

Monomers and Polymers of 4-(*N,N*-Diallylamino)pyridine Functions

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ABSTRACT: 4-(*N,N*-Diallylamino)pyridine (DAAP), *N,N*-diallylaminobenzene (DAAB), *N,N,N',N'*-tetrallyl-4,4'-diaminobenzidine (AAB), *N,N,N',N'*-tetrallyl-4,4'-diaminodiphenyl sulfone (AABS), and *N,N,N',N'*-tetrallyl-4,4'-diaminodiphenyl ether (AABE) were prepared by sodium substitution and *N*-allylation. Moreover, linear polyDAAP, 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 in the cyclopolymerization. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 363–367, 2000

Key words: 4-(*N,N*-Dimethylamino)pyridine; 4-(*N,N*-diallylamino)pyridine; supernucleophilic agent

INTRODUCTION

4-(*N,N*-Dialkylamino)pyridines are effective as supernucleophilic catalysts in a wide range of organic reactions including acylation, esterification, silylation, and related reactions.^{1,2} In 1979, while doing a research on benzylation kinetics of benzyl alcohol, Litvinenko et al.³ discovered that 4-(*N,N*-dimethylamino)pyridine (**1**, DMAP) has an activity 3.7×10^4 higher than that of pyridine. In 1986, Mathias⁴ obtained the monomer 4-(*N,N*-diallylamino)-pyridine (**2**, DAAP) by attacking 4-chloropyridine with diallylamine. Then, the homopolymer (**3**) and several copolymers of DAAP were prepared on the basis of the results from Butler's cyclopolymerization.⁵ In 1991, Rubinsztajn et al. succeeded in grafting DAAP to polysiloxanes (**5**).⁶ Vaidya and Mathias proved that a polymer with a 4-pyrrolidinopyridine (**4**, PPY)

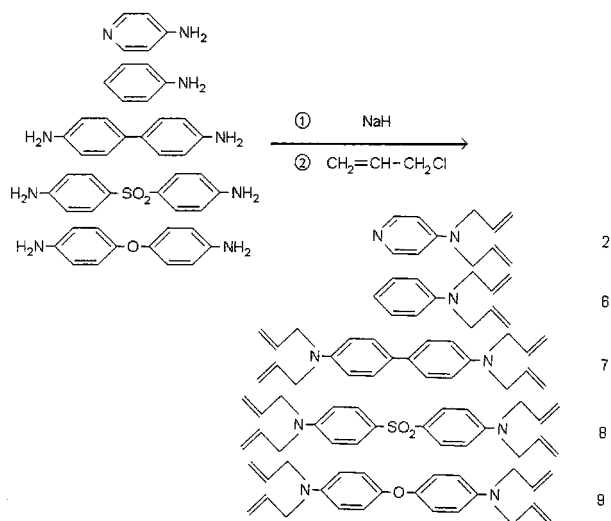
structure possesses higher catalytic activity than that of the compound PPY.⁷

Commercial polymeric catalysts are products which are easily separated from a reaction system and are capable of repeated use. This entails a network structure to exist in a polymer such as would allow it only to swell rather than dissolve in good solvent. We reported a new method which differs from that of Mathias' and have, likewise, succeeded in producing DAAP through *N*-allylation, which is a reaction involving 3-chloropropene and sodio 4-aminopyridine.⁸ Now, by using sodium substitution and *N*-allylation, several monomers, *N,N*-diallylaminobenzene (DAAB) (**6**), *N,N,N',N'*-tetrallyl-4,4'-diaminobenzidine (AAB) (**7**), *N,N,N',N'*-tetrallyl-4,4'-diaminodiphenyl sulfone (AABS) (**8**), and *N,N,N',N'*-tetrallyl-4,4'-diaminodiphenyl ether (AABE) (**9**), were also prepared (Scheme 1).

The benzene ring present in the copolymer poly(DAAP-*co*-DAAB) (**10**) is in a position to be attached to other functional groups (Scheme 2). Poly(DAAP-*co*-AAB) (**11**), poly(DAAP-*co*-AABS) (**12**), and poly(DAAP-*co*-AABE) (**13**), as cross-

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Scheme 1

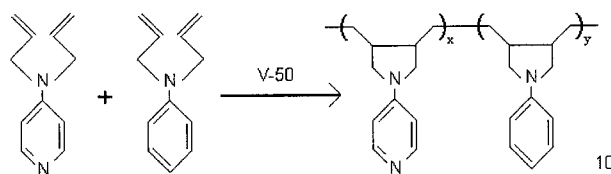
linked polymers, can be obtained in the copolymerization (Scheme 3).

EXPERIMENTAL

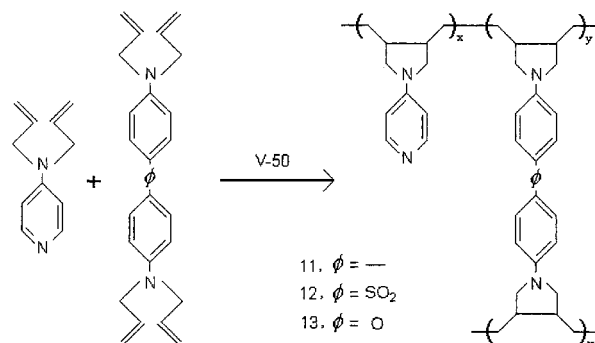
4-Aminopyridine was supplied by the Sigma-Aldrich WI, USA Chemical Co. Tetrahydrofuran (THF) was dried and distilled from sodium/benzophenone before use. The cyclopolymerization reaction was initiated by water-soluble 2,2'-azobis(2-amidinopropane)hydrochloride (**V-50**) as an initiator. IR spectra were recorded on a Nicolet 205 infrared spectrometer. $^1\text{H-NMR}$ spectra were recorded at 200 MHz on a Bruker AC-P200 spectrometer. A PE-2400 model elemental analyzer was used for the C, H, and N analyses.

4-(*N,N*-Diallylamino)pyridine (**2**, DAAP)

Crude NaH (60 wt % in mineral oil) was placed and washed with hexane twice to remove the mineral oil. To a solution of 9.4 g (0.1 mol) of 4-aminopyridine in 60 mL of THF under nitrogen at room temperature was added 8.0 g (0.2 mol) of



Scheme 2



Scheme 3

NaH. The mixture was stirred until the evolution of hydrogen was complete. A solution of 15.4 g (0.2 mol) of 3-chloropropene in 20 mL of THF was added dropwise to the mixture at 0°C and the mixture was refluxed under a nitrogen atmosphere for 5 h, filtered, and evaporated. The product was purified by fractional distillation under reduced pressure to give 11.1 g of **2** (in a 64% yield) as a yellowish or bright red liquid.

ANAL. Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2$: C, 75.82%; H, 8.10%; N, 16.08%. Found: C, 75.81%; H, 8.11%; N, 16.06%.

IR: 1652, 1607, 1523, 1239, 993, 805 cm^{-1} . NMR (CDCl_3 , 200 MHz) δ : 3.87(d, 4H), 5.23(q, 4H), 6.06(m, 2H), 7.90(m, 2H), 8.18(m, 3H).

N,N-Diallylaminobenzene (**6**, DAAB)

DAAB was prepared by a similar process to that used for DAAP, using 9.3 g (0.1 mol) of aniline, 8.0 g (0.2 mol) of NaH, 15.4 g (0.2 mol) of 3-chloropropene, and 80 mL of THF. The mixture was refluxed to give 5.2 g of **6** as a dull red liquid (in a 30% yield).

ANAL. Calcd for $\text{C}_{12}\text{H}_{15}\text{N}$: C, 83.19%; H, 8.73%; N, 8.08%. Found: C, 83.16%; H, 8.73%; N, 8.06%.

IR: 1645, 1605, 1512, 1321, 991, 807 cm^{-1} . NMR (CDCl_3 , 200 MHz) δ : 3.80(d, 4H), 5.21(q, 4H), 5.92(m, 2H), 6.79(m, 3H), 7.18(m, 2H).

1,4-Bis(*N,N*-diallylamino)benzene

The reaction involved 10.0 g (0.42 mol) of processed NaH, 10.8 g (0.10 mol) of 4-phenylenediamine, and 40 mL of 3-chloropropene. The processes of the reaction and purification of the product were the same as those used for preparing DAAP to give 3.5 g (in a 13% yield) of the product

as a yellowish liquid. Its color promptly deepened at room temperature.

ANAL. Calcd for $C_{18}H_{24}N_2$: C, 80.55%; H, 9.01%; N, 10.44%. Found: C, 80.52%; H, 9.03%; N, 10.43%.

***N,N,N',N'*-Tetrallyl-4,4'-diaminobenzidine (7, AAB)**

Under the same conditions as those for preparing DAAP, a reaction was effected by adding to the solution of 18.4 g (0.10 mol) of 4,4'-diaminobenzidine, 10.0 g (0.42 mol) of NaH, and 40 mL of 3-chloropropene in THF. Excess THF was evaporated and added to an Al_2O_3 (50 g) column made up in benzene. Elution of the column with a solution of 7 : 8 alcohol/toluene gave 15.9 g (in a 46% yield) of **7** as a thick viscose brownish red liquid.

ANAL. Calcd for $C_{24}H_{28}N_2$: C, 83.68%; H, 8.19%; N, 8.13%. Found: C, 83.66%; H, 8.20%; N, 8.10%.

IR: 1642, 1601, 1511, 1380, 990, 804 cm^{-1} . NMR ($CDCl_3$, 200 MHz) δ : 3.86(d, 8H), 5.13(q, 8H), 5.89(m, 4H), 6.69(m, 4H), 7.28(m, 6H).

***N,N,N',N'*-Tetrallyl-4,4'-diaminodiphenyl sulfone (8, AABS)**

A mixture of 17.2 g (0.05 mol) of 4,4'-diaminodiphenyl sulfone, 5.0 g (0.21 mol) of NaH, and 20 mL of 3-chloropropene in THF were reacted under the same conditions as those for yielding DAAP. The product was repeatedly washed by saturated aqueous KOH and filtered to remove the solvent. Then, the solid was dissolved in acetone, filtered, and the insoluble substance removed. The filtrate was poured into water to precipitate. Drying in a vacuum to gave 23.00 g (in a 56% yield) of **8** as a yellowish powder.

ANAL. Calcd for $C_{24}H_{28}N_2O_2S$: C, 70.56%; H, 6.91%; N, 6.86%. Found: C, 70.54%; H, 6.89%; N, 6.85%.

IR: 1649, 1600, 1507, 1313, 1145 cm^{-1} . NMR ($CDCl_3$, 200 MHz) δ : 2.53(d, 8H), 5.41(q, 8H), 6.01(m, 4H), 6.64(m, 4H), 7.47(m, 6H).

***N,N,N',N'*-Tetrallyl-4,4'-diaminodiphenyl ether (9, AABE)**

A reaction under the same conditions as those for preparing DAAP was carried out in a solution into which were added 20.0 g (0.1 mol) of 4,4'-diaminodiphenyl ether, 10.0 g (0.42 mol) of NaH, and 40 mL of 3-chloropropene. The product was washed with

saturated aqueous NaOH. The residual was recrystallized from acetone–water (100 mL, 2 : 1) to give 11.5 g (in a 32% yield) of **9** as a white powder.

ANAL. CALCD for $C_{24}H_{28}N_2O$: C, 79.96%; H, 7.83%; N, 7.77%. Found: C, 79.98%; H, 7.80%; N, 7.75%.

IR: 1642, 1593, 1504, 1225, 1025 cm^{-1} . NMR ($CDCl_3$, 200 MHz) δ : 3.36(d, 8H), 5.11(q, 8H), 5.74(m, 4H), 6.36(m, 6H), 7.08(m, 4H).

PolyDAAP (3)

To a solution of 50 g (0.029 mol) of DAAP in 8 mL of 15% diluted HCl at 0°C under nitrogen was added 0.1 g of **V-50**. The mixture was stirred for 10 h at 60°C under nitrogen. The product was washed with a 5% aqueous NaOH three times and dissolved in alcohol and filtered. The filtrate was precipitated in ether to give 3.7 g of **3** as reddish brown powder (in a 75% yield).

ANAL. Calcd for $C_{11}H_{14}N_2$: C, 75.82%; H, 8.10%; N, 16.08%. Found: C, 75.75%; H, 8.03%; N, 16.05%.

IR: 1599, 1518, 1478, 1402, 1223, 999 cm^{-1} .

Poly(DAAP-co-DAAB) (10)

To a mixture of 5.0 g (0.029 mol) of DAAP and 4.97 g (0.029 mol) of DAAB in 15 mL of 15% diluted HCl was added 0.02 g of **V-50** at 0°C under nitrogen. The system was stirred at 60°C under nitrogen for 10 h. The mixture was washed three times with 5% aqueous NaOH. The solid was dissolved in *N,N*-dimethylformamide and filtered. The filtrate was precipitated in water to give 7.3 g (in a 81% yield) of **10** as a dark brown solid.

ANAL. Calcd for $C_{23}H_{29}N_3$: C, 79.50%; H, 8.41%; N, 12.09%. Found: C, 79.55%; H, 8.46%; N, 12.15%.

IR: 2996, 1580, 1502, 1230, 981 cm^{-1} .

Poly(DAAP-co-AAB) (11)

An equal mol of DAAP and AAB were dissolved in a small quantity of *N,N*-dimethylformamide. The conditions were the same as those for yielding [poly(DAAP-co-DAAB)]. The mixture was washed with 5% aqueous NaOH three times. After filtration, the insoluble substance was washed with alcohol for 10 h in a Soxhlet extractor and dried in vacuum to give **11** as a brown solid (in a 77% yield).

ANAL. Calcd for $C_{35}H_{42}N_4$: C, 81.04%; H, 8.16%; N, 10.80%. Found: C, 80.98%; H, 8.13%; N, 10.76%.

The solid was degraded at 250°C under nitrogen. The degraded residue was dissolved in alcohol and precipitated by petroleum ether and dried in a vacuum.

IR: 1602, 1515, 1322, 905 cm^{-1} .

Poly(DAAP-co-AABS) (12)

A equal mol of DAAP and AABS were added a small quantity of *N,N*-dimethylformamide. The reaction thus induced and the operation for purifying the product were the same as those for yielding [poly(DAAP-co-AAB)]. The product **12** was a yellow solid (in a 80% yield).

ANAL. Calcd for $C_{35}H_{42}N_4O_2S$: C, 72.13%; H, 7.26%; N, 9.61%. Found: C, 72.16%; H, 7.21%; N, 9.58%.

The solid was degraded at 250°C under nitrogen. The degraded residue was dissolved in alcohol and precipitated by petroleum ether and dried in a vacuum.

IR: 1600, 1508, 1320, 1140, 901 cm^{-1} .

Poly(DAAP-co-AABE) (13)

A equal mol of DAAP and AABE were added to a small quantity of *N,N*-dimethylformamide. The action thus induced was not different from that for yielding [poly(DAAP-co-AAB)]. The residue was dissolved in *N,N*-dimethylformamide and precipitated by petroleum ether and dried in a vacuum. The product **13** was a yellow solid (in a 74% yield).

ANAL. Calcd for $C_{35}H_{42}N_4O$: C, 78.61%; H, 7.92%; N, 10.49%. Found: C, 78.57%; H, 7.89%; N, 10.50%.

The solid was degraded at 250°C under nitrogen. The degraded residue was dissolved in alcohol and precipitated by petroleum ether and dried in a vacuum.

IR: 1596, 1505, 1231, 1020, 899 cm^{-1} .

RESULTS AND DISCUSSION

4-Aminopyridine is a weak nucleophilic reagent and ineffective for attacking the substrate 3-chloropropene. However, its nucleophilic ability can be markedly raised when sodium substitution takes place in the amino group in 4-aminopyridine in such a way as to increase the density of the electron cloud around its N atom and form the $N-Na_2$ ion. 3-Chloropropene, as an efficient nucleophilic substrate or electrophile, can react with sodio aromatic amines at a mild temperature. The reaction takes about 10 h. But 4,4'-bis(*N,N*-dialkylamino)benzene is not a stable compound.

The DAAP and polyDAAP that we synthesized are identical to Mathias' products in spectra analysis. The monomers demonstrate in the IR spectra a double-bond stretching band in the spectral region of 1650–1640 cm^{-1} . Benzene rings or pyridine rings were proved by bands 1610–1500 cm^{-1} . The band at 1313 cm^{-1} is ascribed to the sulfone groups. The bands at 1225 and 1025 cm^{-1} were assigned to C—O ether bonds. The absence of bands at 3400–3250 cm^{-1} indicates a lack of N—H in the compounds.

In terms of percentage of yield from the synthesizing reaction, it may be concluded that DAAP > AABS > AAB > DAAB > AABE. That is because the electron effect of the linked group ϕ between two anilines can, in a way, bear upon the *N*-alkylation reaction involving amine compounds and 3-chloropropene. It is generally considered that the nucleophilicity of the amine is directly influenced by the density of nitrogen lone pair, and the resonance interaction between the nitrogen lone pair and the aromatic π -system modifies the electron density at nitrogen. In this case, the sodio-amines group is an ionic structure. When the group ϕ is an electron-attracting one, the electron density of amino nitrogen on the aromatic ring will be decreased. That would stabilize the $N-Na$ structure, because an electron-attracting group is conducive to stabilizing anionic nitrogen and facilitates the occurrence of a nucleophilic reaction and an electron-donating group ϕ would hamper a nucleophilic reaction.

In the reaction system, although an excess amount of 3-chloropropene was used, primary or secondary amines still exist as by-products. Oxidation of amines and other unclear by-reactions would also occur in the reaction system itself. Some unpurified products tend to change in color or viscosity. Therefore, in addition to the method of high-vacuum reduced-pressure distillation,

some suitable solvent may be used for bringing about a solution/precipitation operation of the unpurified products. Sometimes, proper elution may also be used for effecting chromatography separation. The crude products were added to an Al_2O_3 column made up in benzene, and elution of the column with 7 : 8 ethanol/toluene mixtures gave pure products. In the structure of the diallylamine derivatives obtained in our reactions, there are two separated double bonds. If a system contains such monomers as acrylates, a crosslinkage structure is to be automatically formed through copolymerization after the yield from the reaction has lain for a few months. Furthermore, a reaction which is similar to that of Wurtz's⁹ and involves NaH (or Na) and 3-chloropropene may take place, which would not only waste the reactants but cause eruptive boiling and form propylene gas in the reaction system. This, however, might, in most cases, be contained by reducing the temperature and adding a reactant in a controlled way or by the use of a solvent.

For preparing various polymers, diallylamino monomers were generally initiated with **V-50** to carry out a cyclopolymerization after DAAP was protonated in an acid. Cyclopolymerization usually proceeds at a slow rate. To form an intramolecule ring of a dipropylene amine, the concentration of monomers has to be confined to a fairly low level in a solution. The polymerization might take a long time and the rate of polymerization might be low.

The IR spectra contain both 1600–1585 and 900- cm^{-1} absorption bands. This testifies to the existence of benzene rings or pyridine rings. There is no absorption peak at the 1670–1640 cm^{-1} region, which would indicate no double olefinic bonds. That poly(DAAP-*co*-AABS) exhibits a strong absorption at 1314 and 1144 cm^{-1} confirms the existence of sulfone. Existence of ether is shown by the demonstrations of the absorption peaks of poly(DAAP-*co*-AABE) at 1220 and 1020 cm^{-1} .

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