

The synthesis of aromatic tetraallylamine

Lei Yi, Jiang Luxia*, Cai Xingxian

(Department of Polymer Science and Materials,
Sichuan University, State key Laboratory of Polymer
Materials Engineering, Chengdu 610065)

Abstract

A kind of aromatic tetraallylamine was prepared by reacting aromatic amine with allyl chloride in an aqueous sodium hydroxide solution and a catalytic amount of a quaternary salt such as tetrabutyl ammonium bromide. The product was characterized by elemental analysis, infrared spectroscopy, and proton nuclear magnetic resonance spectroscopy.

Introduction

Since 1980's, the investigation about the modified bismaleimide resin with allylphenol compounds had given a great progress. The novel bismaleimide resin could be used widely at the aspect of high performance composite's matrix resin with good toughness, high hot-wet resistant properties and impact strength.

In 1992, somebody⁽¹⁻²⁾ found that aromatic diallylamine or triallylamine could be synthesized by reacting aromatic amine with allyl chloride in an aprotic solvent such as dimethylsulfoxide in the presence of an aqueous sodium hydroxide solution. Further the aromatic tetraallylamine could be synthesized by reacting aromatic triallylamine with allyl chloride in a solvent such as dichloridimethane in the presence of triethylamine. Latter we developed a new route to synthesize aromatic tetraallylamine by a one-step method with a phase transfer catalyst⁽³⁾. This paper described the investigation of the synthesis and characterization.

Experimental

Characterization Methods

IR spectra was recorded on Nicolet FTIR 20 SXB spectrometer, ¹H-NMR spectra was obtained by Varian FT-80A NMR spectrometer system at 80 MHz and DMSO-d₆ as a solvent, and C, H, N elemental analysis was carried out with Carlo Erba 1160 elemental analyser.

Materials

Toulene, sodium hydroxide, anhydrous magnesium sulfate and tetrabutyl ammonium bromide were used as chemical pure products, but allyl chloride and bis(4-aminophenyl)methane were used as industrial products.

Synthesis of tetraallyl bis(4-aminophenyl)methane

In a 1000-ml, 3-necked round-bottom glass flask equipped with a controlled heating means, a stirring apparatus, a thermometer, a condenser and a funnel. A mixture of 99g bis(4-aminophenyl)methane and 10g tetrabutyl ammonium bromide were added to the flask, then 350ml toluene and 320g 50% aqueous sodium hydroxide were added, stirring was started. The contents of the flask were heated to a temperature of 50°C-52°C. At the point, 185ml allyl chloride was added, dropwise, over a period of an hour, to the mixture in the flask. After a 7-hours period during which the temperature was maintained, the product was held at ambient temperature. The resulting organic and aqueous layers were resolved in a separatory funnel and the nonaqueous layer was removed. The organic oil product was dried over anhydrous magnesium sulfate, then filtered and gave 150g red-brown liquid product in vacuum distillation.

Results and Discussion

The elemental analysis of tetraallyl bis(4-aminophenyl)methane (C₂₅H₃₀N₂) showed that the found

value(calculated value):C83.89(83.80),H8.39(8.38),N7.95(7.82).

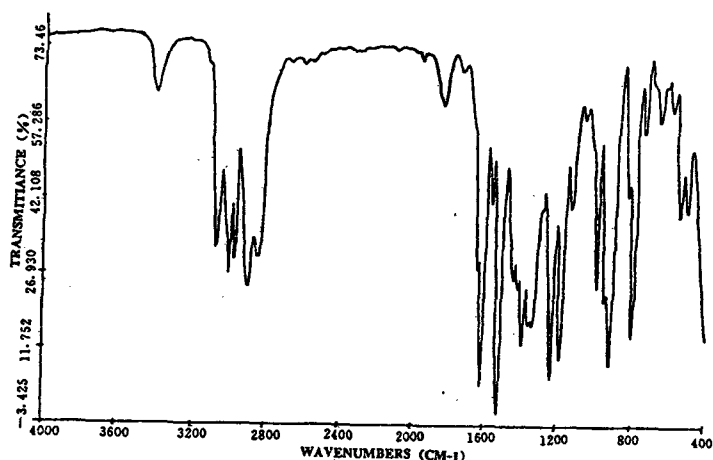


Figure 1 IR spectra of tetraallyl bis(4-aminophenyl)methane
 1638cm^{-1} (c = c), 1336cm^{-1} , 1231cm^{-1} (Ar-N-R₂), 1613cm^{-1} , 1517cm^{-1} (phenyl ring), 3079cm^{-1} , 991cm^{-1} , 917cm^{-1} (allyl).

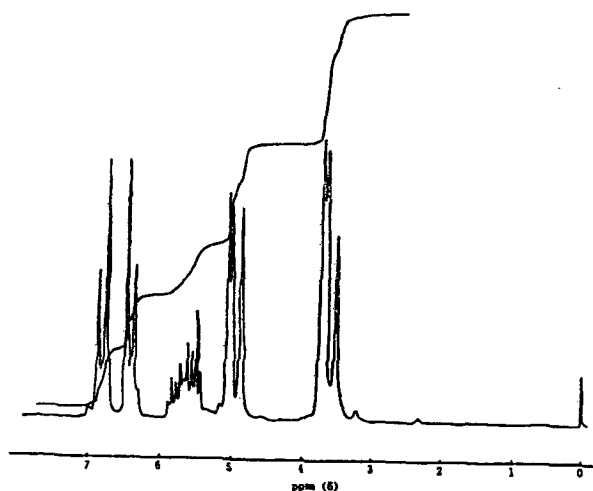
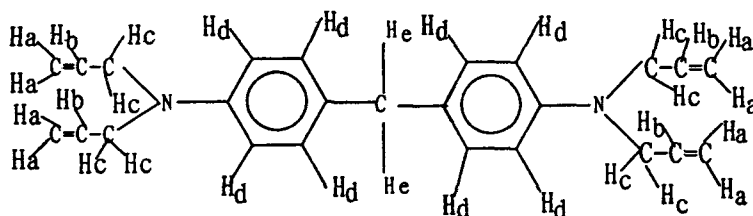


Figure 2 ¹H-NMR spectra of tetraallyl bis(4-aminophenyl)methane
¹H-NMR [tetraallylbis (4-aminophenyl) methane]: 6.5-7.0ppm (4H, phenyl ring, H^d), 6.0ppm (2H, =CH-, H^b), 5.0-5.2ppm (4H, CH₂=, H^a), 3.75-3.9ppm (4H, -CH₂-N, H^c), 3.6ppm (1H, Ar-CH₂-Ar, H^e), and H^a : H^b : H^c : H^d : H^e = 4 : 2 : 4 : 4 : 1.



Conclusions

The tetraallylbis(4-aminophenyl)methane was synthesized and characterized. Additional work needed to be performed to copolymerize the allylamine with BMI resin.

References

- 1 Naito, shigeki; EP378457, 1989
- 2 Naito, shigeki; JP0474156, 1992
- 3 Lei Yi, PhD Dissertation, Dept. of Polymer Science and Materials, Sichuan University, 1995.

* To whom correspondence should be addressed.