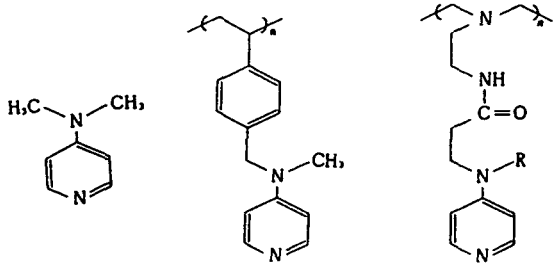
The Synthesis of Epoxide Resin with Alkylaminopyridine Functions

INTRODUCTION

Alkylaminopyridine compounds have been inviting extensive interest as highly efficient catalysts in relation to acylation reactions since Litvinenko and Kirichenko[1] discovered in 1967 the highly efficient catalytic activity 4-(*N,N*-dimethylamino)pyridine (**1**, DMAP) possessed toward the acylation reaction. In the 1980s, Shinkai et al.[2] succeeded in linking alkylaminopyridine groups to polystyrene (**2**) for the purpose of facilitating the separation process and ensuring the repeated usage of such catalysts.



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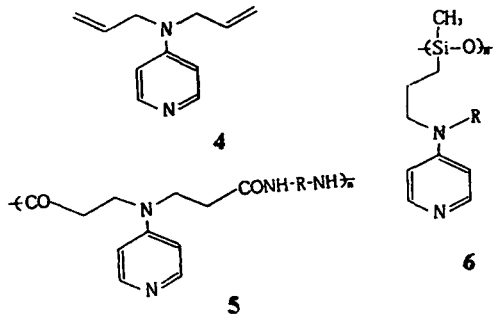
Afterward, Delaney et al.[3] succeeded in grafting the catalytic groups to polyethylenimines (**3**). Then, Mathias et al.[4] succeeded in preparing 4-(*N,N*-diallylamino)pyridine (**4**, DAAP) and in obtaining its polymeric compounds. Now what remained crucial was to have its macromolecular backbone endowed with an appropriate degree of hydrophilicity and lipophilicity so as to increase the affinity between catalysts and the reaction system undergoing the catalytic process. In 1985, Klotz et al.[5] succeeded in preparing polyamide containing alkylaminopyridine groups (**5**). In 1991, Rubinsztajn et al.[6] succeeded in preparing polysiloxanes containing the DAAP structure (**6**):



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We intended to synthesize a new kind of epoxide resin containing alkylaminopyridine groups. This meant bringing about a reaction involving 4-aminopyridine and epoxychloropropane, both being of the equimolar number. The final yield was linear epoxide resin of the aromatic amine type (**7**):

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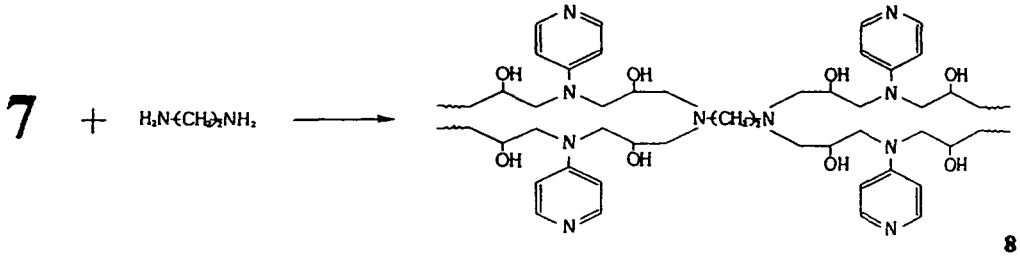
Then, a crosslinked polymer was effected by involving multiamines; this gave epoxide resin of a network structure (**8**):



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The polymeric supernucleophilic reagent that we intended to synthesize, which possessed remarkable approachability and was capable of being repeatedly used, was prepared, as a result of utilization of the great strength, chemical stability, and hydrophilicity which is inherent in the hydroxyl groups contained in the structure of the resin.

EXPERIMENTAL

The 4-aminopyridine was supplied by Sigma Chemical Co. As a means of representation, the FTIR of the Nicolet 5 DX Model was adopted for effecting the analysis of functional groups. ^{1}H-NMR spectra were recorded on a Bruker AC-P 200 Model spectrometer. The C, H, and N analyses were achieved on an elemental analyzer, the PE-2400 Model.

Linear Poly(AP-*co*-ER)

Epoxychloropropane, 20.35 g (0.22 mol), was added to a 100 mL four-necked flask which contained a solution of 20.00 g (0.21 mol) of 4-aminopyridine in *N,N*-dimethylformamide. The contents of the flask were stirred to make them fully mixed. Then, 40 mL of 15% NaOH solution was added to the flask. The reaction system proceeded at room temperature for 2 h under the protection of nitrogen. Then, the surplus epoxychloropropane was evaporated. After that, the temperature of the reaction system was raised to 80°C and the reaction was carried on for 4 h.

The contents of the flask were condensed in a rotatory evaporator. The residual fluid was now dissolved in methanol, and anhydrous $MgSO_4$ was added to the solution. Then, the solution was put aside for the night. After that, the solution was filtered. The filtrate was poured into acetone and left to precipitate. The final product was 38.10 g (in a 96% yield) of white powder. IR: 3420, 2941, 1598, 1507, 1206 cm^{-1}. ^{1}H-NMR(D_2O): δ 2.89 (m, 4H), 3.64–4.17 (m, H), 6.87 (d, 2H), 8.00 (d, 2H).

ANAL: Calcd for $C_8H_{10}N_2O$: C, 64.00%; H, 6.67%; N, 18.67%.
Found: C, 64.03%; H, 6.68%; N, 18.70%.

Crosslinked Poly(AP-*co*-ER)

First, the epoxide number of linear poly(AP-*co*-ER) was taken. The aqueous solution of ethylenediamine and linear poly(AP-*co*-ER), both being of the same mole number, were mixed in accordance with the epoxide number. The mixture was stirred violently at room temperature until the vicosity in the reaction system obviously rose. Then, the vicose fluid was poured into a container and left to ripen at 80°C for 6 h. The resultant yield was solid matter.

The solid matter underwent a process of extraction with methanol for 10 h. The extracted matter was left to vacuum drying. The final product was a yellowish solid matter (in a 95% yield). IR: 3424, 2928, 1603, 1509, 1213 cm^{-1}.

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JINGWU SUN[1,*]
JITAO HUANG[2]
JIAQI ZHANG[2]
SIHUA ZHENG[2]

[1]Department of Applied Chemistry
Tianjin University
Tianjin 300072
People's Republic of China
[2]Department of Chemical Engineering
Tianjin Institute of Technology
Tianjin 300191
People's Republic of China

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* To whom correspondence should be addressed.