# Polymerization of benzyl alcohol in anhydrous hydrogen fluoride: an efficient synthesis of poly(phenylenemethylene)

**R. Eric Banks***
*Department of Chemistry, UMIST, Manchester M60 1QD, UK*

**and Pierre-Yves François and Peter N. Preston***
*Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK*
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It has been shown that benzyl alcohol is transformed rapidly and almost quantitatively into poly(phenylenemethylene) by adding it to anhydrous hydrogen fluoride at 16°C; the product is the so-called 'soluble poly(phenylenemethylene)' with a degree of polymerization of ~20. *p*-Methylbenzyl alcohol has also been oligomerized by a similar procedure. The potential for adaption to industrial-scale use is highlighted.

**(Keywords: benzyl alcohol; poly(phenylenemethylene); anhydrous hydrogen fluoride)**

## *Introduction*

The formation of hydrocarbon materials of composition $[C_7H_6]_n$ via the action of acidic entities (e.g. $BF_3$, $H_2SO_4$ or $P_2O_5$) on benzyl alcohol was discovered nearly 140 years ago by Cannizzaro[1]. Subsequently it was recognized that the material was poly(phenylenemethylene), PPM (**1**), of relatively low molecular weight[2]. It is now established that PPM can be formed via oligomerization of benzyl alcohol or benzyl halides.

In principle, phenylenemethylene groups can be joined in a head-to-tail fashion to give an oligomer or polymer $[C_6H_4CH_2]_n$ (**1**) in which the bonding can be *ortho*, *meta* or *para*. Originally, the substance was listed in *Chemical Abstracts* as 'polybenzyl', but since 1970 has been referred to as poly(phenylenemethylene) with prefixes [1,2], [1,3] or [1,4] to indicate the regiochemistry of substitution. PPM can be synthesized regioselectively: for example, ring-opening polymerization of benzocyclopropene gives [1,2] PPM[3], whereas transition metal-mediated coupling of *p*-chlorobenzylmagnesium chloride affords an oligomer believed to be [1,4] PPM[4]. In contrast, we have shown that PPM prepared by oligomerization of benzyl alcohol in concentrated sulphuric acid is a regioisomeric mixture[5].

So-called 'soluble PPM' can be prepared from benzyl alcohol via treatment with, for example, concentrated $H_2SO_4$ (ref. 2) or a catalytic amount of a heteropolyacid such as $H_3PMo_{12}O_{40}$ (ref. 6). This oligomer has a low molar mass (degree of polymerization ~20) and softening point (~80°C), and is soluble in common organic solvents [e.g. $CHCl_3$, dimethylformamide (DMF)]; hence its name. An oligomer with similar properties is also formed from benzyl chloride and stannic chloride[7]. 'Insoluble PPM' can be prepared by treating benzyl chloride with aluminium trichloride either neat[7] or in chloroethane[8]. We have shown that the spectral characteristics (i.r., solid state $^{13}C$ n.m.r.) of 'soluble' and 'insoluble' PPM are almost identical, which suggests that the latter has a higher molecular weight distribution[5].

Commercial interest has been shown in PPM for a variety of potential applications, for example, in electrostatic toner compositions[9], semiconductor devices[10,11] and coatings for enhancing $MoS_2$ lubrication[12]. However, developments centred on PPM and related oligomers have been hampered by lack of an inexpensive synthesis for such materials. Here we describe a method which ought to change this situation.

## *Experimental and Results*

We have discovered that benzyl alcohol can be converted rapidly and quantitatively into 'soluble' PPM simply by adding it to cold commercial anhydrous hydrogen fluoride (AHF; b.p. 19.5°C). In an isolated literature reference devoid of experimental detail, Calcott *et al.*[13] reported long ago that benzyl alcohol cyclo-oligomerized in AHF to give a product believed to be 1,2,3,4,5,6-hexaphenylcyclohexane.

The method we used was as follows: benzyl alcohol (10.0 g) was added slowly to stirred AHF (60 $cm^3$) maintained at ambient temperature (16°C) in a polyethylene beaker. A vigorous reaction occurred with the addition of each drop, with the result that some HF was lost by evaporation, and the mixture became red in colour then pale pink. The AHF was allowed to evaporate slowly (overnight), leaving an off-white solid; this material was washed repeatedly with water until neutral (litmus), then dried in air (5 h at 45°C) and finally *in vacuo* over $P_2O_5$.

The crude material (7.25 g, 87% yield) was purified by reprecipitation from DMF with methanol. The resulting PPM (found: C, 93.3, H, 6.7%; calculated for $[C_7H_6]_n$: C, 93.3; H, 6.7%) had a m.p. of 88–110°C, molar mass of 2339 (v.p.o., $CHCl_3$) and 3728 [g.p.c., tetrahydrofuran (THF), based on polystyrene equivalents], a glass transition temperature of 53°C (d.s.c.) and suffered 25% weight loss under a nitrogen atmosphere at 560°C (t.g.a.). It was almost identical in every respect (e.g. m.p., i.r., $^1H$ and $^{13}C$ n.m.r.) with PPM prepared laboriously from benzyl alcohol in concentrated sulphuric acid using a published procedure[2]. Note that, in contrast to

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* To whom correspondence should be addressed

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concentrated $H_2SO_4$ [b.p. 338°C (98.3%)], HF is easily recovered quantitatively using our method.

In preliminary experiments *p*-methylbenzyl alcohol has also been oligomerized in AHF by a similar procedure; the resulting pale cream oligomer, $[CH_3C_6H_3CH_2]_n$, has a m.p. of ~120°C (softens, darkens) and molar mass of 2428 (g.p.c., THF).

## *Summary*

AHF converts benzyl alcohol efficiently to PPM in a simple inexpensive procedure clearly capable of adaption for industrial-scale use. It is absolutely essential that anyone wishing to use this method who is not skilled in the use of AHF should take advice from experts on how to handle this hazardous material.

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