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Synthesis and polymerization of unsaturated derivatives of halogenated phenols

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Summary

The preparation of p-styrenesulfonic and methacrylic acid esters of the microbiocides 2,4,6-trichlorophenol and 4-chloro-m-cresol, and their characterization by IR, ^{1}H and ^{13}C NMR spectroscopy are described. The radical homopolymerization of the biocidal monomers, and their copolymerization with various vinyl monomers have been studied. The polymerization gives polymers in which the microbiocide moieties are covalently attached to the polymer backbone chain by ester links.

Introduction

Polymers with a functional group of known microbiocidal activity have received increasing interest as drugs or disinfectants (1,2). Furthermore, this subject has attracted wide attention in the field of protection of paint polymers against micro attack or animal or vegetable fouling (3). Thus biocidal paint binders are produced by covalent binding of biocides such as organotin compounds or phenols to synthetic polymers by a variety of hydrolysable linkages (amide or ester); but examples of anchoring of biocides to polymers by nonhydrolysable groups are few (4,5).

In the present paper the synthesis and radical-initiated polymerization of hydrolytic stable p-styrenesulfonic esters from halogenated phenols are studied. In addition, the preparation and polymerization of 4-chloro-m-cresyl methacrylate is also described.

Experimental

Materials

p-(2-Bromoethyl)benzenesulfonyl chloride (1) was prepared by reacting 2-phenylethylbromide (6) with chlorosulfonic acid (7).

4-chloro-m-cresyl p-(2-bromoethyl)benzenesulfonate (2a): To a mixture of 0.5 mol 1 and 0.5 mol of purified 4-chloro-m-cresol a solution of 20 g NaOH in 70 ml water was added with stirring at 50°C. The stirring was continued at 70°C. After one hour the reaction mixture was cooled to 0°C to precipitate the crude product, which was taken up in ether, washed with water and dried about calcium chloride. The residue remaining on evaporation of the ether was recrystallized from ethanol, giving white crystals (m.p. 83°C) in 42% yield.

$C_{15}H_{14}BrClO_3S$ (389.7) Calc. C 46.33 S 8.23
Found C 46.40 S 8.25
IR (KBr) 1176 (s-SO_2) and 1368 cm^{-1} (as-SO_2).
Mass (m/e) 389 (M^+, 13), 185 (100), 104 (81)

The same procedure as for 2a was applied for preparation of 2,4,6-trichlorophenyl p-(2-bromoethyl)benzenesulfonate (2b) to afford a white solid (m.p. 108°C) in 39% yield.
$C_{14}H_{10}BrCl_3O_3S$ (444.6) Calc. C 37.83 S 7.21
Found C 38.14 S 7.20
Mass (m/e) 444 (M^+, 8), 249 (100), 185 (60)

For the dehydrobromination a KOH solution in ethanol (3 wt.%) was added with stirring to the filtrated solution of 2a or 2b at 50°C. After refluxing for one hour, the formed KBr was filtered off, the filtrate was concentrated and cooled (-50°C) to precipitate the product. A final recrystallization from ethanol gave 4-chloro-m-cresyl p-styrenesulfonate (3a, m.p. 48°C) or 2,4,6-trichlorophenyl p-styrenesulfonate (3b, m.p. 71°C) in yields of 88 and 85%, respectively.
3a: $C_{15}H_{13}ClO_3S$ (308.7) Calc. C 58.35 S 10.38 Cl 11.48
Found C 57.69 S 10.41 Cl 10.77
IR (KBr) 1170 (s-SO_2) and 1390 cm^{-1} (as-SO_2)
Mass (m/e) 308 (M^+, 19), 167 (85), 103 (100)
3b: Mass (m/e) 362 (M^+, 6) 167 (108), 103 (53)

4-Chloro-m-cresyl methacrylate (4): 0.10 mol of purified 4-chloro-m-cresol, 0.11 mol triethylamine (TEA), and 0.2 g N,N-dimethylaminopyridine (DMAP) were dissolved in 250 ml of anhydrous benzene and kept stirred at 10°C. Then a solution of 0.12 mol of freshly distilled methacryloyl chloride in 50 ml benzene was added. After 2 hr, the reaction mixture was filtered, the benzene solution washed with water and dried over calcium chloride. After filtration, benzene was evaporated under reduced pressure. Then the crude product was fractionally distilled through a Vigreux column, yielding a transparent liquid (b.p. 90-92°C at $4 \cdot 10^{-4}$ atm) in 64% yield.
$C_{11}H_{11}ClO_2$ (210.7) Calc. C 62.72 Cl 16.83
Found C 62.64 Cl 16.74
IR (KBr) 1740 cm^{-1} (C=O)
Mass (m/e) 210 (M^+, 45), 107 (79) 69 (100)

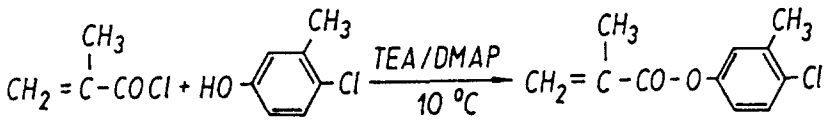
Acrylonitrile, styrene (St), methyl methacrylate, n-butyl methacrylate, 2-hydroxyethyl methacrylate (HEMA), and vinyl acetate (Vac) were purified by conventional methods. The monomers were freshly distilled under argon before use. Toluen was purified in the usual manner and stored over sodium metal. Dimethylformamide (DMF), and 2,2-azobisisobutyronitrile (AIBN) were purified as described previously (8).

Polymerization

The polymerization reactions were carried out in sealed glass tubes containing a given amount of AIBN dissolved in toluen or DMF. Subsequently, the biocidal monomer and comonomer were introduced. The tubes were degassed through three freeze-thaw cycles (liquid nitrogen) before they were placed in a constant-temperature bath (60°C). After a certain time, homopolymerizations or copolymerizations were terminated by the addition of excess methanol. The copolymerizates with HEMA or Vac, were poured into excess ether. The monomer conversions were calculated from the gravimetrically determined yields of the

zenesulfonates 2a or 2b, which can be carefully purified by recrystallization. Conversion to p-styrenesulfonates 3a or 3b was accomplished by treatment with KOH. In addition, the synthesis of p-styrenesulfonates was carried out by esterification of p-styrenesulfonyl chloride with the biocidal phenols, but the yields were low and all attempts to isolate pure sulfonates failed.

The methacrylic acid ester of 4-chloro-m-cresol was synthetized by the reaction of methacryloyl chloride with 4-chloro-m-cresol according to the following scheme.



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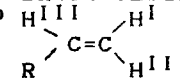
The characterization of biocidal monomers was carried out by ^{1}H NMR, ^{13}C NMR, IR and mass spectroscopy. Numeric ^{1}H NMR spectral data are presented in Table 1 and confirm the expected structure of synthetisized monomers. Furthermore, ^{13}C NMR data (Table 2) are in good agreement with expections. Several criteria were used to assign the observed ^{13}C signals. Firstly, chemical shift increments compiled by Pretsch et al. (10) were used. Secondly, the attached proton test (APT) technique (11, 12) was applied for assigment of the ^{13}C signals to the building groups CH_n (n = 0,1,2,3) of 3a. Finaly, our assigment of the ^{13}C signals was compared with that of 4-chloro-m-cresyl acrylate (5) in accordance with Ref. (5).

Table 1 ^{1}H NMR shift data of 4-chloro-m-cresyl and 2,4,6-trichlorophenyl p-styrenesulfonate (3a and 3b), and 4-chloro-m-cresyl methacrylate (4)

Monomer	Chemical shifts (multiplicity)[a]					
	Vinyl protons[b]					
	I	II	III	Ar-H	Ar-CH_3	=C(CH_3)-
3a	5.37(d)	5.79(d)	6.60(dd)	7.06-7.75(m)	2.23(s)	-
3b	5.24(d)	5.64(d)	6.66(dd)	7.17-7.83(m)	-	-
4	5.75(s)	6.60(s)	-	6.85-7.37(m)	2.30(s)	2.04(s)

[a] Shift value in ppm down field from internal HMDS

[b] 

dried polymers. The polymers were reprecipitated twice and then dried under vacuum at 40°C to constant weight. Copolymer composition was determined by elemental analysis.

Measurements

^1H NMR spectra were recorded on an KRH-100R (Academy of Science of the GDR) using hexamethyldisilane (HMDS) as the standard. ^{13}C NMR spectroscopic measurements were performed with a HX 90-R spectrometer (BRUKER, 90 MHz) using $CDCl_3$ or dimethylsulfoxide-d_6 as a solvent. Mass spectra were measured with a spectrometer, CH 6 (VARIAN). An infrared spectrometer M 80 (Carl Zeiss Jena GmbH, GDR) was used to record IR spectra.

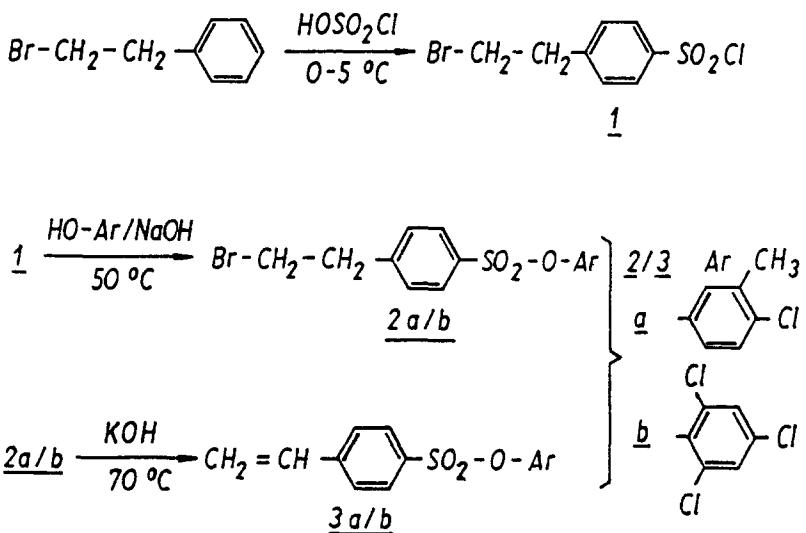
The number-average molecular weights of polymers were determined osmometrically. Molecular weights determinations were also done by GPC (commercial Knauer gel chromatograph) by using colums calibrated with polystyrene standards. The eluent was tetrahydrofuran; the temperature was 40°C.

Differential scanning calorimetry (DSC) measurements were performed by using a Perkin-Elmer DSC-2C thermal analyzer. Scanning rates of 10 °C/min were used.

Results and discussion

Synthesis of biocidal monomers

The route of synthesis of p-styrenesulfonates (3a/3b) is shown in the following scheme.

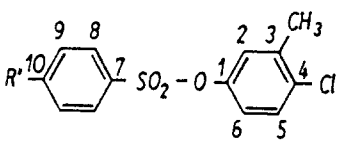


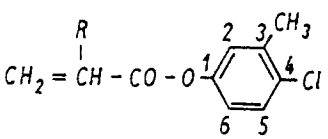
The starting material for the synthesis of 3a or 3b was 2-phenylethyl bromide. p-(2-Bromoethyl)benzenesulfonyl chloride (1) was prepared from the reaction of 2-phenylethyl bromide with chlorosulfonic acid. The next step in the reaction scheme was the esterification of the sulfonyl chloride 1 with the halogenated phenols according to a modification to the procedure described by Whicher et al. (9) yielding the p-(2-bromoethyl)ben-

Table 2 ^{13}C NMR shift data of 4-chloro-m-cresyl esters of p-(2-bromoethyl)benzenesulfonic, p-styrenesulfonic, and methacrylic acid (2a, 3a, and 4)[a]

Carbon atom	Chemical shift 2a obs.[b]	2a calc.[c]	3a obs.[b]	3a CH_n (APT)[d]	4 obs.[b]	5 (5)[e]
1	148.1	142.1	148.3	C	149.1	149.2
2	124.9	128.4	125.0	CH	123.8	124.0
3	138.2	139.2	138.4	C	137.2	137.2
4,7	133.1 133.9	142.3 143.2	133.2 134.3	C C	131.1	131.2
5	130.1	129.9	130.2	CH	129.6	129.6
6	121.2	127.8	121.2	CH	120.2	120.4
8	128.9	127.2	127.1	CH	-	-
9	129.9	129.3	129.1	CH	-	-
10	146.5	144.5	144.0	C	-	-
Ar-CH_3	20.1	21.4	20.2	CH_3	20.0	19.0
-CH_2-	32.2 38.9	31.8[f] 38.6[g]	- -	- -	- -	- -
CH_2=	-	-	118.6	CH_2	127.4	-
-C(R)=	-	-	135.4	CH	135.6	132.3
-CO-	-	-	-	-	165.6	163.8
Alk-CH_3	-	-	-	-	18.2	-

a





R' : 2a : Br - CH_2 - CH_2 -

3a : CH_2 = CH -

R : CH_3 (4) , H (5)

b Shift value in ppm down field from internal HMDS
c Chemical shift increments taken from (10)
d Assigment of ^{13}C signal by APT technique
e 4-chloro-m-cresyl acrylat
f Br-$\underline{C}H_2$-CH_2-
g Br-CH_2-$\underline{C}H_2$-

Polymerization of biocidal monomers

The homopolymerization of p-styrenesulfonates was carried out with AIBN in toluen at 60°C. The results given in Figure 1 demonstate, that the monomers 3a and 3b are radically polymerizable and monomer conversion increases with the polymerization time. Furthermore, it is remarkable that 3b as compared with 3a showed, a high tendency for thermal polymerization which was observed during purification of 3b. As a consequence, further

investigations were done only with 3a. The obtained polymers of 3a are well soluble in benzene, tetrahydrofuran, dioxane and methylene chloride. The number-average molecular weight of poly(3a) obtained after 4 hr (conditions see Figure 1) was esti-

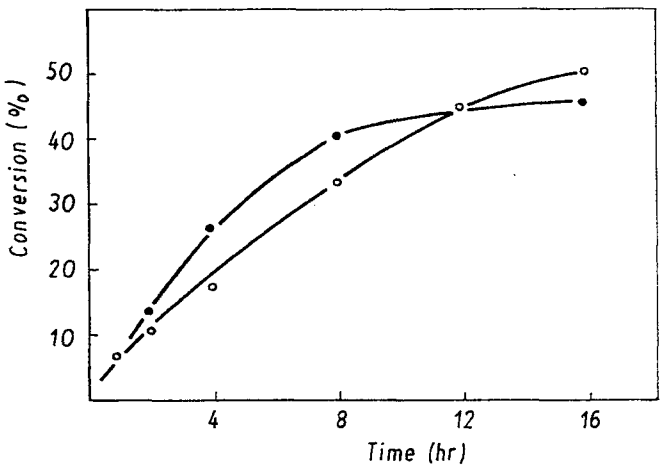


Figure 1 Polymerization of 4-chloro-m-cresyl (o, 3a) and 2,4,6-trichlorophenyl p-styrenesulfonate (•, 3b) in the presence of AIBN (2.5 mmol/l) in toluene at 60°C. [Monomer] = 0.5 mol/l

mated to be 5930 g/mol. The glass transition temperature of this polymer sample determined by DSC analysis was 98°C. The hydrolysis stability of poly(3a) was investigated in bidistilled water at room temperature. It was found that within 30 days a hydrolytic release of 4-chloro-m-cresol did not occur.

The homopolymerization of 4-chloro-m-cresyl methacrylate (4) was carried out in DMF at 60°C. Figure 2 shows that the monomer conversion increases with polymerization time and that polymers with a number-average molecular weights in the range of 41 to 266 kg/mol are obtained. The glass transition temperature of a polymer sample (M_n = 91 kg/mol) was estimated to be 113°C. This temperature is somewhat higher than the value of 110°C for poly(phenyl methacrylate) (13).

The radical copolymerization of biocidal monomers with St (M_1) was carried out in toluene (3a) or DMF (4) as a solvent. The results in Figure 3 show that the composition of copolymers can cover a wide range by varying the monomer feed composition. From the curves, the monomer reactivity reactions r_1 and r_2 were calculated according to the method of Kelen and Tüdös (14): r_1 = 0.31, r_2 = 2.37 (3a) and r_1 = 0.15, r_2 = 0.33 (4). The results of the copolymerization of 3a and 4, respectively, with various vinyl monomers are summerized in Table 3.

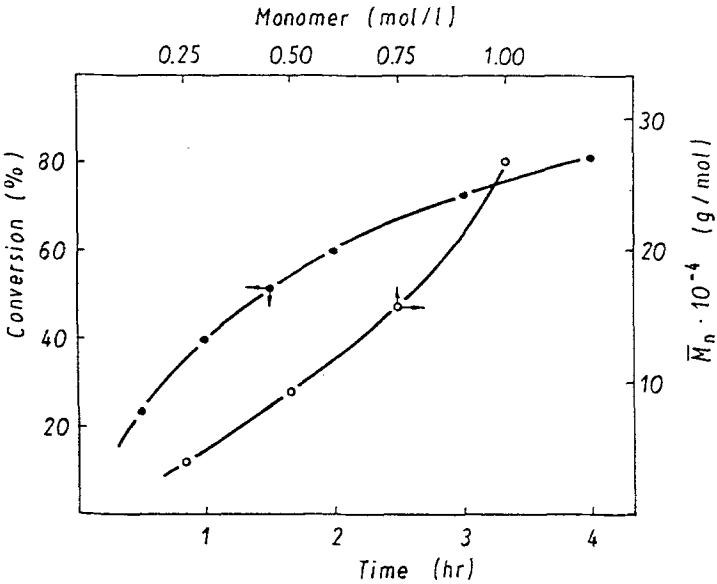


Figure 2 Polymerization of 4-chloro-m-cresyl methacrylate (●, 0.5 mol/l) in the presence of AIBN (2.5 mmol/l) in DMF at 60°C. Time: 1 hr (o)

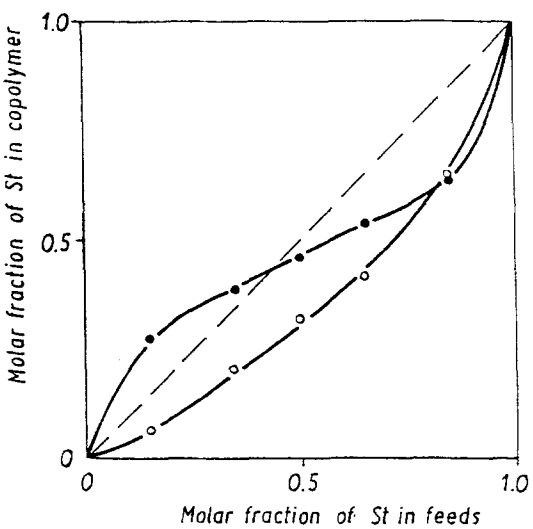


Figure 3 Composition diagramm for the copolymerization of St with 3a (●) and 4 (o) in the presence of AIBN (2.5 mmol/l) at 60°C. [St] + [Comonomer] = 1.0 mol/l

Table 3 Copolymerization of 3a or 4 with various vinyl monomers initiated by AIBN (0.025 mol/l) in toluene. [Monomer] = 1.0 mol/l; molar monomer ratio = 1/1.

Comonomer	Conversion (%)	
	3a (4 hr)	4 (1 hr)
Methyl methacrylate	28.7	9.2
n-Butyl methacrylate	28.3	18.1
2-Hydroxyethyl methacrylate	49.7	25.3
Styrene	31.2	6.1
Vinyl acetate	17.8	14.7
Acrylonitrile[a]	29.9	28.5

[a] DMF as a solvent

It can be seen that the copolymerization of biocidal monomers with all vinyl monomers yields polymers with pendant 4-chlor-m-cresyl groups and different hydrophilicity.

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