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SITE-SITE INTERACTIONS IN A POLYMER MATRIX. FUNCTIONALIZATION OF PYRIDINE RINGS WITH DIBROMOALKANES IN CROSSLINKED POLY(STYRENE-*co*-4-VINYLPYRIDINE)

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ABSTRACT

Pyridine ring functionalization and additional crosslinking in crosslinked poly(styrene-*co*-4-vinylpyridine) with various dibromoalkanes depend on the chain length of the dibromoalkane, the solvent polarity, and the molar ratio between the pyridine rings and the dibromoalkane. The effect of chain length on additional crosslinking becomes more pronounced when the good swelling solvent dimethylformamide is replaced by dibromoalkane. On the other hand, the degree of crosslinking of poly(styrene-*co*-4-vinylpyridine) influences both the reactivity and the additional crosslinking.

INTRODUCTION

Functionalization of polymer resins represents an interesting technique for the preparation of new reagents, catalysts, separation media, etc. [1–3]. Chemical reactions of polymer resins with reagents where difunctionalization is possible could result in additional crosslinking, and the change in the polymer backbone structure could significantly influence the physical properties of carriers, which would be reflected in changed behavior of catalysts, reagents, or carriers for separation media [3–6].

The most widely studied polymer resins are based on various crosslinked styrene backbones and have been used in a number of areas. In spite of the fact that pyridine

by itself or in conjunction with other reagents has wide application, the corresponding resins containing pyridine instead of benzene rings have received much less attention [7]. We now report further investigations [8, 9] into the behavior of crosslinked poly(styrene-*co*-4-vinylpyridine) with various dibromoalkanes.

EXPERIMENTAL SECTION

Materials

Commercially available 1,3-dibromopropane (Merck), 1,4-dibromobutane (Merck), 1,5-dibromopentane (Merck), 1,6-dibromohexane (Merck), styrene (Aldrich Chemical), and 4-vinylpyridine (Merck) were distilled before use. Poly(vinyl alcohol) (Wacker, Polyviol W 28/20) and azobisisobutyronitrile (AIBN) were used without purification. Divinylbenzene (Merck, 45% isomeric ethylvinylbenzene) was washed with NaOH (5%) and water before use. The solvents were purified and stored over Molecular Sieves [15].

Preparation of Crosslinked Poly(Styrene-*co*-4-Vinylpyridine) (1a, 1b, 1c)

In a 1500-mL four-necked flask, equipped with a reflux condenser, thermometer, stirrer, and an inlet for oxygen-free nitrogen, 250 mL of a 1% water solution of poly(vinyl alcohol), 0.6 g AIBN, 36 g styrene, 24 g 4-vinylpyridine, and various amounts of divinylbenzene (50% in ethylvinylbenzene), namely, 2.5 g for 1a, 15 g for 1b, and 40 g for 1c, were stirred for 5 min under a constant flow of nitrogen and then heated under stirring so that the reaction mixture reached 70°C in 1 h. The stirring velocity was then increased and continued for 3 h, and finally for 30 min at 95°C. Various amounts of products were isolated.

Crosslinked poly(styrene-*co*-4-vinylpyridine) was activated by the following procedures: The polymer beads were stirred successively in methanol (T 50°C, t 2 h), NaOH (5%, T 50°C, t 2 h), washed with water, stirred successively in dimethylformamide (T 50°, t 2 h), methanol (T 50°C, t 2 h), and chloroform (T 50°C, t 2 h), dried at room temperature for 19 h, and finally *in vacuo* at 80°C for 3 h. The concentration of pyridine rings was determined by combustion analysis, and the following values were found: 1a, 44% pyridine rings (5.88% nitrogen); 1b, 32% pyridine rings (4.32% nitrogen); and 1c, 25% pyridine rings (3.28% nitrogen). Polymer beads with a distribution of particle sizes in the range of 400–800 μm were used for further investigations.

Reactions with Dibromoalkanes (2a–2d)

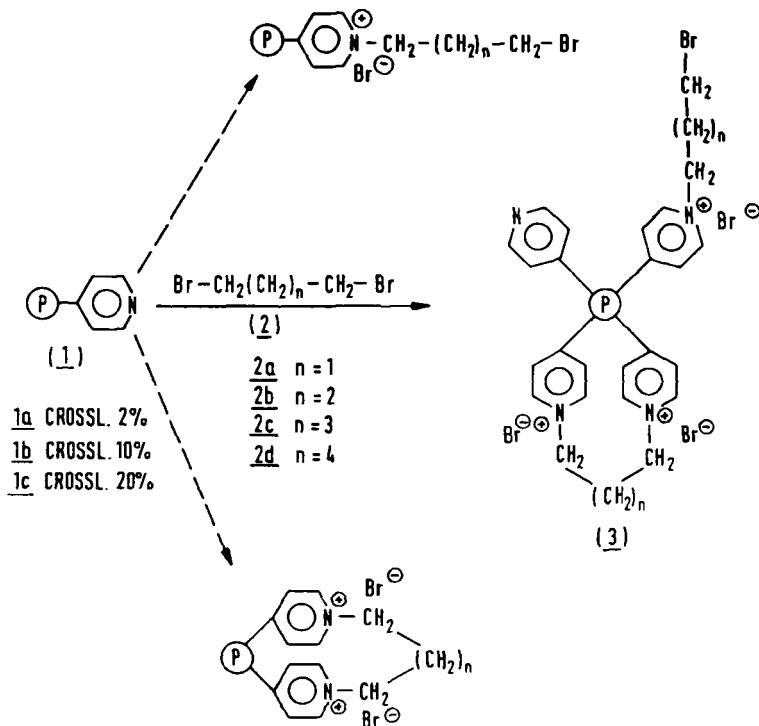
Dry crosslinked poly(styrene-*co*-4-vinylpyridine) (1a, 1b, 1c), containing 2 mmol pyridine rings, was mixed with 8 mL solvent, left to swell at room temperature for 18 h, and thermostated for 1 h at a specified temperature. Then a solution of different amounts of dibromoalkane in 2 mL solvent was added and stirred for various times. In the cases of bulk dibromohalide, 6 mL dihalide were used. The polymer beads were filtered off, washed three times with 5 mL solvent and 10 times with 5 mL methanol, dried at room temperature for 18 h, pulverized, and dried *in vacuo* at 80°C for 3 h.

Ionically bonded bromide was determined as follows: 0.2 g sample was suspended in 30 mL of a 50% water solution of acetic acid, 5 mL concentrated HNO₃ was added, and the suspension was potentiometrically titrated with 0.1 N AgNO₃. The total amount of bromine, i.e., ionically and covalently bonded bromine, was determined as follows: 0.2 g sample was suspended in 4 mL pyridine, heated for 2 h at 100°C and cooled to room temperature. Then 6 mL dimethylformamide was added, the sample was cooled on ice before the slow addition of 6 mL HNO₃ and, after the addition of 10 mL distilled water, the suspension was potentiometrically titrated with 0.1 N AgNO₃.

RESULTS AND DISCUSSION

Boucher and coworkers [10] studied reactions of alkylhalides with various soluble polyvinylpyridines, while Nishide and coworkers [11] studied the complexation properties of polyvinylpyridine which was partly crosslinked by 1,4-dibromobutane. Sherrington and Greig [12] studied the reactions of several poly(styrene-*co*-4-vinylpyridines) with various degrees of crosslinking, and they found that the polymer resins behave like Molecular Sieves.

The importance of the constancy of the degree of crosslinking of the polymer resins in the preparation of new supports initiated our investigations into site-site interactions in poly(styrene-*co*-4-vinylpyridine) resins with various degrees of crosslinking. Poly(styrene-*co*-4-vinylpyridine) resins with various degrees of crosslinking were prepared by suspension polymerization of styrene, 4-vinylpyridine, and 1,4-divinylbenzene (DVB), and after activation the following beads were used: 2% crosslinked beads containing 44% pyridine rings (1a), 10% crosslinked beads containing 32% pyridine rings (1b), and 20% crosslinked beads containing 25% pyridine rings (1c). Pyridine rings in crosslinked poly(styrene-*co*-4-vinylpyridine) could be functionalized with dibromoalkanes in two ways (see Scheme 1): monofunctionalization of pyridine rings or crosslinking of the polymer backbone. However, competition between the two processes could be expected, resulting in a polymer backbone (3) with the structure shown in Scheme 1.



SCHEME 1.

This induced us to study the effect of the chain length of the dibromoalkane, i.e., 1,3-dibromopropane (2a, $n = 1$), 1,4-dibromobutane (2b, $n = 2$), 1,5-dibromopentane (2c, $n = 3$), 1,6-dibromohexane (2d, $n = 4$), and the degree of crosslinking of the polymer backbone (1) on the mode of functionalization, as well as to a study of the possibility of directing the reaction either toward only monofunctionalization, or to crosslinking, by variation of the reaction conditions. Both possible processes could be differentiated by determination of ionically bonded bromine in proportion to the total bromine content of the polymer resin. In the case of complete additive crosslinking with no monofunctionalization, all the bromine contained would be found in the ionic state, while only half of the total bromine bonded would appear in the ionic form when only monofunctionalization occurred.

The amount of ionically bonded bromine was established by potentiometric titration with AgNO_3 in the presence of acetic acid and nitric acid [13]. The amount of covalently and ionically bonded bromine was also determined by potentiometric titration, but the beads were heated for 2 h in pyridine at 100°C prior to titration [14]. Conversions of covalently bonded bromine to the ionic form were confirmed by independent experiments with pyridine and dibromoalkanes (2a–2d). In several cases the functionalization of pyridine rings was also confirmed by nitrogen content determination by combustion analysis, but the values obtained were of very limited use for determining the degree of additional crosslinking because the differences in the expected values were too small. Thus 1a contained 5.88% nitrogen; in the monofunctionalized form the expected nitrogen content would be 2.9%, and 3.89% in the completely crosslinked form, in the reaction of 1a with 1,6-dibromohexane (2d). The corresponding values for reactions with 2a would be 3.18% nitrogen for the monofunctionalized and 4.13% for the crosslinked form.

In a typical experiment an exact amount of dry poly(styrene-co-4-vinylpyridine) (1) containing 2 mmol pyridine rings was suspended in 8 mL purified dry solvent, the beads were swollen for 18 h at room temperature, and then thermostated at the appropriate temperature for 1 h. Then a measured amount of dibromoalkane (2) in 2 mL solvent was added, the reaction mixture stirred for a given time, the solvent and excess halide filtered off, and the polymer beads washed 5 times with the solvent used in the reaction and 10 times in methanol (several washings are necessary to remove all the unbonded dibromoalkane from the polymer backbone). It was then dried for 18 h at room temperature, pulverized, and after drying *in vacuo* at 80°C for 3 h, finally analyzed for total and ionically bonded bromine content.

First we studied the effect of the chain length of the dibromoalkane on the functionalization of pyridine rings in dimethylformamide (DMF), known to be a good swelling solvent. The effect of the chain length is presented in Table 1. It is evident that, after 24-h reaction at 70°C , almost all the pyridine rings in 1a are functionalized, with additional crosslinking of the polymer backbone being the predominant process. The chain length does not have a very important effect on the degree of monofunctionalization; however, the highest degree of crosslinking (78%) was observed with 1,3-dibromopropane, and it diminished to 69% with 1,6-dibromohexane.

Further, we studied the effect of dibromoalkane concentration on the functionalization of pyridine rings in 1a in DMF (molar ratio of pyridine rings to dibromoalkane, 1:3) and in pure dibromoalkane. After 2-h reaction at 70°C , higher functionalization was observed in bulk, dibromoalkane, but the degree of additional crosslinking changed markedly when the reaction was carried out in DMF. The effect of the chain length of the dibromoalkane on the monofunctionalization of pyridine rings became more pronounced than in the case of the reaction in DMF. The reaction with pure 1,3-dibromopropane resulted in equal amounts of monofunctionalization and addi-

TABLE 1. Effect of Chain Length of Dibromoalkanes on Functionalization of Pyridine Rings and on Additional Crosslinking in Crosslinked Poly(Styrene-*co*-4-Vinylpyridine)^a

Dibromoalkane, <i>n</i>	Functionalization of pyridine rings, %	Monofunctionalization, %	Crosslinking, %
1	96	18	78
2	97	22	75
3	98	19	79
4	96	27	69

^aSolvent, dimethylformamide; mole ratio pyridine:dibromoalkane, 1:3; crosslinking of polymer resins, 2%; reaction time, 24 h; reaction temperature, 70°C.

tional crosslinking, while monofunctionalization became much more pronounced on reaction with pure 1,6-dibromohexane (Table 2).

The chemical transformations of the polymer backbone are influenced by two important parameters: the swelling of the resins and the polarity of the solvent. In addition, we studied the effect of solvent polarity and the degree of crosslinking of the poly(styrene-*co*-4-vinylpyridine) on the functionalization of the pyridine rings and the degree of additional crosslinking. Solvents were chosen in the following way: DMF is polar and swells the resins very well, benzene is nonpolar but its swelling capacity is very similar to that of DMF, while the polymer beads remain nearly

TABLE 2. Effect of Chain Length and Concentration of Dibromoalkanes on Functionalization of Pyridine Rings and on Additional Crosslinking in Crosslinked Poly(Styrene-*co*-4-Vinylpyridine)^{a,b}

Dibromoalkane, <i>n</i>	Functionalization of pyridine rings, %		Monofunctionalization, %		Crosslinking, %	
	A	B	A	B	A	B
1	88	89	13	46	75	43
2	89	93	21	50	68	43
3	94	96	18	45	76	51
4	89	98	19	72	70	26

^aCrosslinking of polymer resins, 2%; reaction time, 2 h; reaction temperature, 70°C.

^bA: solvent, dimethylformamide; mole ratio pyridine:dibromoalkane 1:3; B: bulk dibromoalkane.

TABLE 3. Effect of the Degree of Crosslinking of Poly(Styrene-co-4-Vinylpyridine) and Solvent Polarity on Functionalization of Pyridine Rings and Additional Crosslinking with 1,6-Dibromohexane at 70°C

Copoly- mer	Solvent	Reaction time h	Functionalization of pyridine rings %	Monofunction- alization, %	Cross- link- ing %
1a (2%)	C ₆ H ₁₂	2	52	6	46
	C ₆ H ₆	2	45	3	42
	DMF	2	88	33	55
	DMF	24	95	27	68
	Br(CH ₂) ₆ Br	2	98	72	26
1b (10%)	C ₆ H ₁₂	2	5	0	5
	C ₆ H ₆	2	24	2	22
	DMF	2	70	3	67
	DMF	24	84	6	78
	Br(CH ₂) ₆ Br	2	47	11	36
1c (20%)	DMF	2	35	13	22
	DMF	24	83	10	73
	Br(CH ₂) ₆ Br	2	26	20	6

unchanged in cyclohexane compared to the dry state. As shown in Table 3, the solvent polarity has a very important influence, not only on the rate of functionalization, but also on the degree of the additional crosslinking. In both nonpolar solvents the reaction is slower and the additional crosslinking is the main process observed. The increased monofunctionalization of pyridine rings observed in the reaction of 2% crosslinked resins in bulk dihaloalkane was lost with both higher crosslinked resins where mainly additional crosslinking was observed.

Finally we studied the effect of the chain length of the dibromoalkane and the degree of crosslinking on the additional crosslinking in bulk 1,3-dibromopropane and 1,6-dibromohexane (Table 4). 1,3-Dibromopropane reacts with pyridine rings at a rate uninfluenced by the degree of crosslinking, while increased crosslinking resulted in diminished functionalization in the case of 1,6-dibromohexane. However, both the chain length of the dibromoalkane as well as the crosslinking were found to influence the degree of additional crosslinking (Table 4).

TABLE 4. Effect of Chain Length of the Dibromoalkane and the Degree of Crosslinking of Poly(Styrene-co-4-Vinylpyridine) on Functionalization of Pyridine Rings and on Additional Crosslinking^a

Copolymer	Functionalization of pyridine rings, %		Monofunctionalization, %		Crosslinking, %	
	<i>n</i> = 1	<i>n</i> = 4	<i>n</i> = 1	<i>n</i> = 4	<i>n</i> = 1	<i>n</i> = 4
1a (2%)	89	98	46	72	43	26
1b (10%)	91	47	67	11	24	36
1c (20%)	83	26	53	20	30	6

^aSolvent: 1,3-dibromopropane (*n* = 1), 1,6-dibromohexane (*n* = 4); reaction temperature, 70°C; reaction time, 2 h.

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