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Functionalized Macroreticular Resins as Effective and Selective Traps for Gaseous Tobacco Smoke Components

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ABSTRACT

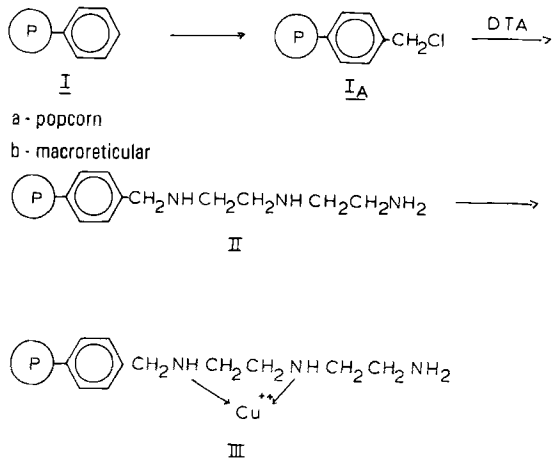
Macroreticular polystyrene resins with polyamine functions and copper (II) ions in chelated form were synthesized and their abilities to selectively remove hydrogen cyanide and volatile aldehydes from tobacco smoke were determined. Up to 80 and 40% reduction was observed. The functionalized fixed-pore macroreticular resins were more efficient than their solvent-swellable "popcorn" counterparts in the removal of these gas-phase components of smoke.

The tobacco smoke produced during the burning of a cigarette is an extremely complex mixture of hundreds of compounds. These are dispersed in a two-phase system consisting of a vapor and a disperse phase (aerosol) [1]. The removal of the particulate matter in the smoke can be achieved by impingement using mechanical filters such as the cellulose acetate tow. The gaseous fraction of tobacco smoke is made up mainly of the so-called permanent gases (chiefly of atmospheric origin), along with extremely small quantities of vapors of compounds with vapor pressures in excess of 0.1 Torr at room temperature. This small fraction is very important in imparting taste and aroma to the smoke. It is also known to contain many of the pharmacologically active materials found in smoke [2]. The removal of a relatively greater percentage of some undesirable components of the gaseous phase without affecting the overall composition of smoke is referred to as selective filtration. A number of research groups are actively involved in the preparation of selective tobacco smoke filters [3].

Small quantities of hydrogen cyanide and volatile aldehydes (such as acrolein) are present in tobacco smoke [4]. These have been blamed for certain ill effects of tobacco smoke [5, 6]. Our efforts have been directed towards the preparation of granular resins with various chemical functions and their utilization as cigarette filter materials for the selective removal of these undesirable components of cigarette smoke. It was shown earlier that chemical reactions can take place between the active functions on the resin and substances in tobacco smoke during the process of smoking a cigarette [7]. Furthermore, "popcorn" polystyrene resins [8] bearing functional groups such as acylimidazole, polyamine, and copper (II) ions in chelated form were able to trap up to 30% hydrogen cyanide and the volatile aldehydes from tobacco smoke without altering its overall composition [9]. As the recently developed macroreticular resins [10] provide extremely large surface area and fixed pore structure, a study of creating the active functions on these resins was undertaken. The resins were evaluated as selective filters for cyanide and aldehydes to observe increased efficiencies, if any, over their "popcorn" polystyrene counterparts.

EXPERIMENTAL

The experimental filter tip assembly used to evaluate the resins has been described in an earlier publication [8]. Each filter tip contained 150 mg of the resin beads (popcorn 40-100, macroreticular 20-40 mesh). The procedures used to functionalize popcorn polystyrene resins have also been dexcribed [8, 11]. The macroreticular polystyrene beads used in the present work (Ib, Amberlite XAD-2)



Scheme 1

were a gift of Dr. Robert Kunin of Rohm and Haas Company, Philadelphia, Pa. These were washed completely according to the procedure described by Relles [12] before being used in the following reactions.

Chloromethyl macroreticular resin (IAb) was prepared from a stirred suspension of Ib (30g) in chloromethyl methyl ether (75 ml) in an ice-bath by adding anhydrous stannic chloride (30 ml) dropwise over 30 min. The mixture was stirred at 0°C for 1 hr and at room temperature for 48 hr. The beads were recovered by filtration and washed completely with chloroform, dioxane, dioxane-water, water and acetone (34 g; 12.6% Cl).

To prepare DTA Resin (IIb), diethylenetriamine (DTA, 35 ml) was added to a suspension of IAb in pyridine (25 g in 70 ml). The mixture was maintained at 115°C for 24 hr. The resin was removed by filtration, washed completely with hot pyridine, pyridine-water, water and methanol (28 g, 1.8% Cl, 5.6% N).

Copper (II) complex (IIIb) was prepared from resin IIb suspended in 300 ml water; the pH was adjusted to 6 with dilute HCl, and in aqueous solution of copper sulfate (8 g in 400 ml) was added while maintaining the pH at 5.5. After 2 hr stirring the green beads were removed by filtration and washed with water until free of copper ions (6% Cu).

RESULTS

"Popcorn" and macroreticular polystyrene resins were functionalized according to the reactions shown in Scheme 1. The former

was prepared by copolymerization of styrene with 0.1% divinylbenzene according to the procedure described by Letsinger et al. [8]. The mesh size was in the 40-100 range. The latter was Amberlite XAD-2 resin manufactured by Rohm and Haas Company [13] (nominal mesh size 20-40). The resins exhibited similar pressure drops (average 2.7 in. of water, measured by Filtrona Pressure Drop Tester Mark 4HP).

The resin beads (150 mg each) were used to fill cigarette tips, and the ensuing smoke was analyzed for total particulate matter (TPM), nicotine, hydrogen cyanide, and volatile aldehydes according to the procedures previously described [9]. The test results shown in Table 1 show that the functionalized macroreticular resins are much more efficient in the removal of cyanide and the aldehydes from fresh cigarette smoke than their "popcorn" counterparts.

DISCUSSION

Popcorn polystyrene [8], a low-density, porous, highly insoluble polymer made by using 0.1% divinylbenzene as the crosslinking agent, was used to prepare the granular filters in the earlier study [9]. It has been reported that solvent-swellable crosslinked polystyrene resins ("gel" type) made by suspension polymerization techniques are more reactive than the macroreticular resins and can be functionalized with relative ease [14]. The same was found to be true of the popcorn resins. Thus under the conditions used to chloromethylate the popcorn beads to an extent of 3.3 meq/g [9] (50% ring substitution), the macroreticular contained less than 1 meq/g CH_2Cl functions. More severe conditions (no solvent, longer reaction time at 25°C) were required to obtain the latter with 3 meq/g functions (resin IAb). Furthermore, the chloromethyl functions on the popcorn resin were more accessible to the reactions with diethylenetriamine (DTA), as resin IIa contained no chlorine while IIb contained 1.8% chlorine, even after 24 hr reaction time. This residual chlorine content was not reduced appreciably by further treatment with DTA. Thus the macroreticular resins used in the study contained about 25% less active functions (DTA, copper ions) than their popcorn counterparts.

A number of cigarette filter tips were filled with the resin beads and subjected to tobacco smoke in an assembly described earlier [9]. The ensuing smoke was analyzed for total particulate matter (TPM), nicotine, and two volatile components (hydrogen cyanide and aldehydes). It should be noted that cyanide partitions about equally between both the TPM and gas phase. The values shown in Table 1 are the sums of the cyanide content in both the phases. This was done for the sake of brevity. The efficiencies of the resin columns to remove a particular component of tobacco smoke was estimated by comparison of the results

TABLE 1. Polystyrene Resins as Cigarette Filters[a]

Filter description	TPM (dry) (mg/cig)[b]	Nicotine (mg/cig)[c]	HCN (total) (μg/puff)[d]	Reduction in HCN by resins (%)	Aldehydes (μg/puff)[e]	Reduction in aldehydes by resins (%)
2R1 cigarette only, no filter[f]	35.2	2.6	37.8	-	149.2	-
2R1 with filter blank	31.8	2.5	37.1	-	145.0	-
Polystyrene						
Popcorn Ia	27.3	2.0	33.7	9.1	144.0	0.1
Macro Ib	28.3	2.2	32.1	13.4	129.0	1.1
Polystyrene-DTA						
Popcorn IIa	27.8	2.2	33.8	8.9	135.1	0.7
Macro IIb	27.6	2.15	17.8	52	81.2	44
Polystyrene-DTA-Cu^{++} complex						
Popcorn IIIa, 8% Cu	26.1	2.0	22.3	40	145	0
Macro IIIb, 6% Cu	26.5	2.2	7.5	80	103	29

[a] 150 mg beads (40-100) per cigarette tip; 9-10 puffs per cigarette.
[b] Standard deviation(s) range 1.1-2.7.
[c] s = 0.1 in all cases.
[d] s range 0.45-2.7.
[e] s range 0.1-0.34.
[f] University of Kentucky reference cigarette no. 2R1.

with those obtained using the filter blank alone. It is evident that all the resins tested have little effect on TPM or the nicotine content, but differ greatly in their abilities to act as traps for the two volatile components. The unfunctionalized polystyrene resins Ia and Ib have unappreciable effect on the levels of these compounds. Hence it is evident that the active functions (DTA and chelated copper ions) immobilized on the polystyrene support are responsible for the removal of the volatile components.

The functionalized macroreticular resins were found to be much more efficient filters than their popcorn counterparts. Thus the resin IIb removed 44% aldehydes while IIa, the popcorn derivative, was totally ineffective. The most remarkable result was that resin IIIb removed 80% cyanide, while resin IIIa removed only half as much.

The present study shows that the functions on the rigid macroreticular resin are more accessible to substances in the vapor state than those on the solvent-swellable counterpart. The selectivity exhibited by resin IIIb was remarkable considering the complexity of the tobacco smoke. Considerable deposition of particulate matter upon the filter material takes place during the smoking process. As a variety of chemical functions can be introduced into the polystyrene matrix, it may be possible to design a filter material for the removal of certain undesirable components from an extremely complex mixture such as tobacco smoke.

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