldehyde.

The addition polymerization of aliphatic aldehydes has been investigated extensively in recent years, while very little has been reported on the corresponding chemistry of aromatic aldehydes. The only such polymers described in the literature are the copolymers of benzaldehyde with ketenes[1] and styrene,[2] while no homopolymer or oligomer of an aromatic aldehyde is known. It has also not yet been determined whether the polymerization of benzaldehyde, for instance, is impossible for thermodynamic reasons or due to the lack of a suitable reaction. The effect of structure on the ceiling temperature of polymerizable aldehydes and related olefins leaves no doubt that this critical temperature will be quite low for the homopolymerization of benzaldehyde. It has been pointed out, however, that the introduction of a second monomer increases the ceiling temperature of the polymerization,[3] and we might therefore expect to be able to prepare copolymers of benzaldehyde even if the homopolymer itself remains unattainable. This paper describes one such copolymer, with dihydropyran, and the preparation of the cyclic trimer of benzaldehyde by an indirect route.

Results and Discussion

Copolymerization. In contrast to aliphatic aldehydes, benzaldehyde shows no tendency to cyclize or polymerize at low temperatures in the presence of an acid catalyst. The monomeric aldehyde can be recovered unchanged from a 30% toluene solution after 24 hr at −78° in contact with boron trifluoride etherate. The other monomer of this study, dihydropyran, has been reported repeatedly to form methanol-soluble low molecular weight polymers with cationic initiators.[4] Thus, Kamio, *et al.*, report the polymerization with Lewis acids at temperatures between −30 and +20° in a variety of solvents to give polymers with a maximum η_{sp}/c of 0.01 (*c* is 10 g/l.). Tamura, *et al.*, prepared a polymer in methylene chloride at −78° with boron trifluoride etherate as catalyst and obtained a product with an average degree of polymerization between 3 and 15. Finally, Sarkio and Nyman obtained a methanol-soluble polymer with a degree of polymerization of 20 by polymerizing dihydropyran in a mixture of methylene chloride and heptane at −25°, using a triethylaluminum–titanium tetrachloride catalyst. We found that no methanol-insoluble polymer is formed when a 30% solution of dihydropyran in toluene is left in contact with 2 mol % boron trifluoride etherate at −78° for 24 hr.

In combination these two monomers are much more reactive. When an equimolar mixture of benzaldehyde and dihydropyran in toluene solution, cooled by a Dry Ice–acetone bath, is treated with a Lewis acid, such as boron trifluoride etherate, the viscosity of the solution increases rapidly and a methanol-insoluble polymer is formed instantly. By terminating the reaction with a small amount of pyridine and isolating the polymer by precipitation in methanol, the time–conversion plot of Figure 1 was obtained. The reaction in about 30% solution is shown to be quite rapid and the molecular weight to be increasing slightly with the conversion. At higher concentrations the reaction becomes too vigorous and the heat of the reaction leads to charred products. It is also possible to carry out the polymerization in excess dihydropyran as the solvent, but in this case the concentration of the benzaldehyde must not exceed 10% to prevent the reaction from running away.

The nmr analysis (60 Mc) of a polymer sample isolated after 1 hr reaction time (η_{sp}/c 0.19) showed a distinct region of aromatic hydrogens, but only un-

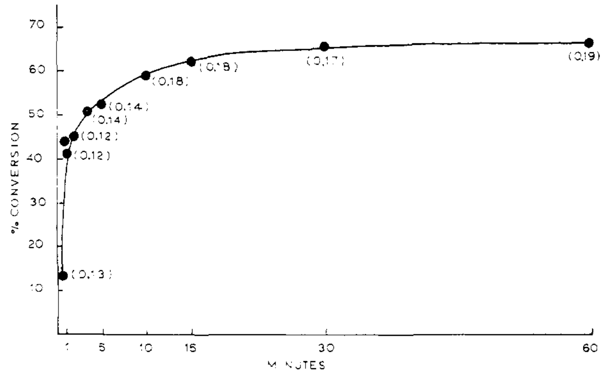

Figure 1. Rate of copolymer formation: charge, 10.6 g of benzaldehyde, 8.4 g of dihydropyran, 40 ml of toluene, 0.5 ml (2 mol %) of boron trifluoride etherate. Numbers in parentheses are reduced specific viscosities (deciliters per gram) measured at 25° in chloroform (concentration, 2 g/l.).

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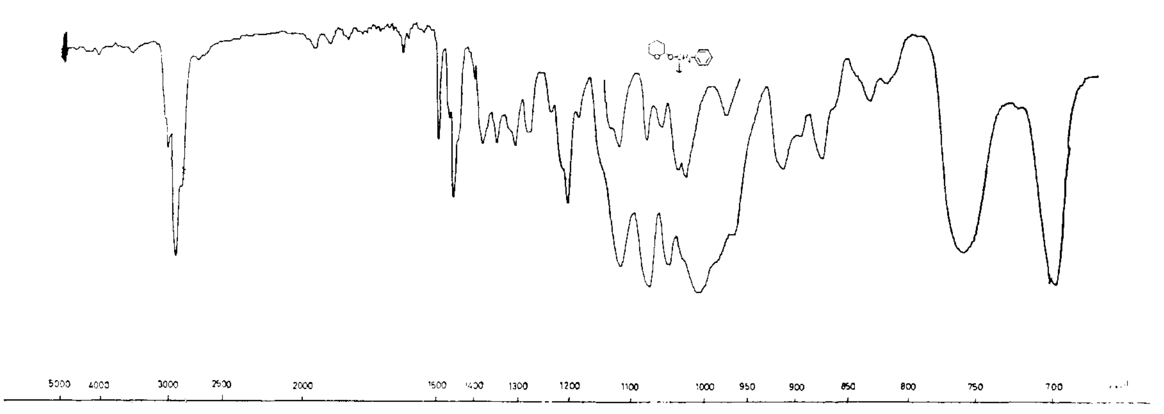


Figure 2. Infrared spectrum of copolymer.

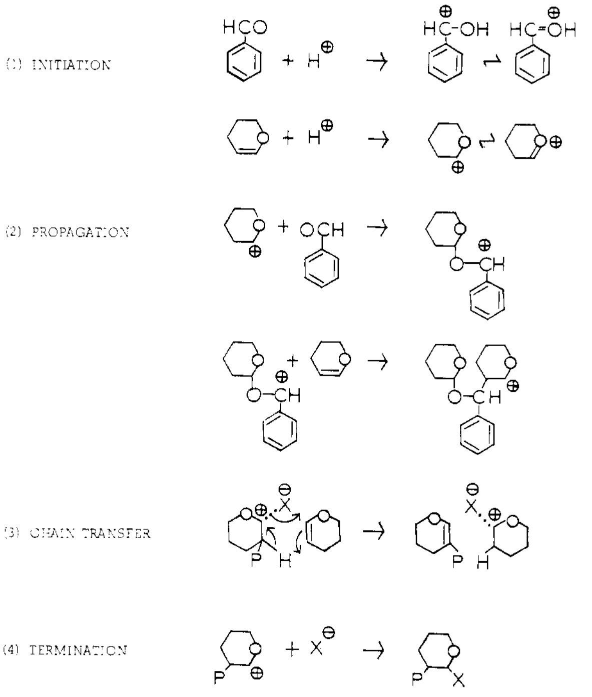


Figure 3. Copolymerization reactions.

resolved broad signals for the aliphatic hydrogens. Although no structural features could be deduced from the spectrum, it was possible to calculate the composition from the ratio of aromatic to aliphatic hydrogens. This ratio was found to be 5:9, corresponding to a 1:1 copolymer.

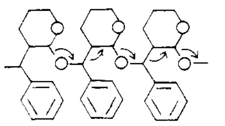
The elemental analysis of a sample isolated during the early stages of the reaction (1 min, η_{sp}/c 0.13) indicated a preponderance of dihydropyran in the product: C, 74.85; H, 7.60; O, 17.18 (calcd for 60% dihydropyran and 40% benzaldehyde: C, 75.00; H, 7.76; O, 17.24). The same composition was found in a sample that had been prepared in excess dihydropyran (3 hr, η_{sp}/c 0.17): C, 74.66; H, 7.88; O, 17.33.

The infrared spectrum of a copolymer film is shown in Figure 2. It has the characteristic absorptions of the benzene ring at 3000, 1600, 1580, 1490, 1450, 760, and 698 cm^{-1}. The presence of a 2-alkoxytetrahydropyran configuration in the polymer is indicated[5] by the absorptions at 962, 910, 872 and 817 cm^{-1}. In addition, the absorption pattern found between 1000 and 1200 cm^{-1} is regarded as characteristic of acetals.[6] The corresponding portion of the spectrum of an authentic sample of 2-benzyloxytetrahydropyran[7] is superimposed on the polymer spectrum in Figure 2 to demonstrate the similarity. A weak band appears at 1243 cm^{-1}, denoting some vinyl ether unsaturation in the polymer, probably in the form of dihydropyran end groups derived from the chain transfer reaction to monomer.

The polymer appears, therefore, to be largely a polytetrahydropyranyl ether as formed by the polymerization reactions 1–4 shown in Figure 3.

Initiation (reaction 1) can conceivably occur on either benzaldehyde or dihydropyran. A third propagation reaction, the addition of dihydropyran to pyranyl cation, is not shown but must also occur to some extent, as shown by the analytical results. The chain transfer to monomer (reaction 3) and the termination through recombination with the counterion (reaction 4) are well-documented cationic polymerization reactions.

Additional evidence for the proposed polymer structure was obtained from mass spectrometry. A sample of the polymer was pyrolyzed at 270° in the direct insertion probe of a Varian M-66 cycloidal mass spectrometer and the spectrum of the pyrolyzate recorded (Figure 4). The spectrum shows that a large portion of the polymer depolymerizes back to the monomers, presumably by an unzipping mechanism such as reaction 5. Consequently, the mass spectrum contains the molecular ion peaks of benzaldehyde (m/e 106) and dihydropyran (m/e 84) plus their established patterns of fragment ions. Thus the peaks at m/e 105, 77 and 51 can be assigned to benzaldehyde[8] while the strong peaks at 56, 55 and 28 are recognizable



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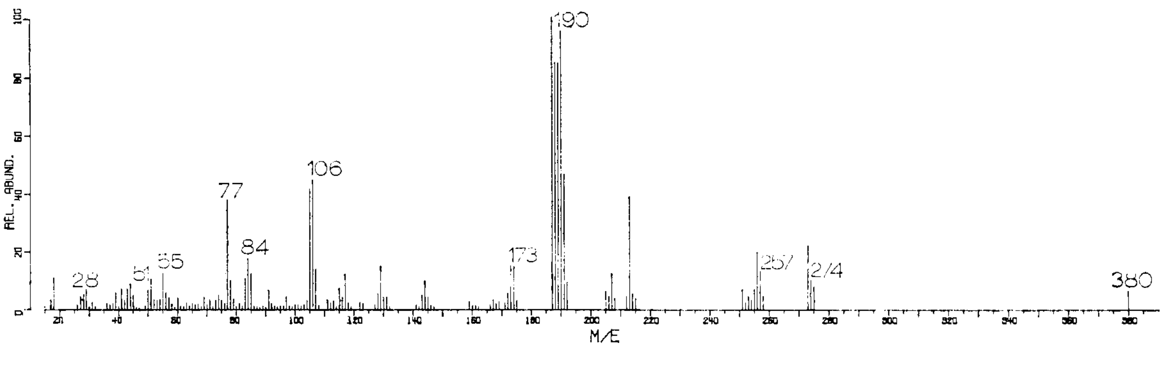
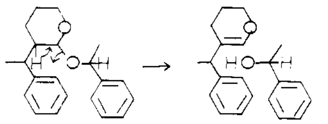


Figure 4. Mass spectrum of copolymer pyrolyzate.

dihydropyran fragments.[9] In addition to this depolymerization, the pyrolytic elimination reaction of acetals by E*i* mechanism is also operative, as illustrated in reaction 6. This reaction leads to a variety of products, some of which are identifiable as molecular ions in the mass spectrum.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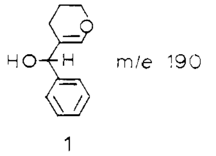
There is a series of intense peaks between *m/e* 187 and 190 which we assign to dimer 1 and its fragment



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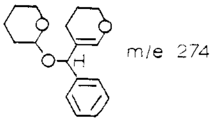
ions. As has been shown for benzyl alcohol,[10] the loss of the hydroxyl group leads to the formation of an M − 17 ion. In our case, loss of the hydroxyl group gave *m/e* 173. The pyrolytic fragment composed of one benzaldehyde and two dihydropyran units, either



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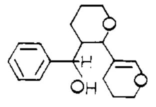

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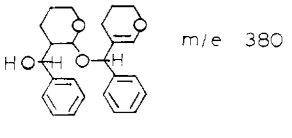
2 or 3, also shows up in the mass spectrum as molecular ion and as the fragments M − 1 and M − 17. Finally, a peak of low intensity appears at *m/e* 380 which can be assigned to a tetrametric molecule of structure 4.



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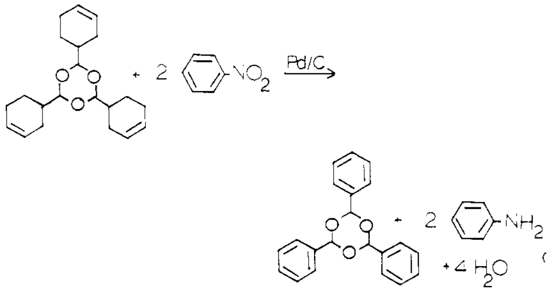
For comparison the mass spectrum of poly(dihydropyran), pyrolized under identical conditions, was recorded. The polymer was prepared by bulk polymerization with 1 mol % boron trifluoride etherate as catalyst. After 4 days at −78° a 7% yield of methanol insoluble polymer with a reduced specific viscosity of 0.08 dl/g (*c* = 2 g/l.) was obtained. In addition to numerous low molecular weight fragments, the spectrum showed peaks at *m/e* 168, 252, 336, and 420, clearly attributable to molecular ions containing two, three, four and five dihydropyran units. Since none of these show up in the mass spectrum of the copolymer, it follows that it does not contain an appreciable amount of long dihydropyran segments in its chains.

The copolymer is amorphous and, in accordance with the proposed structure, easily hydrolyzed. However, the low molecular weight oily hydrolysis product has so far resisted all attempts at fractionation into pure products.

Benzaldehyde Trimer. All our attempts to prepare a trimer or a polymer from benzaldehyde alone were unsuccessful. Since tetrahydrobenzaldehyde can easily be trimerized or polymerized it offers the possibility of obtaining benzaldehyde polymers indirectly by dehydrogenation. The cyclic trimer of tetrahydrobenzaldehyde was prepared in methylene chloride at Dry Ice temperature with boron trifluoride etherate[11] and dehydrogenated by hydrogen exchange[12] according to reaction 7.



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The formation of a larger than stoichiometric amount of water indicated the occurrence of a side reaction. The product was identified as the cyclic trimer of benzaldehyde by elemental analysis, molecular weight determination, infrared spectrum, nmr analysis and by hydrolysis to benzaldehyde.

Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.20; H, 5.70; mol wt, 318.36. Found: C, 79.09; H, 5.76; mol wt, 321.

In the infrared spectrum the C=C stretching vibration of tetrahydrobenzaldehyde (1652 cm^{-1}) has dis-

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(10) Reference 8, p 119.

(11) A. Chayanov, *Zh. Obshch. Khim.*, **8**, 460 (1938); *Chem. Abstr.*, **32**, 79056 (1938).

(12) E. A. Braude, R. P. Linstead, and K. R. H. Wooldridge, *J. Chem. Soc.*, 3586 (1954).

appeared and is replaced by four aromatic bands (1600 and 1540 cm^{-1} weak, 1490 and 1450 cm^{-1} strong). The four strong acetal bands of tetrahydrobenzaldehyde trimer at 1145, 1100, 1070 and 1040 cm^{-1} have shifted in the benzaldehyde trimer to 1130. 1080, 1025, and 1000 cm^{-1}. In addition, the benzaldehyde trimer has four strong absorptions between 765 and 685 cm^{-1}, characteristic of aromatic compounds. The nmr spectrum shows a multiple signal at τ 2.5 for the aromatic hydrogens and a single peak at τ 3.7 for the heterocyclic hydrogen, in the expected ratio of 5:1. Heating a sample of the compound in alcohol with a trace of hydrochloric acid, in the presence of 2,4-dinitrophenylhydrazine, gave a hydrazone which was identical with an authentic sample of the benzaldehyde derivative.

A large amount of low-melting solid can be isolated as dehydrogenation by-product from the mother liquor of the benzaldehyde trimer. The infrared spectrum, nmr analysis and comparison with an authentic sample identify this compound as N-benzylidineaniline. It is formed either by direct attack of aniline on cyclic trimer or by depolymerization to benzaldehyde followed by condensation with aniline. This reaction is responsible for the excess water formed during the dehydrogenation.

An attempt was also made to dehydrogenate poly(tetrahydrobenzaldehyde) to poly(benzaldehyde), using the method of hydrogen exchange to nitrobenzene. The starting polymer was prepared in toluene at −110° with boron trifluoride etherate as catalyst. The product obtained under these conditions contains about 30% polymer which can be separated from the trimer by preferential precipitation from chloroform with acetone. A sample of this polymer was recovered unchanged after 12 hr in refluxing toluene, in the presence of nitrobenzene and palladium catalyst. We assume that the macromolecules cannot adopt the right configuration on the catalyst surface to allow the hydrogen exchange to take place.

The benzaldehyde trimer was found to depolymerize rapidly above its melting point, even in the absence of a catalyst. This inherent instability of the benzal acetal group is likely to be even greater in a linear polymer. It is therefore safe to conclude that poly(benzaldehyde), if it can be prepared, will be thermally very unstable.

Experimental Section

1. Polymerization. Benzaldehyde was purified by distillation, dihydropyran and toluene by distillation followed by passage through Linde 4A Molecular Sieves. The polymerizations were carried out in erlenmeyer flasks, sealed with serum stoppers and magnetically stirred. The catalyst, freshly distilled boron trifluoride etherate, was introduced with a hypodermic syringe. The reaction was quenched with sufficient pyridine to neutralize the catalyst and the polymer precipitated with methanol.

2. Dehydrogenation. A solution of 58.75 g (0.178 mol) of tetrahydrobenzaldehyde trimer and 65.8 g (0.535 mol) of nitrobenzene in 300 ml of toluene, containing 5 g of palladium on charcoal (10%), was refluxed in a round-bottomed flask equipped with a Dean–Stark trap and a reflux condenser. After 15 ml of water had been collected (8 hr) the reaction was stopped, the solution filtered hot and the toluene removed under vacuum. Methanol (50 ml) was added, the mixture cooled to 0° and the precipitated crystals were filtered off, yield of crude benzaldehyde trimer 28.6 g. Recrystallization from cyclohexane–benzene 7:1 gave 17.9 g of long needles, mp 175–176°, and 6.1 g of coarse needles, mp 173–174°. Both compounds were identical by nmr and infrared analysis.

Removing the methanol and excess nitrobenzene left a brown oil which solidified on standing. Recrystallization from hexane gave N-benzylideneaniline, mp 52°.

Acknowledgment. I am indebted to Miss V. Boyle for the nmr analysis and Mr. J. W. Lewis for the mass spectra.