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Synthesis and polymerization of diallylaromatic amines as supernucleophilic reagents

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4-(*N,N*-Diallylamino)pyridine (DAAP) and *N,N*-diallylaminobenzene (DAAB), each having only a single diallylamino group, and *N,N,N′,N′*-tetrallyl-4,4′-diaminobenzidine (AAB), *N,N,N′,N′*-diaminodiphenylsuflone (AABS) and *N,N,N′,N′*-tetrallyl-4,4′-diaminodiphenyl ether (AABE), each of which has two diallylamino groups, were prepared by means of *N*-alkylation reaction involving aromatic amines and allyl chloride in the presence of a phase-transfer catalyst. Linear poly(DAAP), poly(DAAP-*co*-DAAB) and network poly(DAAP-*co*-AAB), poly(DAAP-*co*-AABS) and poly(DAAP-*co*-AABE), all being polymers containing supernucleophilic groups, were synthesized by cyclopolymerization and copolymerization.

(Keywords: polymer catalyst; diallylaromatic amines; *N*-allylation; cyclopolymerization)

INTRODUCTION

4-(*N,N*-Dialkylamino)pyridines are efficient and universal catalysts for acylation reactions that have aroused much interest in the synthesis of pharmaceuticals, polymers and fine chemicals. Thus, in 1967 Litvinenko and Kirichenko discovered that the activity of 4-(*N,N*-dimethylamino)pyridine (**1**, DMAP) was 10^3 times higher than that of conventional pyridine catalysts[1]. In 1969 Steglich and Hofle showed that the catalytic activity of 4-pyrrolidinopyridine (**2**, PPY) was even higher than that of DMAP[2]. Subsequently, alkylaminopyridine, as a supernucleophilic catalyst, has been applied to scores of different organic reactions such as acylation, hydrolysis, isomerization, alkylation and silylation.

In 1986 Mathias obtained 4-(*N,N*-diallylamino)pyridine (**3**, DAPP) by reaction of 4-chloropyridine with diallylamine[3]. Results from Butler's research[4] indicate that diallylamine compounds, as monomers with a low activity of polymerization, are in a position to undergo cyclopolymerization. Therefore, under the action of a water-soluble azo initiator, DAAP can undergo not only homopolymerization (**4**) but also copolymerization with other monomers. Catalytic tests have shown that the polymers of DAAP possess a more powerful catalytic activity than PPY, and can be counted as one of the alkylaminopyridine catalysts with the greatest activity found so far[5].

All commercial polymeric catalysts, however, must be capable of being readily separated from the reaction systems for repeated use. This requires that such polymeric catalysts should be network macromolecules characterized by their tendency to swell rather than to dissolve. In the work reported in this paper, we addressed ourselves to finding a method for effecting *N*-alkylation by means of a phase-transfer reaction; 4-aminopyridine was reacted with allyl chloride in the presence of a phase-transfer catalyst to give DAAP.

The monomers *N,N*-diallylaminobenzene (**5**, DAAB), *N,N,N′,N′*-tetrallyl-4,4′-diaminobenzidine (**6**, AAB), *N,N,N′,N′*-tetrallyl-4,4′-diaminodiphenylsulfone (**7**, AABS) and *N,N,N′,N′*-tetrallyl-4,4′-diaminodiphenyl ether (**8**, AABE) were obtained in a similar way.

The copolymer poly(DAAP-*co*-DAAB) (**9**) has been prepared, along with crosslinked polymers containing supernucleophilic PPY structure resulting from the copolymerization between DAAP and AAB, AABS and AABE (**10–12** respectively).

EXPERIMENTAL

General

With tetrabutyl ammonium chloride as a phase-transfer catalyst, reaction of allyl chloride and any of the various aromatic amine compounds yielded monomers. The cyclopolymerization was initiated by 2,2′-azobis(2-amidinopropane)hydrochloride (V-50), a water-soluble initiator. Structural identification was carried out by means of Fourier transform infra-red spectroscopy (*FT*i.r.) (Nicolet 205 spectrometer), ^{1}H nuclear magnetic resonance spectroscopy (n.m.r.) (Brucker AC-P 200 spectrometer) and elemental analysis (PE-2400 instrument).

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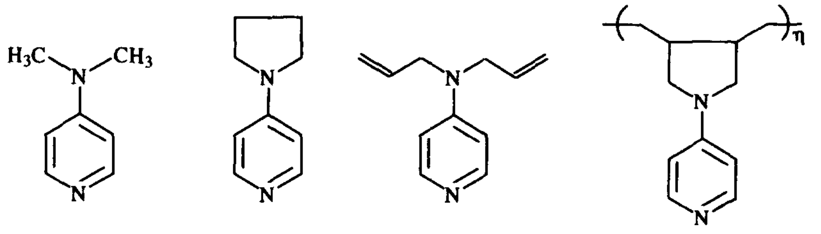
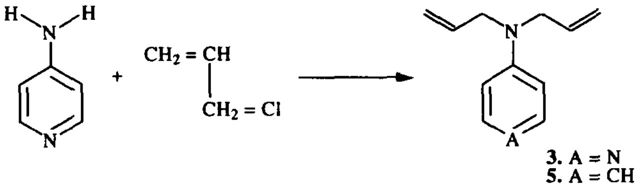


1 2 3 4

Scheme 1

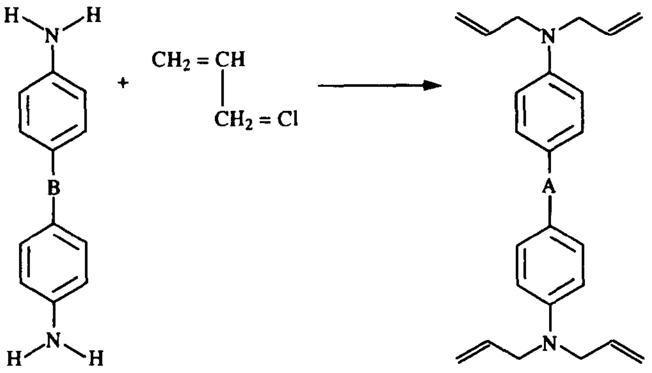


3. A = N
5. A = CH

Scheme 2

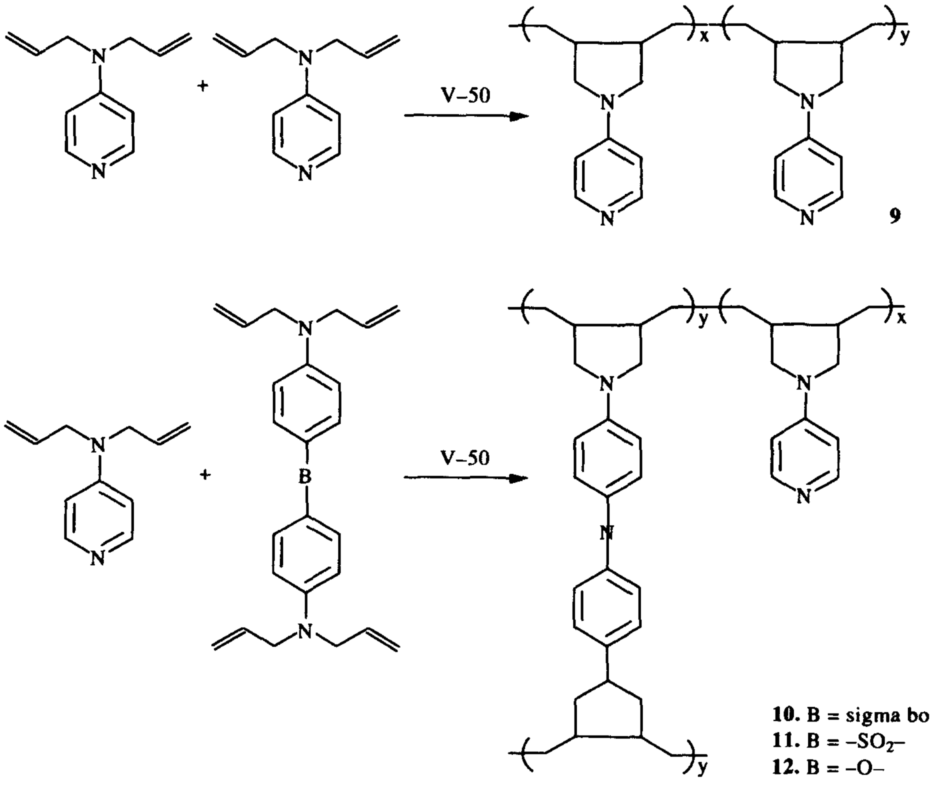
*Preparation of 4-(*N,N*-diallylamino)pyridine* (**3**)

A mixture of 4-aminopyridine (5.00 g, 0.053 mol), allyl chloride (16 ml) and a small quantity of KI was placed in a four-necked flask which contained saturated aqueous KOH (30 ml), the flask was heated gently before tetrabutyl ammonium chloride (1 ml of 50% solution) was added, then the mixture was stirred for 15 h at room temperature. The contents of the flask were treated with NaCl and the upper organic layer separated and dried with anhydrous $MgSO_4$ overnight. After filtration,



6. B = empties
7. B = $-SO_2-$
8. B = -O-

Scheme 3



9

10. B = sigma bond
11. B = $-SO_2-$
12. B = -O-

Scheme 4

reduced pressure distillation gave a yellowish liquid (4.35 g, 47%) which turned red on standing. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.80; H, 8.10; N, 16.11.

Preparation of N,N-*diallylaminobenzene* (**5**)

Freshly distilled aniline (5.00 g, 0.054 mol), allyl chloride (17 ml), saturated aqueous KOH solution (30 ml) and a small quantity of KI were mixed in a four-necked flask at low temperature and tetrabutyl ammonium chloride (1 ml of 50% solution) was added. The mixture was stirred vigorously at room temperature for 10 h before treatment with NaCl. The upper organic layer was separated and dissolved in acetone prior to filtration to remove all solid residues. The filtrate was dried overnight by anhydrous $MgSO_4$, filtered to remove $MgSO_4$ and distilled under reduced pressure. The liquid obtained from the distillation was separated by column chromatography (methanol/toluene eluent, 3:8) to give a red liquid (5.95 g, 64%). Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.20; H, 8.74; N, 8.06.

Preparation of N,N,N′,N′-*tetrallyl-4,4′-diallylamino-benzidine* (**6**)

Benzidine (6.00 g, 0.033 mol), a small quantity of KI and allyl chloride (10 ml) were mixed in a four-necked flask and gently heated before the mixture was placed in saturated aqueous KOH (20 ml). Tetrabutyl ammonium chloride (1 ml of 50% solution) was added and the mixture was stirred at room temperature for 10 h. The upper organic part of the liquid was separated and dissolved in ether prior to filtration to remove the insoluble matter. After evaporation of the ether, the residual liquid was separated by column chromatography on an alkaline Al_2O_3 column using alcohol/toluene in the ratio of 7:8 as eluent. After that, the liquid was dried to give the final product as a brownish red, viscous liquid (60% yield). Calcd for $C_{24}H_{28}N_2$: C, 83.68; H, 8.19; N, 8.13. Found: C, 83.71; H, 8.20; N, 8.17.

Preparation of N,N,N′,N′-*tetrallyl-4-4′-diamino-diphenyl sulfone* (**7**)

4,4′-Diaminodiphenyl sulfone (10.00 g, 0.040 mol), allyl chloride (15 ml), saturated aqueous KOH (30 ml), tetrabutyl ammonium chloride (1.5 ml of 50% solution) and a small quantity of KI were mixed in a four-necked flask. The contents of the flask were stirred vigorously at room temperature for 15 h and then filtered. The filtrate was washed repeatedly with saturated KOH solution and then dried. The dried matter was dissolved in acetone and the resulting solution was filtered. The filtrate was mixed with water which caused precipitation of a solid. The precipitates were recovered by filtration. The filter cake was repeatedly rinsed with water. The whole operation was repeated many times. The residue was dried under vacuum to give a yellowish powder as the final product (8.55 g, 52%). Calcd for $C_{24}H_{28}N_2O_2S$: C, 70.56; H, 6.91; N, 6.86. Found: C, 70.52; H, 6.92; N, 6.82.

Preparation of N,N,N′,N′-*tetrallyl-4,4′diaminodiphenyl ether* (**8**)

4,4′-Diaminodiphenyl ether (5.00 g, 0.025 mol), allyl chloride (8 ml), benzene (5 ml), saturated aqueous KOH (20 ml), tetrabutyl ammonium chloride (1 ml of 50% solution) and a small quantity of KI were mixed in a four-necked flask and mixture was stirred vigorously at room temperature for 10 h. After removal of water and excess allyl chloride, the residual liquid was dissolved in boiling acetone/water (2:1), the solution was filtrated while hot and left to crystallize. The operation specified above was repeated before the product was dried under vacuum. The final product was a white powder (6.12 g, 69%). Calcd for $C_{24}H_{28}N_2O$: C, 79.96; H, 7.83; N, 7.77. Found: C, 79.92; H, 7.79; N, 7.74.

Synthesis of poly(DAAP) (**4**)

In a sealed reactor DAAP (5.00 g, 0.029 mol), 15% hydrochloric acid (8 ml) and V-50 (0.1 g) were mixed at 0°C. Before the reaction system was sealed, nitrogen was bubbled through the mixture. Then it was stirred at 60°C for 10 h. A further portion of V-50 (0.1 g) was added and, after nitrogen purging, the reaction was continued for 10 h. The mixture in the flask was washed three times with a 5% aqueous NaOH solution before it was dissolved in alcohol. After filtration, the mixture was added to ether to precipitate the product. The operation specified above was repeated three times prior to vacuum drying. The final product was a reddish brown solid (3.9 g, 78%). Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.78; H, 8.13; N, 16.12.

*Synthesis of poly(DAAP-*co*-DAAB)* (**9**)

DAAP (5.00 g, 0.29 mol) and DAAB (4.97 g, 0.029 mol) were mixed in a sealed reactor and cooled. Aqueous hydrochloric acid solution (15 ml of 15% solution) was added to the mixture at 0°C, followed by V-50 (0.02 g). The mixture was purged with nitrogen for 10 min before the reaction system was sealed. The mixture was then heated at 60°C for 10 h, and V-50 (0.02 g) was added. The process specified above was repeated three times. Then the mixture was washed three times with 5% aqueous NaOH solution and three more times with water. The solid matter thus obtained was dissolved in *N,N*-dimethylformamide, then the solution was filtered and poured into water to precipitate the product. The operation specified above was repeated three times prior to vacuum drying. The final product was a deep brown solid (7.49 g, 82%). Calcd for $C_{23}H_{29}N_3$: C, 79.50; H, 8.41; N, 12.09. Found: C, 79.46; H, 8.42; N, 12.13.

*Synthesis of poly(DAAP-*co*-AAB)* (**10**)

An equimolar mixture of DAAP and AAB was dissolved in a limited amount of *N,N*-dimethylformamide. The rest of the conditions for reaction were the same as for the synthesis of **9** (above). The mixture was washed with 5% aqueous NaOH three times. After filtration, the insoluble matter was placed in a Soxhlet extractor, extracted with alcohol for 10 h and then dried in a vacuum system. The final product was a brown solid (79% yield). Calcd for $C_{35}H_{42}N_4$: C, 81.04; H, 8.16; N, 10.80. Found: C, 80.99, H, 8.15; N, 10.85.

The solid was degraded at 250°C under N_2. The degraded residues were dissolved in alcohol, precipitated by petroleum ether and dried in vacuum. I.r. (ν, cm^{-1}): 1592, 1510, 1331, 900, 812.

Table 1 Spectroscopic characterization of the monomers

Monomer	*FT*i.r. (ν, cm^{-1})	N.m.r. (δ, ppm)
DAAP	1645, 1599, 1518, 1229, 989, 804	3.83 (d,4H), 5.19 (q,4H), 5.91 (m,2H), 7.86 (m,2H), 8.12 (m,3H)
DAAB	1642, 1601, 1504, 1317, 991, 804	3.79 (d,4H), 5.18 (q,4H), 5.89 (m,2H), 6.74 (m,3H), 7.15 (m,2H)
AAB	1641, 1611, 1506, 1386, 991, 806	3.92 (d,8H), 5.14 (q,8H), 5.82 (m,4H), 6.70 (m,4H), 7.30 (m,6H)
AABS	1642, 1609, 1501, 1314, 1146	2.50 (d,3H), 5.37 (q,8H), 5.99 (m,4H), 6.59 (m,4H), 7.45 (m,6H)
AABE	1643, 1590, 1500, 1223, 1022	3.31 (d,8H), 5.14 (q,8H), 5.75 (m,4H), 6.30 (m,6H), 7.02 (m,4H)

*Synthesis of poly(DAAP-*co*-AABS)* (**11**)

An equimolar mixture of DAAP and AABS were mixed in a limited amount of *N,N*-dimethylformamide. The reaction of and the refining process were the same as those used for the synthesis of **10** (above). The final product was a yellow solid (80% yield). Calcd for $C_{35}H_{42}N_4O_2S$: C, 72.13; H, 7.26; N, 9.61. Found: C, 72.10; H, 7.26; N, 9.60.

The solid was degraded at 250°C under N_2. The degraded residues were dissolved in alcohol, precipitated by petroleum ether and dried in vacuum. I.r. (ν, cm^{-1}): 1598, 1510, 1314, 1146, 904.

*Synthesis of poly(DAAP-*co*-AABE)* (**12**)

A small quantity of *N,N*-dimethylformamide was added to an equimolar mixture of DAAP and AABE. The reaction and purification were the same as those for the synthesis of **10** (above). The final product was a yellow solid (75% yield). Calcd for $C_{35}H_{42}N_4O$: C, 78.61; H, 7.92; N, 10.49. Found: C, 78.64; H, 7.94 N, 10.53.

The solid was degraded at 250°C under N_2. The degraded residues were dissolved in *N,N*-dimethylformamide, precipitated by petroleum ether and dried in vacuum. I.r. (ν, cm^{-1}): 1585, 1510, 1223, 1022, 896.

RESULTS AND DISCUSSION

According to our method, contrary to that of Vaidya and Mathias[6] 4-aminopyridine is used as a nucleophilic reagent to attack the substrate allyl chloride. 4-Aminopyridine is a rather weak nucleophile, the reaction involving 4-aminopyridine and allyl chloride failed to take place in 7 days. However, when we dissolved 4-aminopyridine in allyl chloride, an organic phase was formed. When saturated aqueous KOH was used as the aqueous phase, reaction was brought about in the presence of tetrabutyl ammonium chloride as a phase-transfer catalyst. The reaction was promoted by KI. The monomers can be obtained by vigorous stirring of the reactants at room temperature.

Moreover, the DAAP and poly(DAAP) we have synthesized are completely identical with those synthesized by Mathias *et al.* as determined by i.r. analysis (see *Table 1*). The i.r. spectra of all the monomers show a double-bond stretching vibration in the 1650–1640 cm^{-1} region. The existence of benzene rings or pyridine rings was confirmed by the band at 1610–1500 cm^{-1}. The peak at 1314 cm^{-1} was characteristic of the sulfone group, with peaks at 1223 and 1022 cm^{-1} indicating ether bonds. There was no sign of the existence of absorption bands due to N–H stretching vibration in the 3400–3250 cm^{-1} region.

The efficiency of the synthesis was in the order AABE > DAAB > AAB > AABS > DAAP. The electron effect of the linking group B between the two anilines exerted an influence on the *N*-alkylation reaction involving amine compounds and allyl chloride. When the group B was an electron-attracting group, the nucleophilicity of the aromatic amines was so reduced as to make allylation very difficult. However, when the group B was an electron-donating group, the allylation reaction was facilitated.

In the presence of a phase-transfer catalyst, the *N*-allylation reaction involving an aromatic amine and a halogenated hydrocarbon is reversible. The halides produced in the reaction have to enter a water phase to become separated from the reaction product. Even with the halides removed in such a way there are still by-products as a result of partial reaction. Additional side reactions, such as the oxidation reaction of amines, are also possible. These problems require elaborate and complex purification protocols as described in the Experimental section. The diallylamine compounds described here can undergo cyclopolymerization, copolymerization and crosslinking with other monomers. The diallylamine monomers used in this work are usually protonated with hydrochloric acid before they are initiated with V-50 to start a cyclopolymerization reaction, the reaction is slow and the concentration of monomers has to remain low to ensure the formation of rings.

I.r. spectroscopic analysis of the copolymers indicates the existence of absorption bands at 1600–1585 cm^{-1} and 900 cm^{-1}, this confirming the existence of benzene rings or pyridine rings. There is no peak in the region of 1670–1640 cm^{-1}, which testifies to that fact that the double bonds have been consumed. Poly(DAAP-*co*-AABS) shows strong absorptions at 1314 and 1146 cm^{-1}, demonstrating the existence of the sulfone unit. Poly(DAAP-*co*-AABE) exhibits peaks at 1223 and 1022 cm^{-1}, confirming the existence of ether links in the polymer.

Elemental analysis and calculations based on n.m.r.[8] show that when an equimolar mixture of DAAP and styrene (St) is copolymerized, the mole ratio of the two structural units in the resulting polymer is St/DAAP = 23:1. Thus, the polymerizing reactivity of DAAP is much lower than that of styrene. However, when equimolar amounts of the monomers DAAP and DAAB are copolymerized, the composition of the polymer was DAAP/DAAB = 5.5:1.

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