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A novel biocidal styrenetriazinedione polymer

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Commercial polystyrene has been modified by chemically attaching 6-methyl-1,3,5-triazine-2,4-dione moieties to it in the *para* position of the aromatic rings. Chlorination of this novel polymer in aqueous base yielded poly(1,3,5-trichloro-6-methyl-6-(4′-vinylphenyl)-1,3,5-triazine-2,4-dione) which functioned as a biocide against the bacterium *Staphylococcus aureas* in a water-filter application. Some preliminary characterization data have been presented. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polystyrene; trichlorotriazinedione; biocide)

Introduction

New soluble biocidal materials generally require extensive and expensive testing procedures before approval is granted by regulatory agencies. This is particularly true for those soluble materials which are intended for use in disinfecting potable and recreational water supplies. However, if an insoluble material could be developed which could be used as a sanitizer in a water-filter application, the costs of obtaining regulatory approval could be reduced substantially. An obvious candidate for such an insoluble biocide would be a high-molecular-weight polymer. In the past polymeric quaternary ammonium anionic-exchange resins[1] and poly(styrenedivinylbenzene) compounds containing N-chlorinated sulfonamide moieties[2] have been used as biocides, but these biocidal polymers generally suffer the limitations of excessive solubility in water and/or the release of concentrations greater than 1 mg l^{-1} of free chlorine into flowing water[1,2].

Considerable work in these laboratories has led to the development of several series of soluble N-halamine biocidal compounds[3], and recently we have shown that a biocidal N-halogenated hydantoin derivative of polystyrene can be prepared which is completely insoluble in water and releases less than 1 mg l^{-1} of free chlorine into flowing water[4]. In the present communication we report a new insoluble biocidal polymer formed by modification of polystyrene by chemically attaching a chlorinated triazinedione moiety at the *para* position of the benzene rings. This is particularly significant because the trichlorotriazinetrione monomer is widely employed as a commercial soluble swimming-pool disinfectant[3].

Experimental

Synthesis. The polymer poly(1,3,5-trichloro-6-methyl-6-(4′-vinylphenyl)-1,3,5-triazine-2,4-dione) (Poly-CTD) was prepared by the synthetic scheme shown in *Figure 1.* The poly(4-vinylacetophenone) formed in the first synthetic step was prepared by a Friedel–Crafts acylation of commercial polystyrene (Aldrich Chemical Co., Milwaukee, WI, with stated molecular weight 45 000) in carbon disulfide with a yield of 98.0%; the procedure used has been described in detail[4]. In the second step 1.46 g (0.01 mol of repeating unit) was dissolved in a mixture of 30 ml of dioxane and 20 ml of ethanol and then reacted with 1.35 g (0.01 mol) of dithiobiuret in the presence of dry HC1 at ambient temperature for 16 h. The solid product poly(6-methyl-6-(4′-vinylphenyl)-1,3,5,-triazine-2,4-dithione) was isolated by suction filtration and purified by washing with distilled water in 46% yield. In the third step 2.11 g (0.008 mol) of the poly(triazine-

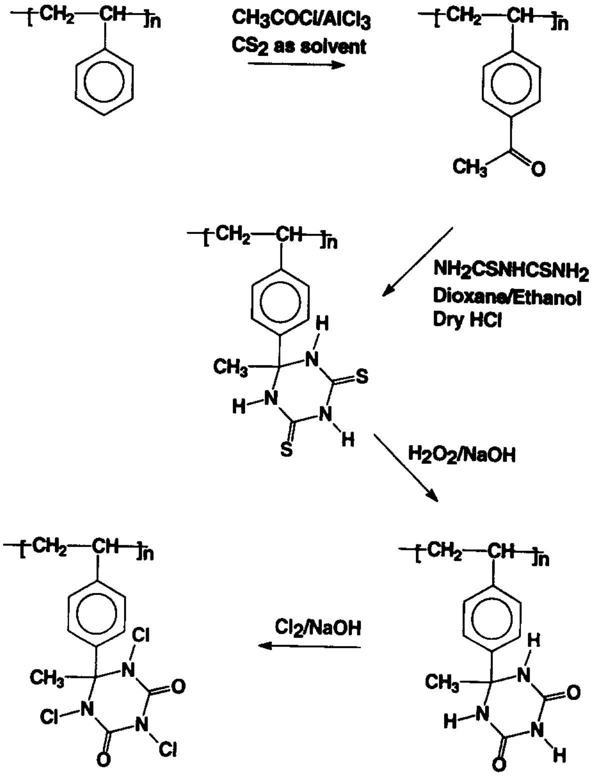

Figure 1 Reaction scheme for preparation of Poly-CTD

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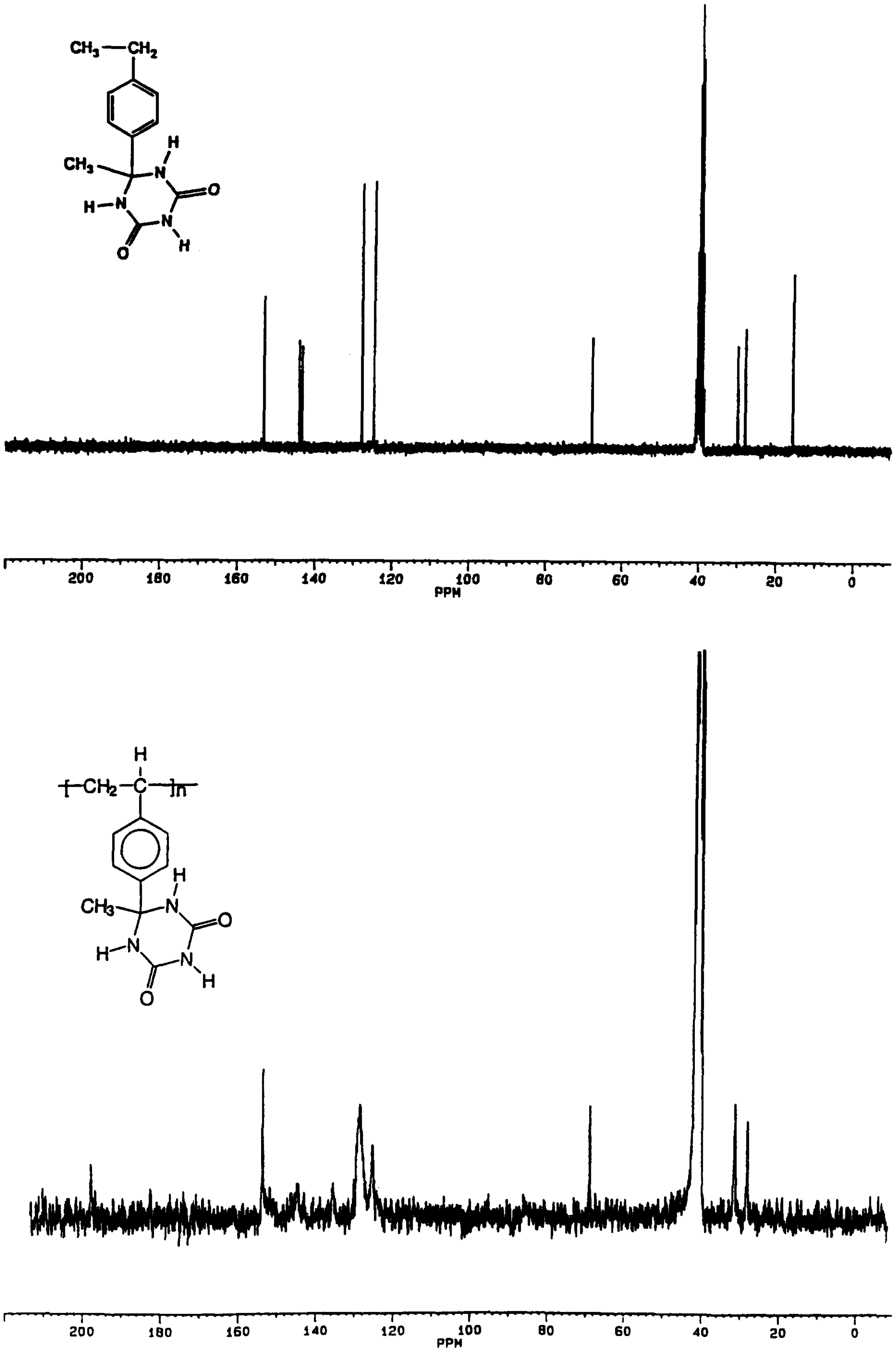

Figure 2 The 250 MHz ^{13}C n.m.r. spectra of the precursor polymer to Poly-CTD and a model monomer compound

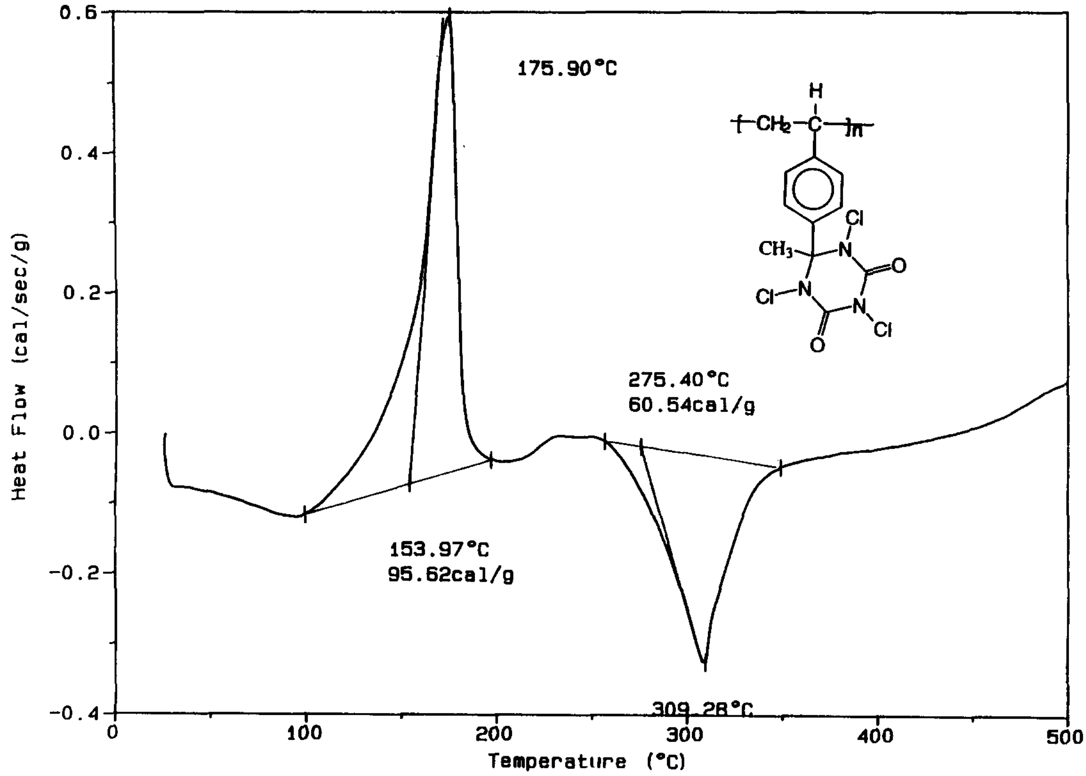

Figure 3 The d.s.c. spectrum of Poly-CTD

dithione) product were dissolved in 50 ml of 2 N NaOH and reacted with 9.2 g (0.08 mol) of 30% hydrogen peroxide at temperatures below 40°C. Following decomposition of excess H_2O_2 at 80°C and neutralization with 2 N H_2SO_4, the yellow poly(dione) product was washed with distilled water and dried in air at ambient temperature; the yield in this step was 89%. In the last step 1 g (0.0043 mol) of the poly(triazinedione) was suspended in 100 ml of 1 N NaOH and chlorinated by bubbling in chlorine gas at temperatures below 10°C until the pH reached 7.0. The final product Poly-CTD was recovered as a light yellow solid by suction filtration and purified by washing with distilled water. After drying at ambient temperature the final product was produced in 71% yield. The overall yield for the whole reaction scheme was thus 28.5%. Other polymer derivatives (6-ethyl- and 6-propyl-(4′-vinylphenyl)-) and 6-methyl-(4′-isopropenylphenyl)-) have also been prepared, the former two with very low yields, the latter in 47% yield, using analogous techniques.

The monomer 6-methyl-6-(4′-ethylphenyl)-1,3,5-triazine-2,4-dione was prepared in this work also to aid in spectroscopic characterization. The synthetic steps were essentially the same as for the polymer, the starting material being 4-ethylacetophenone (Aldrich Chemical Co.).

Characterization. The new polymer Poly-CDT which was insoluble in water and all organic solvents attempted was characterized by several means. Infrared analysis (IBM 32 FTIR) of the solid material in a KBr pellet showed prominent bands at 1269, 1358, 1604 and 1732 cm^{-1}. Although the chlorinated material was not soluble in the usual n.m.r. solvents, it was found that the unchlorinated precursor triazinedione polymer was sparingly soluble in DMSO, as was the monomer compound 6-methyl-6-(4′-ethylphenyl)-1,3,5-triazine-2,4-dione. The ^{13}C n.m.r. spectra (Bruker AM-250) for the monomer and polymer are shown in *Figure 2*. The monomer displayed sharp resonances at δ 153.0 (carbonyl carbons); 143.8, 143.2, 127.7, 124.5 (aromatic carbons); 67.7 (C_6); 29.8 (methylene carbon); 27.8, 15.6 (methyl carbons). The polymer spectrum was more poorly resolved, but resonances can be discerned at δ 152.8, 144.0, 136.0, 128, 124, 68, 30 and 27, leaving little doubt that we have, in fact, produced the precursor to Poly-CTD. The resonance of low intensity near δ 200 corresponds to a small amount of unreacted poly(4-vinylacetophoneone). It should be noted that the precursor polymer exhibits a broad infra-red band at 3245 cm^{-1} (KBr) corresponding to the N–H stretching modes which virtually vanishes upon chlorination indicating that most of the triazinedione nitrogens are chlorinated in Poly-CTD.

The thermal stability of Poly-CTD was determined by DSC (DuPont 2000). The d.s.c. spectrum of Poly-CTD is shown in *Figure 3*. The exothermic band at 176°C corresponds to loss of chlorine from the polymer, and the endothermic band near 275°C corresponds to decomposition of the triazinedione ring. It would appear that Poly-CTD is stable at least up to 100°C and is thus a potential biocide for heated as well as general water disinfectant applications.

Unfortunately the molecular weight of Poly-CTD could not be determined here due to its insolubility. However, the results can be inferred from the starting polystyrene molecular weight.

Microbiology. A Pasteur pipette of length 14.6 cm and inside diameter of 0.64 cm was packed to a length of 2.54 cm with Poly-CTD particles of size 25–60 mesh. The sample had been stored at ambient temperature for 29 days before testing. The column was washed with distilled deionized water at pH 7.0 until free chlorine could not be detected in the effluent as evidenced by colouring of KI solution (i.e. less than 1 mg/l^{-1} free chlorine). Then 1 ml of an aqueous pH 7.0 solution of *Staphylococcus aureus* (ATCC 6538) bacterial suspension at 10^6 CFU ml^{-1} was flowed through the column using a gravity feed. The contact time of flow was 30 s. The effluent was quenched with 0.02 N sodium thiosulfate to prevent inactivation of bacteria by free chlorine in the effluent. Aliquots of the effluent were plated on nutrient agar, and the plates were incubated at 37°C for 48 h before examination for viable organisms. It was found that no bacteria survived, i.e. a 6 log inactivation occurred in a contact time of less than 30 s.

Discussion and conclusions

The insolubility of the new polymer Poly-CTD in water renders it a candidate for a biocidal water filter. It has been suggested that its insolubility may be due to radical crosslinking induced during the final chlorination step*. We consider this unlikely because upon reaction of Poly-CTD with 0.1 N sodium thiosulfate to titrate the chlorine moieties, a polymer with the same properties, including solubility in aqueous NaOH and in DMSO, as the unchlorinated precursor triazinedione polymer is obtained. Had radical crosslinking occurred, the unchlorinated polymer obtained after reaction with the reducing agent would not have had identical properties to the unchlorinated precursor to Poly-CTD. The performance of Poly-CTD as a biocide in a water filter application was very encouraging. Not only does it inactivate *S. aureus* efficiently with brief contact time, but also it is stable in storage at an ambient temperature for at least one month. Its component moieties (polystyrene and trichlorotriazinetrione) are both approved materials for human and animal contact, so it is logical that the new polymer will also be safe for use in disinfection applications, particularly since it is insoluble; this could be preferable to N-halamine monomers and free chlorine which can only be used at concentrations of a few mg/l^{-1} in water because of their appreciable solubilities. The primary limitation of Poly-CTD as a commercial biocide is probably the cost of its synthesis due to the rather low overall yield. In this respect the chlorinated polystyrene hydantoin developed earlier in these laboratories[4] may be preferable. Work is continuing in these laboratories on development of novel N-halamine polymeric biocidal compounds.

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