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Synthesis of Polymer-Attached Triphenylamine Cation Radical

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Polymer-Attached Triphenylamine 양이온 라디칼의 합성

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Abstract: A very useful cation radical, triphenylaminium hexachloroantimonate, was quantitatively incorporated into insoluble polymer framework. The polymer cation radical was found to be effective as a catalyst in the Diels-Alder type dimerization and then shown to be reusable through several cycles of use.

요 약: 매우 유용한 양이온 라디칼인 triphenylaminium hexachloroantimonate가 불용성 폴리머체에 정량적으로 접합되어졌다. 그 폴리머 양이온 라디칼은 딜스-알더 반응형태의 이분자화 반응에 촉매로서 효과적이었으며 여러번 재사용되어질 수 있음을 알 수 있었다.

1. Introudction

The discovery of the cation-radical catalyzed Diels-Alder reaction opened a field of cation radical chemistry[1]. The inefficiency of reactions involving neutral or electron-rich dienophiles imposes a major constraint on the Diels-Alder reaction. This reactivity constraint might be relieved by using cation radical which converts these dienophiles to their corresponding electron-deficient species.

Recently, several cation-radicals have been attached to a polymer support by polymer modification[1f, g]The attachment of organic reagents to an insoluble polymer support gives an advantage which they can be separated by filtration[2]. The reagent is easily regenerated for latter use which is attractive from an economical viewpoint as well as a simplified workup procedure.

There are two methods in incorporating an organic reagent into a polymer structure[2a]. The first method is polymer modification. In this method, a reactive polymer such as chloromethylated cross-linked polystyrene is chemically modified in one or several steps, allowing incorporation of the reagent. The second method involves preparation of a monomer containing the reagent which can be polymerized. Both methods which have advantages and disadvantages should be considered for each individual reagent. Because the functional group of the former polymer is subjected to chemical damage the latter has stronger durability property. This paper describes a new synthesis of polymer cation radical by the second method which has not been reported so far.

2. Experimental

General All manipulations of compounds and solvents were carried out by using standard schlenk techniques. Solvents were degassed and purified by distillation under nitrogen prior to use. Reagent grade chemicals were used as received. Spectroscopic measurements utilized the following instrumentation: ^{1}H NMR, Varian XL 30Q; ^{13}C NMR, Varian XL 300(at 75.4 MHz). NMR chemical shifts are reported in δ vs Me_4Si in ^{1}H NMR and assigning the $CDCl_3$ resonance at 77.00ppm in ^{13}C spectra. Infrared spetra were recorded on a Brucker IFS 48 infrared spectrometer.

1-[4-Bis(phenyl)aminophenyl]ethanone (1): To a cooled (0℃) CH_2Cl_2 (50ml) solution containing triphenylamine (3g, 12.2mmol) and acetyl chloride (0.87ml, 0.96g, 12.2mmol) was added $FeCl_3$ (1.4g, 8.5mmol). The mixture was stirred at 0℃ for an additional 1h. The cooling bath was removed and the mixture was allowed to reflux for 4h. Water (50ml) was slowly added to the mixture. The mixture was diluted with CH_2Cl_2 (150ml) and an additional H_2O (50ml) and the layers were separated. The organic layer was washed with H_2O (100ml) and brine (100ml). The organic layer was dried (K_2CO_3), filtered, and the solvents were removed under reduced pressure. The residue was chro-matographed on silica gel (4(W)×20(H)cm) with a gradient eluant of 0–15% ethyl acetate in hexanes(V/V). Fractions containing the product were combined and the solvents removed under reduced pressure to yield pure product 1 (2.0g, 58%): ^{1}H NMR($CDCl_3$): δ=7.79(d, J=9.0Hz, 2H), 7.31(d, J=5.9 Hz, 4H), 7.14(m, 6H), 6.98(d, J=9.0 Hz, 2H), 2.54(s, 3H, $COCH_3$); ^{13}C NMR($CDCl_3$): δ =196.5, 152.2, 146.5, 129.9, 129.8, 126.0, 124.7, 119.6, 116.3, 26.3. Anal. Calcd: C, 83.45; H, 5.98%. Found: C, 83.54; H, 5.92%.

1-[4-Bis(4-bromophenyl)aminophenyl]ethanone (2): A DMF (50ml) solution of the acylated triphenylamine from above (2.5g, 8.4mmol) was treated with NBS (3.1g, 17.4mmol). The mixture was stirred at room temperature for 1h and then heated to 50℃ for an additional 10h. The mixture was diluted with water (100ml) and CH_2Cl_2 (120ml) and the layers separated. The organic layer was washed with water (3×100ml). The organic layer was dried (K_2CO_3), filtered, and the solvent removed under reduced pressure to afford crude 2 (3.6g, 94%) as a dark brown oil. The product was crystallized from boiling ethanol (15ml) and then flash chromatographed on silica gel (4(W)×8(H) cm) with 20% ethyl acetate in hexanes(V/V) affording pure 2(3.1g, 81%) as a yellow solid: ^{1}H NMR ($CDCl_3$): δ=8.03(d, J=8.5 Hz, ^{2}H), 7.63(d, J =8.6 Hz, 4H), 7.20(m, 6H), 2.75(s, 3H, $COCH_3$); ^{13}C NMR($CDCl_3$) : δ=186.5, 151.3, 145.3, 132.8, 130.0, 129.9, 129.7, 120.7, 117.5, 28.3. Anal. Calcd : C, 53.93; H, 3.37%. Found: C, 54.77; H, 3.57%.

1-[4-Bis(4-bromophenyl)aminophenyl]ethanol (3) : To 50ml 3-neck flask equipped with a condenser and dropping funnel containing lithium aluminum hydride (0.15g, 4.0mmol) and anhydrous diethyl ether (10ml), 2 (2.5g, 5.5mmol) dissolved in diethyl ether (20ml) was slowly added at 0℃ . The mixture was heated to 40℃ and allowed to react for 12h. 10% NaOH/H_2O (2ml) was added cautiously to destroy the excess lithium aluminum hydride. The mixture was diluted with diethyl ether (60ml) and water (60ml), and the layers were separated. The organic layer was washed with brine (50ml), dried (K_2CO_3), filtered, and the solvents were removed under reduced pressure to afford crude 3 (2.4g, 95%) as a light yellow solid. Purification of 3 was achieved by flash chromatography on silica gel(4(W)×8(H)cm) with 20% ethyl acetate in hexanes(V/V). Removal of the solvents under reduced pressure gave pure 3 (2.3g, 91%) as a light yellow powder : ^{1}H NMR($CDCl_3$) : δ=7.34 (d, J=8.9 Hz, 4H), 7.28(d, J=8.1 Hz, 2H), 6.99(m, 6H), 4.41(m, 1H), 1.76(br s, 1H, OH), 1.51(d, J=6.4 Hz, 3H, $CH(OH)CH_3$); ^{13}C NMR($CDCl_3$) : δ= 146.4, 141.0, 132.3, 132.1, 126.7, 125.3, 124.6, 115.4, 69.9, 25.0. Anal. Calcd : C, 53.66; H, 3.89%. Found : C, 53.73; H, 3.83%.

1-[4-Bis(4-bromophenyl)aminophenyl]ethene (4) : A DMF (30ml) solution containing 3 (2.0g, 4.4mmol) was treated with a catalytic amount of *p*-toluenesulfonic acid (0.04g, 0.21mmol). After 10min of reaction, the mixture was allowed to reflux over a period of 50min. The mixture was diluted with hexanes (100ml) and washed with water (100ml) and finally brine (100ml). The organic layer was dried (K_2CO_3), filtered, and the solvents removed under reduced pressure to afford crude 4. Purification of 4 was achieved by column chromatography on silica gel (3(W)×12(H)cm) with 5% ethyl acetate in hexanes(V/V). Removal of the solvents yielded 4 (1.1g, 60%) as a light yellow power : ^1H NMR($CDCl_3$) : δ=7.35(m, 6H), 6.98(m, 6H), 6.68 (dd, J=17, 11Hz, 1H, $C\underline{H}=CH2$), 5.69(d, J=17 Hz, 1H, $CH=C\underline{H_2}$), 5.22(d, J=11Hz, 1H, $CH=C\underline{H}2$); ^{13}C NMR($CDCl_3$) : δ=146.4, 146.3, 136.0, 132.4, 132.2, 127.3, 125.5, 124.2, 115.7, 112.9. Anal. Calcd : C, 55.97; H, 3.50%. Found : C, 55.87; H, 3.53%.

Copolymerization of 4 with styrene and DVB : 2% solution (ca. 0.1ml) of boron trifluoride etherate was added to a degassed solution of monomer 4 (0.42g, 0.95mmol), styrene (0.79g, 7.60mmol), and divinylbenzene (0.12g, 0.95mmol) in CH_2Cl_2 at -78 ℃ under nitrogen. After 30min the cooling bath was removed, and the mixture was slowly allowed to warm to 10℃ and to react for 5h. The suspension was treated with ether and methanol, and stirred for 20min. The polymer was filtered, washed with methanol and ether. The polymer was dried under reduced pressure at 65℃ for 6h to afford 5 (1.25g, 95%) as gray color : IR(KBr) 2824, 1697, 1624, 1581, 1489, 1451, 1312, 1265cm^{-1}; Anal. Calcd : C, 80.50; H, 6.31; N, 1.12%. Found : C, 77.98; H, 7.27; N, 0.98%.

Polymer Cation Radical (6) : Polymer 5 (0.26g) was suspended in CH_2Cl_2 (4ml), and $SbCl_5$ (0.2ml) was slowly added at -20℃. The mixture immediately turned deep blue. After stirring for 20min, the polymer was collected on a glass frit and washed with CH_2Cl_2 (20ml), ether (20ml), and then dried under reduced pressure at 65℃ for 6h to yield 6 (0.34g, 100%) : IR(KBr) 2824, 1581, 1481, 1451, 1312, 1265cm^{-1}; Anal. Calcd: C, 64.99; H, 5.11; N, 0.82%. Found : C, 64.70; H, 5.11; N, 0.77%.

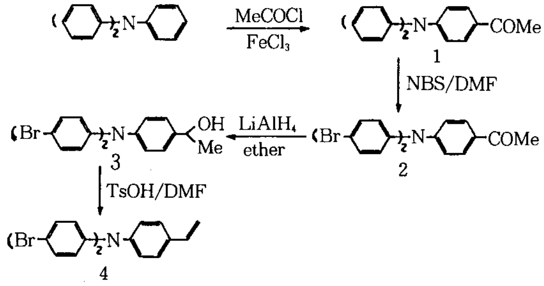
Diels-Alder Reaction of Cyclohexadiene in the presence of polymer cation radical : To a CH_2Cl_2 (2ml) solution of 1, 3-cyclohexadiene (250mg) was added the polymer cation radical 6 (50mg). The mixture was allowed to stir at room temperature for 2h. The polymer was filtered and washed with CH_2Cl_2, and solvent of the filtrate and the remaining 1, 3-cyclohexadiene was removed under reduced pressure to give cyclohexadiene dimer (175 mg) in ca. 70% yield after flash chromatography on silical gel with hexanes.

3. Results and Discussion

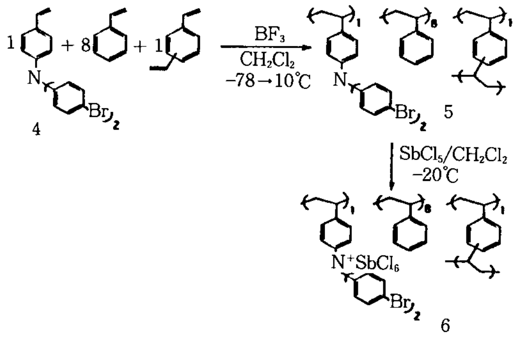
A polymer-attached reagent consists of two parts, a functional group and a polymer support. Tris-(*p*-bromophenyl)amine (TPA) moiety was selected as the functional group because it can be easily converted to the cation radical which has considerable thermal stability[3]. We prepared TPA monomer which contains a reactive double bond and then copolymerizes with styrene and divinylbenzene.

The Friedel-Crafts reaction of triphenylamine with acetyl chloride provided 1 in 68% yield. 1 was treated with NBS to give 2, followed by reduction with lithium aluminum hydride to give 3. Attempts to drive the next step to 4 by treatment of 3 with conventional dehydrating reagents DMSO[4a], H_2SO_4[4b], $KHSO_4$[4c], Al_2O_3[4d], and $POCl_3$/pyridine[4e] failed due to too low yield. In the case of TsCl/excess t-BuOK, the formation of the monomer was accompanied by several by-products which could not be purified to a satisfactory level for further polymerization studies. We could find an efficient dehydrating condition, TsOH(cat)/refluxing DMF, which afforded the desired compound 4 as a colorless heavy oil in 60% yield (Scheme 1).

Radical copolymerization[5] of 4 was attempted with styrene and divinylbenzene. However, most of 4 was isolated with a small amount of polymer compound. Elemental analysis of the polymer showed that this was a cross-linked polystyrene and 4 was not incorporated into the polymerization. 4 might act as a radical scavenger. We turned to cationic copolymerization[6]. 4, divinylbezene, and sytrene (1 : 1 : 8) was copolymerized in the presence of BF_3 cation initiator to give the insoluble cross-linked polymer 5 containing 10mol% of 1-[4-bis(4-bromophenyl)aminophenyl]ethene moiety(Scheme 2). 5 was converted to the aminium cation radical polymer 6 upon reaction with antimony pentachloride ($SbCl_5$) in quantitative yield. The cation radical is dark purple in color and appears to be stable in air for several days. Elemental analysis (C, H, N) and weight gain were used to confirm the purity of polymer 5 and 6.

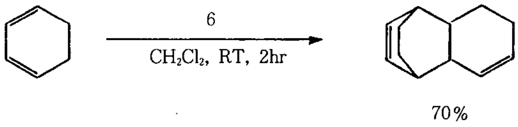


Scheme 1



Scheme 2

The Diels-Alder cyclodimerization of 1, 3-cyclohexadiene requires ca. 20h at 200℃ to give 30 % yield[7]. When cation radical 6 was employed the reaction was quite effective (Scheme 3). The reaction was detected by GC with the aid of ^1H NMR and the product was compared with authentic sample.



Scheme 3

Using the method of Bauld[11] cation radical 6 could be easily regenerated and recycled several times. Elemental analysis verified they are unchanged in their makeup.

4. Summary and Conclusion

Polymerizable vinyl triphenylamine has been prepared through four steps from triphenylamine. The monomer was not polymerized under the condition of radical polymerization but under the condition of cationic polymerization. The polymer was converted to very stable aminium cation radical polymer upon reaction with antimony pentachloride($SbCl_5$). The Diels-Alder cyclodimerization of 1, 3-cyclohexadiene was achieved in the presence of the cation radical polymer to give 70% yield in ca. 2h at room temperature. The polymer-attached cation radical could relieve inefficiency of Diels-Alder reaction involving neutral or electron-rich dienophile as well as it could be easily regenerated for reuse.

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