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THE SYNTHESIS OF POLYURETHANE WITH (ALKYLAMINO)PYRIDINE FUNCTIONS

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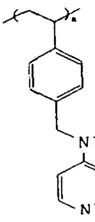
INTRODUCTION

4-(N,N-Dialkylamino)pyridines, as a supernuleophilic catalyst, can increase the rates of various acylation reaction by 10-10^4 times.[1] Therefore it was particularly fit for catalyzing the esterification involving secondary or tertiary alcohol with high steric hindrance and could be used extensively for making pharmaceutical products and in fine synthesis of organic compounds.

In 1982, following the method for preparing ion exchange resin, Shinkai et al. succeeded in linking alkylaminopyridine groups to chloromethylated polystyene (PS) (1). However, as the approachability of such a polymeric catalyst was marred by the hydrophobic property inherent in the backbone ofPS as a carbon chain polymer, the activity of such a catalyst is lower than that of some others of the same type and with low molecular weight compounds.[2] Hierl et al. succeeded in having alkylaminopyridine side-linked to polyethylenimines (2).[3] Verducci succeeded in inducing the side chains of amides(3).[4] In 1985, Klotz et al. succeeded in preparing polyamides by involving dicarboxylic ester containing alkylaminopyridine and diamines in a condensed polymerization reaction(4).[5] In 1991, Rubinsztajn et al. effected a cross-linkage of 4-(N,N-diallylamino)pyridine to polysiloxanes (5).[6] It is generally believed that the backbone of a hetero chain polymeris not so stable during a catalytic process as a carbon chain polymer. However, a catalytic process initiated by alkylaminopyridine as a highly efficient catalyst generally takes place at room temperature or in a rather mild environment. During the course of such a polymeric catalysts is in operation, the degradation of chain rupture could usually be neglected.



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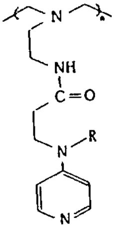

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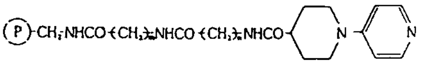

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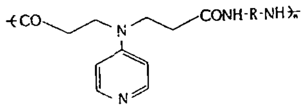

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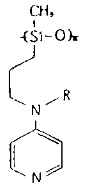

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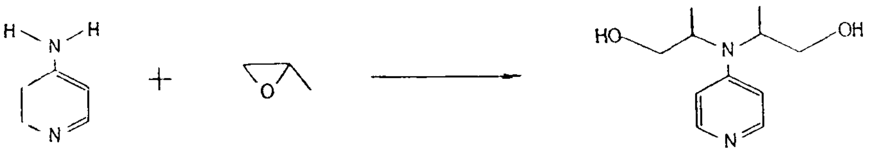
The focus of our research was preparing such a new kind of polyurethane possessing excellent solubility, chemical stability, and mechanical properties in order that alkylaminopyridine group could be linked to them. For this purpose we had a reaction in which 4-aminopyridine and epoxypropane were involved. This furnished each of the molecule of 4-aminopyridine with two hydroxyl groups, that is 4-[N,N-bis(1-methyl-2-hydroxylethyl)amino]pyridine (6, MHEAP).



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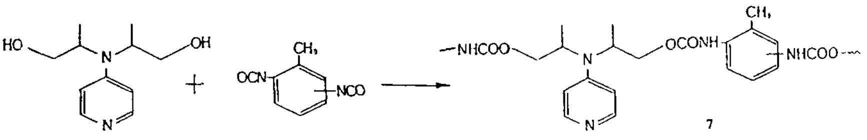
The reaction of MHEAP (6) and toluene diisocyanate (TDI) yielded linear polyurethane (7).



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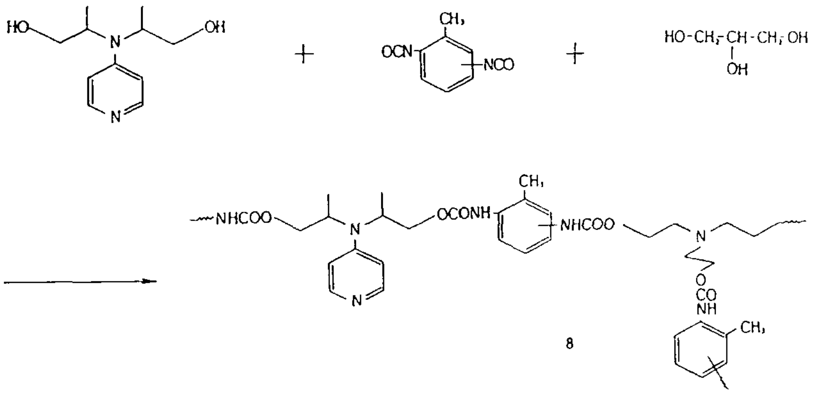
Further, we report here a synthesis of network polymer with alkylaminopyridine function(8). The synthesis involves the condensation polymerization of MHEAP with TDI and triethanolamine.



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EXPERIMENTAL

4-Aminopyridine was supplied by Sigma Chemical Co. For characterisation,FTIR model of Nicolet DX was used. ^{1}H-NMR, Brucker AC-P 200 was used. An element analyser PE-2400 model was used.

4-[N,N-Bis(1-methyl-2-hydroxylethyl)amino]pyridine (6): 34.8 g (0.6 mol) of epoxy propane, 1.5 mL of acetic acid, and 200 mL of water were mixed in a 100 mL four-necked flask. Then a solution of 18.8 g (0.2 mol) of 4-aminopyridine in 8 mL of N,N-dimethylformamide was slowly added by drops into the flask, within half an hour under the protection of nitrogen. After that the system was stirred and left to reflux at room temperature for 3 h.

The solution was left to condense in a rotatory evaporator. After that acetone was added and left to crystallize. The resultant solid matter was washed with ether before it was filtered and left to a vacuum drying. The final product was (29.8 g, 81% yield) of white solid matter. mp. 254-255℃ IR(KCl): 3300, 2905, 1600, 1519, 1478, 1406, 1196;NMR (CDCl$_3$): δ 1.12 (d, 6H), 2.50 (s, 2H), 3.89-4.01 (m, 2H), 4.18-4.27 (m, 4H), 6.85 (d, 2H), 8.20 (d, 2H);Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.85; H, 8.62; N, 13.30.

Linear Polyurethane (7): MHEAP was dissolved in a few N,N-dimethylformamide. Then its hydroxyl group number was determined by a testing. TDI with its isocyanate groups and hydroxyl groups being of the same mole number – was added by drops to the four-necked flask. After that the mixture was stirred at 60℃ for 3 h. The final product was a pink, viscose, soft matter. Yield 81%.

IR: 3405, 1650, 1598, 1513, 1150. Anal. Calcd for $C_{20}H_{24}N_4O_4$: C, 62.49; H, 6.29; N, 14.57. Found: C, 62.45; H, 6.30; N, 14.65.

Cross-linked Polyurethane (8): 18.4 g (0.1 mol) of MHEAP was dissolved in N,N-dimethylformamide. The solution was slowly added by drops to a 100 mL four-necked flask which contained a solution of 34.8 g (0.2 mol) ofTDI in DMF. The mixture was stirred for 2 h at 60℃. Then to the reaction system was added by drops 10.9 g (0.07 mol) of triethanolamine. After all the reactants were fully mixed in the flask, the mixture was poured into a container, there they were left to solidify at 80℃ for 3 h.

The solidified matter was pulverized before it was placed in a Soxhlet extractor to undergo a process of purification with alcohol for 10 h. The solid matter that had undergone a process of swelling was left to a vacuum drying. The final product was 60.2 g (94%) white solid matter.IR: 3309, 2951, 1647, 1601, 1519, 1230.

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