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Site—site Interactions in a Polymer Matrix. The Effect of Reaction Conditions on the Functionalization of Pyridine Rings in Crosslinked Poly(Styrene-4-Vinylpyridine) with 1,6-Dibromohexane

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SITE—SITE INTERACTIONS IN A POLYMER MATRIX. THE EFFECT OF REACTION CONDITIONS ON THE FUNCTIONALIZATION OF PYRIDINE RINGS IN CROSSLINKED POLY(STYRENE-4-VINYLPYRIDINE) WITH 1,6-DIBROMOHEXANE

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ABSTRACT

Functionalization of pyridine rings in crosslinked poly(styrene-4-vinylpyridine) containing 37-43% pyridine rings and crosslinked by 2% divinylbenzene with various alkylbromides depends on the structure of the alkylbromide, the swelling of the resins, the solvent polarity, the reaction temperature, and the molar ratio of the alkylbromide to the pyridine rings. 1,6-Dibromohexane is found to be much more reactive than 1-bromohexane. However, monofunctionalization is accompanied by additional crosslinking. The degree of additional crosslinking depends on the backbone swelling, the solvent polarity, the reaction temperature, and the molar ratio of pyridine rings to 1,6-dibromohexane.

INTRODUCTION

Chemical functionalization of polymer resins represents an interesting future direction for the preparation of new reagents, catalysts, separation media, etc. [1, 2]. On the other hand, it is believed that solid-phase synthesis provides isolation of reactive sites, offering an alternative to the use of the high-dilution technique. The few available results for transformations of cross-

linked polystyrene resins with substrates where difunctionalization is possible have, on the contrary, demonstrated that a certain or even a complete degree of additional crosslinking of the polymer backbone could occur [3-9].

The change in the polymeric backbone structure, caused by additional crosslinking, can significantly influence the physical properties of the carrier, which may be reflected in the different behavior of the catalysts, the reagents, or the carriers for the separation media.

Crosslinked polystyrene beads have found a wide range of use, while crosslinked polyvinylpyridine or crosslinked copolymers of styrene and 4-vinylpyridine have received much less attention [10] in spite of the fact that pyridine, by itself or in conjunction with other reagents, has wide application. We now report our investigation of the behavior of crosslinked poly(styrene-4-vinylpyridine), containing 37-43% of pyridine rings, with mono- and dibromo-substituted alkanes.

EXPERIMENTAL

Material

Commercially available 1-bromohexane, 1-bromododecane, and 1,6-dibromohexane were distilled before use, and the solvents were purified and stored over Molecular Sieves [11]. Crosslinked poly(styrene-4-vinylpyridine) was prepared [12] and activated by the following procedure: The polymer beads were stirred in MeOH (T 50°C, t 2 h), NaOH (5%, T 50°C, t 2 h), washed with water, stirred in DMF (T 50°C, t 2 h), MeOH (T 50°C, t 2 h), and CHCl_3 (T 50°C, t 2 h), dried at room temperature for 19 h, and finally dried in vacuum at 80°C for 3 h. The amounts of pyridine rings were determined by combustion analysis. Resins, containing 37-43% pyridine rings, were used for further studies.

Reactions with 1-Bromohexane and 1-Bromododecane

Dry crosslinked poly(styrene-4-vinylpyridine) (containing 2 mmol pyridine rings, 2% crosslinking) was mixed with 8 mL solvent, left to swell at room temperature for 18 h, and thermostated for 1 h at a given temperature. Then solutions of different amounts of alkylhalide (3 mmol, 6 mmol, etc.) in 2 mL solvent was added and stirred for various times. 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 vacuum at 80°C for 3 h. The amount of ionic bromide was determined as follows [13]:

0.2 g of the sample was suspended in 30 mL of 50% water solution of acetic acid, 5 mL concentrated HNO_3 was added, and the suspension was potentiometrically titrated with 0.1 *N* AgNO_3 .

Reactions with 1,6-Dibromohexane

Reaction procedures were the same as for 1-bromohexane and 1-bromododecane. The amount of ionically bonded bromine was also determined in the same way, while the total amount of bromine, i.e., ionically and covalently bonded, was measured as follows [14]: 0.2 g sample was suspended in 4 mL pyridine, heated for 2 h at 100°C, cooled to room temperature, and then 6 mL DMF was added. The sample was cooled on ice before the slow addition of 6 mL HNO_3 and, after the addition of 10 mL distilled water, the suspension was potentiometrically titrated with 0.1 *N* AgNO_3 .

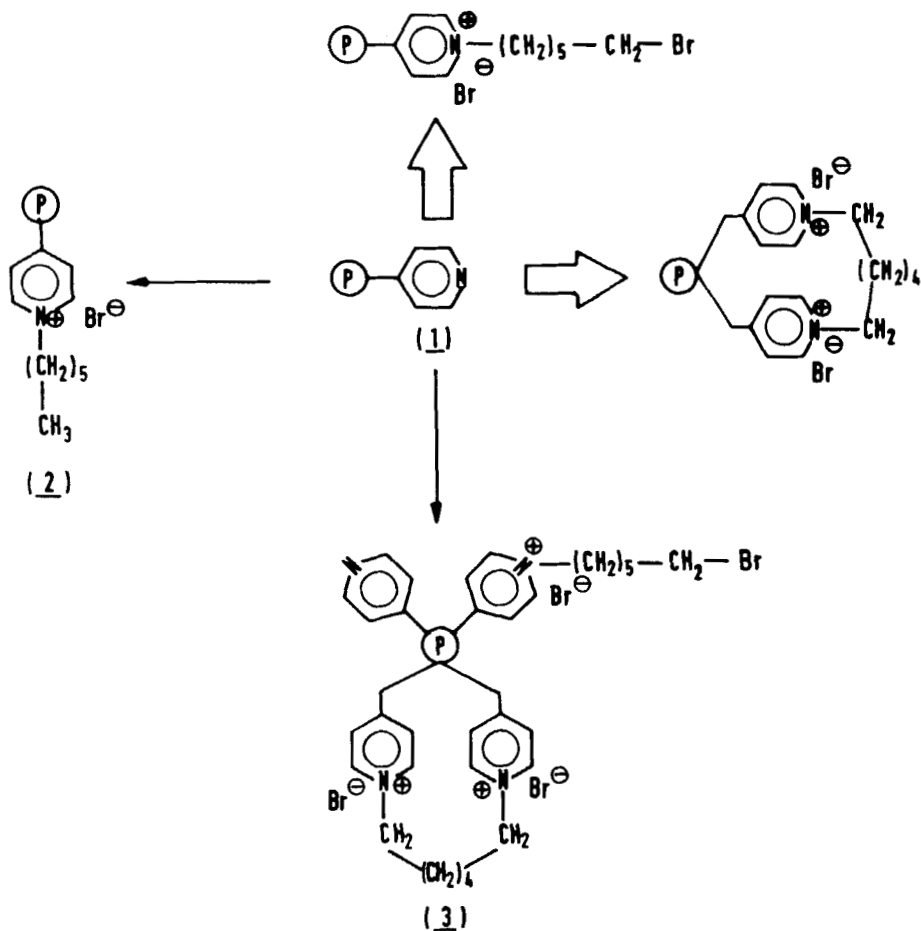
Swelling of the polymer beads was determined by the following procedure: 1-2 mL dry polymer resin was placed in a graduated cylinder, 5-10 mL solvent was added and, after 24 h, the volume of the swollen beads was measured ($q = V_{\text{swollen beads}}/V_{\text{dry beads}}$).

RESULTS AND DISCUSSION

Nucleophilic attack of the pyridine ring in various soluble polyvinylpyridines to alkylhalides has been studied by Boucher and coworkers [15], while Nishide and coworkers studied the complexation properties of polyvinylpyridine which was partly crosslinked by 1,4-dibromobutane [16]. Sherrington and Greig [17] found a behavior like Molecular Sieves for various crosslinked polystyrene-4-vinylpyridines. They studied reactions of copolymers with various degrees of crosslinking (5, 10, 20, 37%) with 2-(bromo-methyl)-naphthalene, 1-iodobutane, and 1-iodooctane in pentan-2-one, toluene, and heptane in detail by following the alkylhalide concentration changes in the reaction mixture, and found that kinetics were first order with respect to pyridine and 0.6 order with respect to alkylhalide [17].

Being interested in site-site interactions in crosslinked poly(styrene-4-vinylpyridine) by functionalization of pyridine rings with 1,6-dibromohexane, we first studied reactions with 1-bromohexane and 1-bromododecane. A degree of functionalization was followed by determining the amount of bromine anion bonded to the polymer resin, which was determined (after a series of washings of the products with solvents in order to remove all the unbonded alkylhalide from the polymer backbone) by potentiometric titration with

AgNO_3 in the presence of acetic acid and nitric acid [13]. In several cases the functionalization was also confirmed by determining the amount of nitrogen by combustion analysis. Pyridine rings in crosslinked poly(styrene-4-vinylpyridine) could be functionalized in two marginal ways: monofunctionalization or crosslinking (see Scheme 1). Two possible forms can be distinguished by comparing the amount of ionically bonded bromine to the total bromine content. In the monofunctionalized form, half of the total bonded bromine



SCHEME 1.

appears in ionic form, while in the crosslinked form all the bromine contained is bonded ionically. The amount of covalently and ionically bonded bromine was determined as before, but the products were heated for 2 h in pyridine at 100°C prior to potentiometric titration [14]. Conversion of covalently bonded bromine to the ionic form was confirmed also by an independent experiment with pyridine and 1,6-dibromohexane. In several cases the functionalization of the pyridine rings was also confirmed by nitrogen determination, 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 crosslinked poly(styrene-4-vinylpyridine) (**1**) contained 5.88% of nitrogen; in the monofunctionalized form the nitrogen content would be 2.9 and 3.89% in the completely crosslinked form for the reaction with 1,6-dibromohexane.

In the chemical transformation of the polymer backbone, the questions of the swelling of resins versus the polarity of the solvent arises. As solvents, dimethylformamide (DMF) is polar and swells crosslinked **1** very well, benzene is nonpolar but its swelling capacity is very similar to that of DMF, while in cyclohexane the polymer beads remain nearly unchanged compared to their dry state. The crosslinked **1** was prepared by suspension copolymerization in the presence of 2% divinylbenzene, activated in several solvents (Experimental Section), dried in vacuum, and the beads containing 37-43% pyridine rings were used for further studies. In a typical experiment an exact amount of dry **1** (containing 2 mmol pyridine rings) was suspended in 8 mL purified and dry solvent, the beads were swollen for 18 h at room temperature, then thermostated at the appropriate temperature for 1 h, and finally a certain amount of alkylhalide in 2 mL solvent was added. The reaction mixture was stirred for a given time, the solvent and excess halide filtered off, the polymer beads washed 5 times with the solvent used in the reaction and 10 times with methanol, then dried for 18 h at room temperature, pulverized, and analyzed after drying in vacuum at 80°C for 3 h.

The effect of the structure of the alkylating agent and the alkylhalide/pyridine molar ratio on the functionalization of **1** in DMF at 70°C is presented in Fig. 1. It is evident that the substrate with the longer chain reacted more slowly, but it is surprising that the reaction of **1** with 1,6-dibromohexane proceeded at a much higher rate than that with 1-bromohexane. Differences in reactivity became still more pronounced in solvents with different degrees of swelling capacity, and Fig. 2 shows the degree of functionalization of the pyridine rings in cyclohexane, benzene, and DMF after a 2-h reaction. The functionalization of pyridine rings in various solvents with 1-bromohexane at 70°C followed first-order kinetics (Fig. 3), while the effect of the solvent and reaction temperature is presented in Fig. 4.

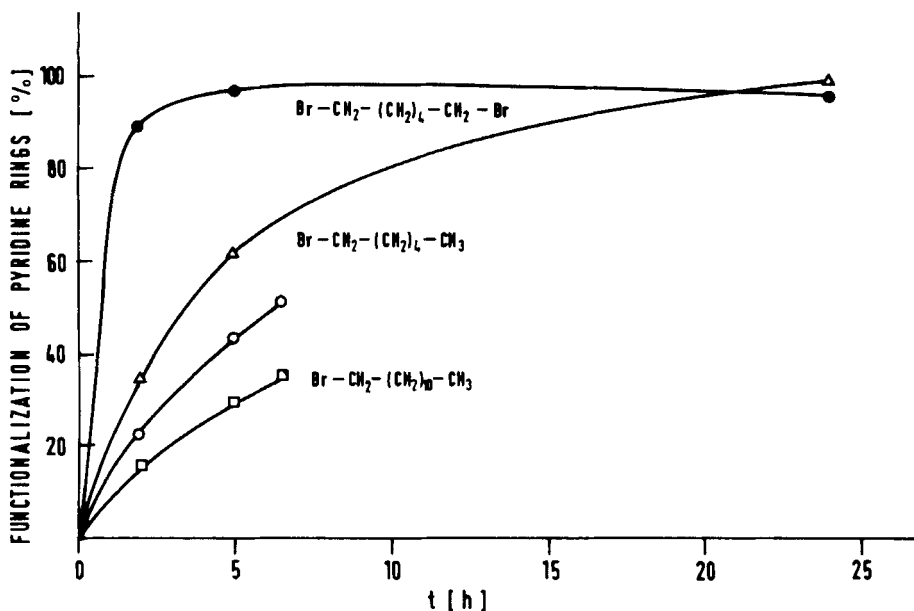


FIG. 1. Effect of the alkylating agent on the functionalization of pyridine rings in crosslinked poly(styrene-4-vinylpyridine) in DMF at 70°C with molar ratios of (●) 1,6-dibromohexane/pyridine = 3:1, (△) 1-bromohexane/pyridine = 3:1, (○) 1-bromohexane/pyridine = 1.5:1, (□) 1-bromododecane/pyridine = 1.5:1.

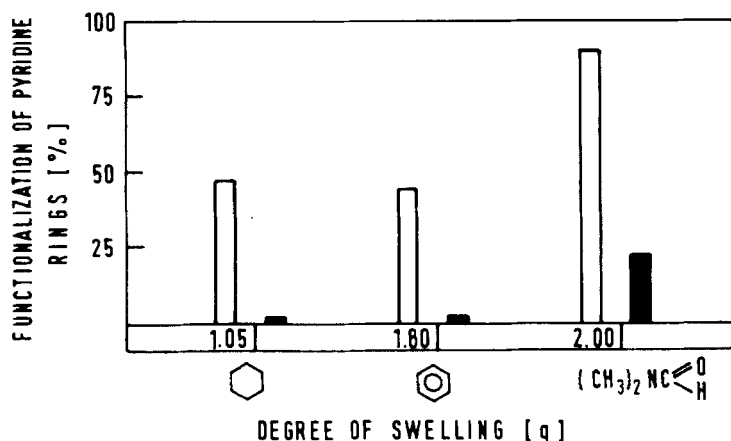


FIG. 2. Effect of swelling of resins and structure of the alkylating agent on the functionalization of pyridine rings in crosslinked poly(styrene-4-vinylpyridine) after 2 h of reaction at 70°C. Alkylating agent: pyridine molar ratio 3:1. (□) 1,6-dibromohexane; (■) 1-bromohexane. Solvents (left to right) cyclohexane, benzene, DMF.

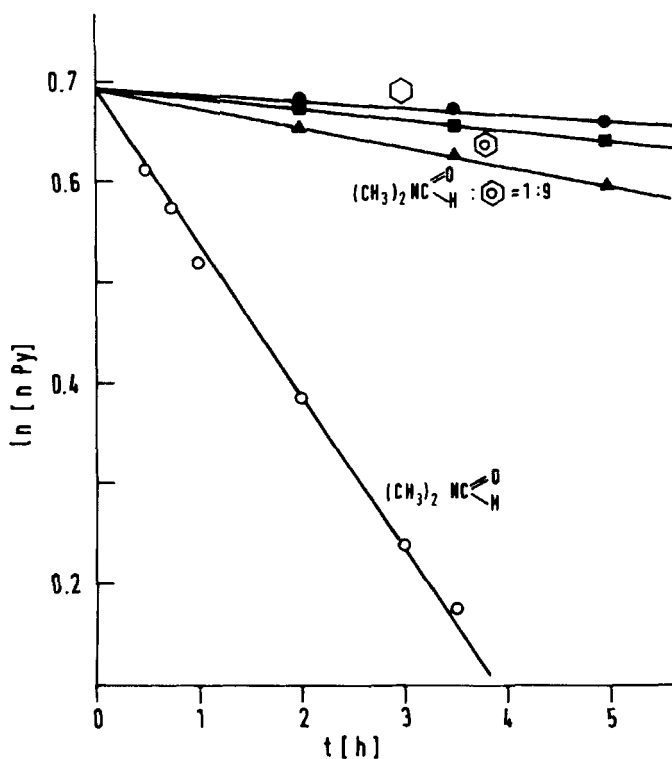


FIG. 3. Effect of solvent on the functionalization of pyridine rings (nPy = mmol unfunctionalized pyridine rings) in crosslinked poly(styrene-4-vinylpyridine) with 1-bromohexane at 70°C ($t = 0$; nPy , 2 mmol; $C_6H_{13}Br$, 3 mmol; solvent, 10 mL).

Further, we have studied the effect of the molar ratio of 1,6-dibromohexane/pyridine rings and the reaction time on the functionalization of pyridine rings, and special attention was paid to the degree of monofunctionalization and crosslinking (see Scheme 1). As is evident from Fig. 5, the reaction time does not play an important role in the functionalization of pyridine or the degree of crosslinking, while an increased amount of the alkylating agent increased the functionalization of the pyridine rings and completely changed the ratio of monofunctionalization to crosslinking, which was 5%/68% for a 1:1 molar ratio and 72%/26% when 1,6-dibromohexane was used as a solvent. Crosslinking was favored even more when 1,6-dibromohexane was added step-

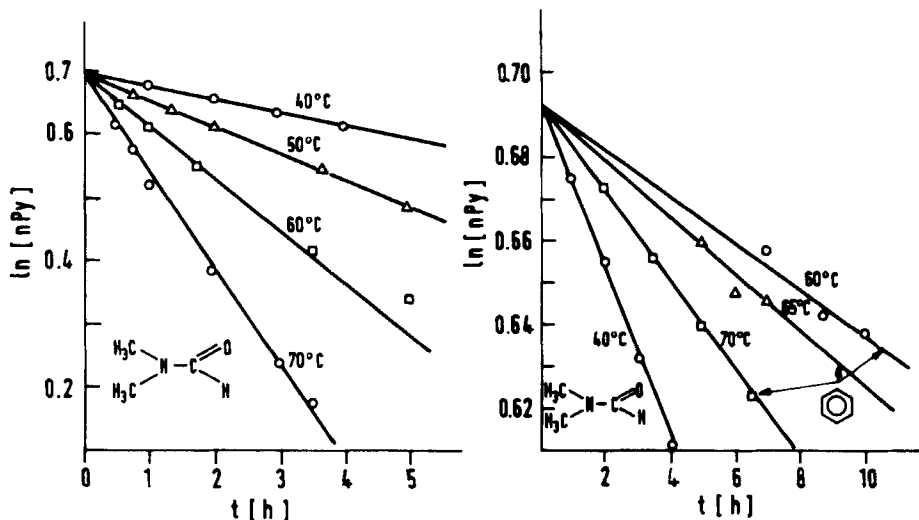


FIG. 4. Effect of solvent and temperature on the functionalization of pyridine rings (nPy = mmol unfunctionalized pyridine rings) in crosslinked poly(styrene-4-vinylpyridine) with 1-bromohexane ($t = 0$; nPy , 2 mmol; $C_6H_{13}Br$, 3 mmol; solvent, 10 mL).

wise in three portions until a molar ratio of 1:1 was reached, and after 6.5 h of reaction a 3%:84% monofunctionalization versus crosslinking ratio was established.

The effect of the reaction time and temperature on the conversion of pyridine rings, monofunctionalization, and crosslinking with 1,6-dibromohexane is presented in Fig. 6. After 24 h reaction in DMF, more than 96% conversion of pyridine rings was observed, while the ratio between monofunctionalization and the additional crosslinking was not influenced very much, and the following ratios were observed: T 40°C, 18:78; T 70°C, 27:68; T 110°C, 22:74. Contrary to the effect of temperature, the swelling of the polymer beads and the solvent polarity have a much greater influence on the degree of the functionalization and crosslinking, which is evident from Table 1.

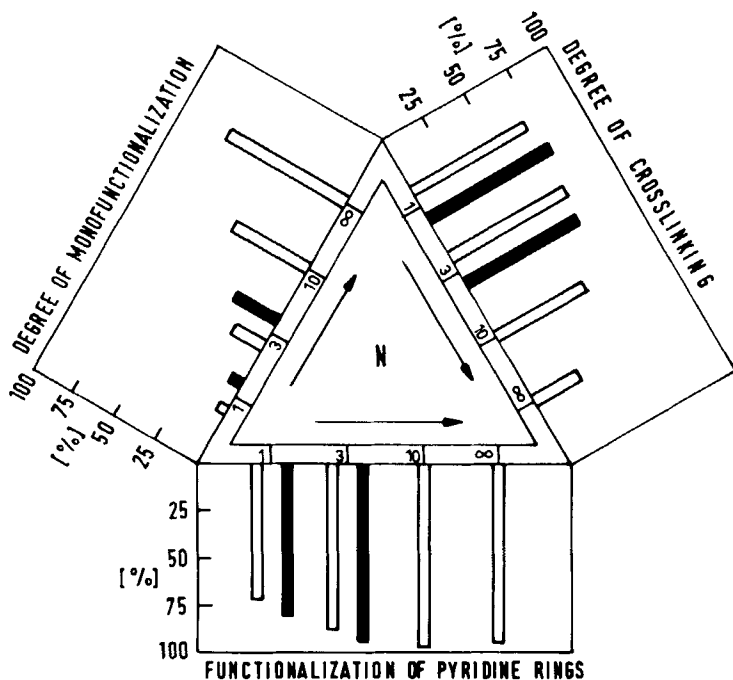


FIG. 5. Effect of reaction time and molar ratio of 1,6-dibromohexane/pyridine rings (abscissas) on the degree of additional crosslinking in (ordinates) crosslinked poly(styrene-4-vinylpyridine) in DMF at 70°C. (□) 2 h reaction, (■) 24-h reaction.

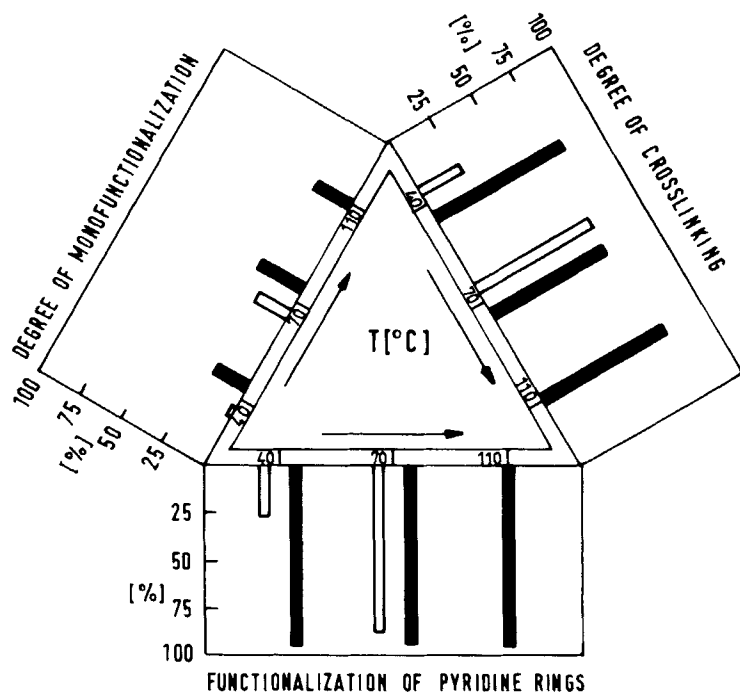


FIG. 6. Effect of reaction time and temperature (abscissas) on the degree of additional crosslinking (ordinates) by reaction of crosslinked poly(styrene-4-vinylpyridine) with 1,6-dibromohexane (molar ratio 1:3) in DMF: (□) 2-h reaction, (■) 24-h reaction.

TABLE 1. Effect of Swelling of Resins on the Degree of Additional Crosslinking by Reaction of Crosslinked Poly(Styrene-4-vinylpyridine) with 1,6-Dibromohexane^a

Solvent	Swelling	Functionalization of pyridine rings, %	Monofunction- alization, %	Crosslinking, %
Cyclohexane	1.05	52	6	46
Benzene	1.80	45	3	42
DMF	2.00	90	20	70
Br-(CH ₂) ₆ -Br	1.80	98	72	26

^aMolar ratio 1:3; reaction time 2 h at 70°C.

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