Dendrimer Functionalized Polysilane: An Efficient and Recyclable Organocatalyst

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ABSTRACT: Polysilane supported dendrimer was efficiently utilized as an organocatalyst for Knoevenagel condensation reaction. Polysilane support was synthesized by the polymerization of trichloromethylsilane. The polypropyleneimine (PPI) dendrimer was grafted on the polymer support by divergent method. The dendrimer was synthesized up to three generations (G3). The dendrimer functionalized polysilane (PS-PPIG3) was found to contain high concentration of terminal amino groups. The catalytic activity of the PS-PPIG3 dendrimer was generalized by conducting the Knoevenagel condensation reaction with diverse sets of substrates, and was found to be an efficient organocatalyst. The condensation product could be easily separated from the reaction medium because of the heterogeneous nature of the polymer support. The reaction conditions were optimized, and the catalyst was found to be reusable. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41593.

INTRODUCTION

Dendrimers are monodisperse large molecules composed of two or more tree-like dendrons. They are highly branched macromolecules,[1–3] obtained by a sequence of reaction steps and are characterized by their structure perfection. A dendrimer is usually symmetric around the core and often accept a spherical three dimensional morphology. The different properties of large dendrimers compared to their conventional polymeric counterparts make these molecules interesting compounds for material science. Dendrimers are mainly used in the area of catalysis and in biotechnology and for medicinal applications.[4–6]

Polymer supported dendrimers can combine the advantages of both homogeneous and heterogeneous catalytic systems. They show the activity and selectivity of a conventional homogeneous catalyst, while they can be recovered from the reaction medium easily. Several scientific groups have utilized the highly branched nature of dendrimeric materials to obtain multivalent ligands for the use in catalysis.[7,8] Dendrimer supported catalysts have the added advantage that the active catalyst and dendrimer are solvated, making the catalytic sites more available in solution (relative to polymers). Catalytic transformations involving organic molecules, known as "organocatalysis", have attracted much interest in recent years.[9–12] These catalysts are more environmental friendly, as they do not involve metals. The heterogenization of organocatalysts provides additional advantages, such as the easy separation of the products and the reusability of the catalysts, which are very important in large scale production. Approaches involving the functionalization of both inorganic and polymer supports with organocatalysts have been reported.[13,14]

In the present study, the catalytic activity of polysilane supported G3-PPI (PS-PPIG3) dendrimer was studied. Polypropyleneimine (PPI) dendrimer was grafted on polysilane by divergent method. The dendrimer synthesis was carried out up to three generations (G3). The Knoevenagel condensation reaction was chosen as the model reaction, which is a well-known classical reaction of condensation between carbonyl compounds and compounds containing active methylene group catalyzed by bases like amines.[10,15–20] Anion-exchange resin, amino group immobilized silica materials, clays, and alkali and alkaline earth carbonates[21–27] have also been reported. However, to the best of our knowledge, there are no reports on the use of polysilane as a support for dendrimer in heterogeneous catalysis. The PS-PPIG3 dendrimer showed higher activity in comparison with the earlier reports.[15,22,28] In this article, we describe the first example of the PPI dendrimer grafted polysilane catalyst; its preparation and application in Knoevenagel condensation reaction. In a previous report,[28] in which the highly cross-linked nature of the polymer support made the catalytic centre less accessible for the active participation in the reaction and took more time for the completion of the reaction.

EXPERIMENTAL

Materials

The monomer, trichloromethylsilane was purchased from Sigma-Aldrich; Magnesium, ethylenediamine, DMSO, and styrene were purchased from Alpha Aeser; Lithium aluminium hydride and sodium hydride (paraffin colloid) were purchased from Loba Chemie Pvt., India. Acetone, diethyl ether, ethyl acetate, glacial acetic acid, hexane, hydrochloric acid, methanol, potassium hydroxide, Toluene, THF, sodium carbonate, and all the substrates for catalytic activity studies were purchased from Spectrochem Pvt., India, and all the solvents were purified according to standard procedures.[29]

Instrumental

FTIR spectra were recorded on JASCO model 4100 FTIR spectrometer as KBr pellets. ^{29}Si-CP-MAS NMR spectra and ^{13}C-CP-MAS NMR spectra were recorded on Bruker 300 MHz instrument and obtained from NMR Research Centre, IISc., Bangalore and National Chemical Laboratory, Pune. ^{1}H NMR spectra were recorded on Bruker 400 MHz instrument with TMS as the internal standard in CDCl$_3$ (SAIF-CUSAT). In catalytic activity study, all the reactions were analyzed, by HPLC on Shimadzu CLASS VP Ver 6.1. Column: Phenomenex Luna 5u C18 (2) 100 Å, for yield and purity of the products. Solvent ratio (CH$_3$OH : H$_2$O) was 70 : 30 with a run time of 30 minutes. The flow rate, detector wavelength, and the temperature were 1 mL/minute, 254 nm and 28°C, respectively.

Preparation of Polysilanes (PS)

The synthesis of polysilane involved the condensation of monomer by Grignard reaction. In a 250 mL round bottom flask, magnesium (1.03 g, 42.36 mmol) in anhydrous THF (50 mL) was refluxed and stirred vigorously to make a dispersion. Trichloromethylsilane (5 mL, 42.36 mmol) was added drop wise. The reaction was exothermic. After the addition of monomer, the reaction mixture was refluxed for 8 h. The whole process was carried out under Nitrogen atmosphere. The reaction mixture was cooled, the suspension obtained was filtered and solvent was removed by fractional distillation. The polysilane obtained was viscous liquid in nature and soluble in toluene. Yield: 45%.

Estimation of Chlorine Capacity of the Polymers. Chlorine analysis was done by the modified Volhard's method.[34] The polysilane (250 mg) was heated with pyridine (2.5 mL) for 1 h at 100°C, and the suspension was diluted with acetic acid : water (1 : 1) (25 mL). The halide was displaced by the addition of Con. HNO$_3$ (5 mL) and precipitated with a measured excess of standard AgNO$_3$ solution. AgCl that was formed was coated with toluene, and the excess AgNO$_3$ was back titrated with standard NH$_4$SCN solution, using ferric alum [FeNH$_4$(SO$_4$).12H$_2$O] as indicator. A red color due to the formation of Fe(SCN)$_3$ indicated that an excess of SCN$^-$ was present and that the end-point was reached.

Introduction of Amino Group on Polysilane

The polysilane (5 g) was taken in a 250-mL round bottom flask with 50 mL of toluene. After adjusting the temperature to 0°C, ethylenediamine (28 mL) was added drop wise to the reaction mixture and followed by 1 g of sodium hydride (sodium hydride, which was obtained as a paraffin colloid, was washed with hexane and dried before use) as base. The reaction mixture was stirred at 0°C for 1 h and the temperature was allowed to rise to the room temperature (30°C) and refluxed for 12 h to ensure the completion of the reaction. The polymer became solid up on cooling and ethyl acetate was added to the reaction mixture in order to destroy the excess sodium hydride. The resin was filtered, washed with ethyl acetate, methanol, 5% aq. KOH solution, water, and finally with methanol. It was dried under vacuum for 24 h and estimation of amino group was carried out. Yield: 95%.

General Procedure for the Solid Phase Synthesis of PPI Dendrimers

First, second, and third-generation PPI dendrimers were synthesized on the aminoethylpolysilane (9.87 mmol NH$_2$ per gram), according to the following procedure.

Procedure for Michael Addition of Acrylonitrile. The aminoethylpolysilane (1 g) was added in three portions to a mixture of excess acrylonitrile (64.7 mL) and catalytic amount of glacial acetic acid with constant stirring.[30] The reaction mixture was kept at 50°C with stirring for 3 days. It was filtered and washed with 5% NaHCO$_3$ solution and followed by washing thoroughly with water, methanol, and acetone. The polymer was dried under vacuum.

Procedure for the Reduction of Nitrile Group to Amino Group. The above polymer was suspended in dry THF taken in a 100 mL round bottom flask kept at 0°C in an ice bath. LiAlH$_4$ (0.75 g, 19.74 mmol) was added in small portions to the reaction mixture with stirring. The reaction mixture was kept at 0°C for 1 h. The temperature was slowly brought to 30°C and stirred for 12 h to ensure complete reduction. Excess LiAlH$_4$ was deactivated by adding ethyl acetate. It was filtered and washed with THF, diethyl ether, THF- dil. HCl, dil. HCl, water, methanol, and acetone. The resin was dried under vacuum. The presence of amino groups was qualitatively detected by ninhydrin test and quantitatively determined by volumetric method.

Repetition of the above two steps of Michael addition and subsequent reduction using LiAlH$_4$ gave second and third generation PPI dendrimer attached to the polysilane. The products were obtained with 95, 92, 92% yields for first, second, and third-generation PPI dendrimers on aminoethylpolysilane, respectively.

Estimation of Amino Groups. Amino group concentration in polysilane supported dendrimer was estimated with aqueous HCl using the acid–base titration method. Typically, the dendrimer attached polysilane (100 mg) was suspended in standard hydrochloric acid (40 mL) for 24 h with occasional stirring. The resin was filtered and washed well with distilled water. The filtrate and the washings were collected. The unreacted hydrochloric acid was estimated by titration against standard Na$_2$CO$_3$ solution using methyl orange as indicator. A blank titration was also carried out. From these values, the amount of amino groups per gram of the resin was calculated.

The first and second generation PS-PPI (PS-PPIG1 & PS-PPIG2) dendrimers were only partially soluble in normal
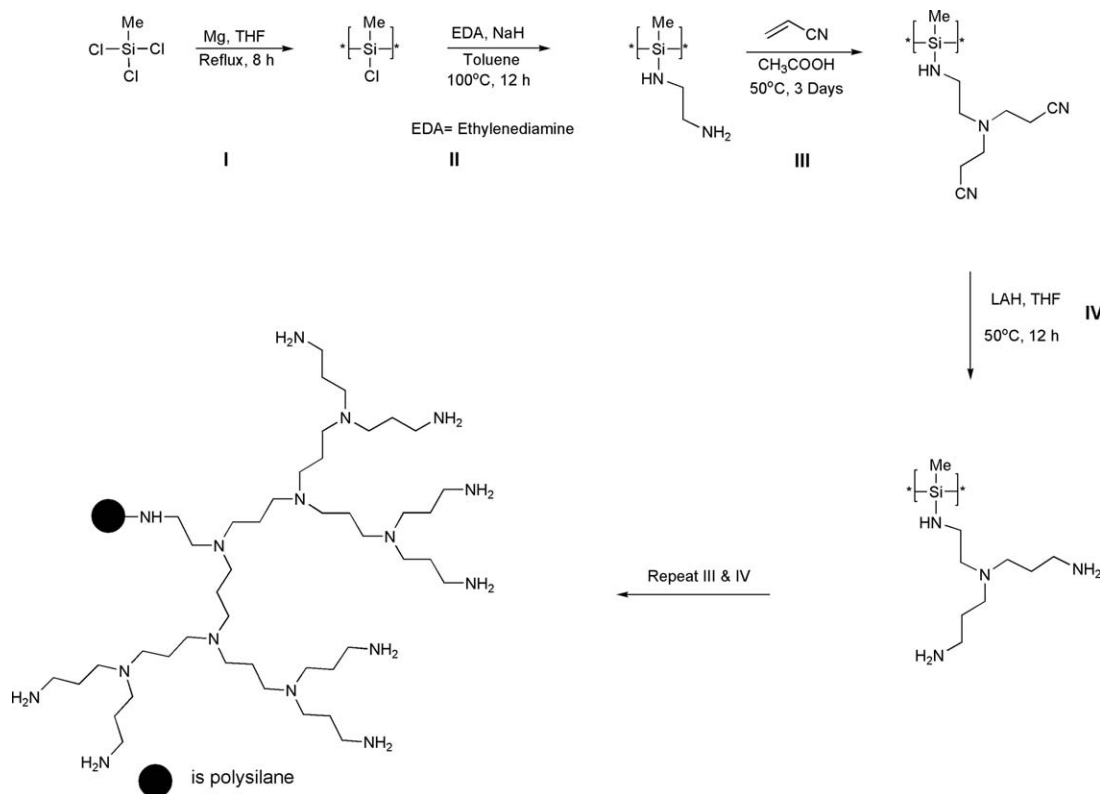
Figure 1. Scheme for the synthesis of PS-PPIG3.

organic solvents. But on Michael addition of the PS-PPIG2 dendrimer results in a product, PS-PPIG2.5 dendrimer, which was soluble in DMSO.

The PS-PPIG3 dendrimer was a viscous liquid and observed that it was soluble in DMSO.

Study of Catalytic Activity

The Knoevenagel Condensation Reaction. An equimolar mixture of carbonyl compound and active methylene compound with PS-PPIG3 dendrimer (3 mol % of amino groups with respect to the substrates) was taken with 10 mL ethyl acetate in a 25 mL round bottom flask. The reaction mixture was stirred at room temperature (reaction with ethyl cyanoacetate was performed at 50°C)[15] for 12 h, and catalyst was removed by filtration and washed with ethyl acetate. Solvent was removed in a rotary vacuum flash evaporator. The products formed were recrystallized from ethyl acetate.

Optimization of Reaction Conditions. An equimolar mixture of benzaldehyde and malononitrile was reacted in the presence of PS-PPIG3 dendrimer. Initially, the reaction time was optimized by conducting the reaction for 5, 10, and 15 min in the presence of 3 mol % of catalyst and at room temperature.

Secondly, to optimize the amount of catalyst, reaction with 1, 2, and 3 mol % of catalyst was conducted. The reaction mixture was stirred for 15 min at room temperature.

Recycling Procedure of the Catalyst. Recycling of the catalyst was performed as follows: The Knoevenagel condensation reaction between benzaldehyde and malononitrile was carried out

under optimized reaction conditions. After the completion of reaction, catalyst was removed from the reaction mixture by filtration and washed thoroughly with ethyl acetate, methanol, and acetone and dried under vacuum for 24 h. The process was repeated in each cycle.

RESULTS AND DISCUSSION

Preparation of Polysilane

The synthesis of polysilane involved the condensation of the monomer by Grignard coupling.[31,32] Polysilane was prepared from trichloromethylsilane monomer in the presence of magnesium in dry THF (Figure 1). The polysilane obtained was viscous liquid soluble in toluene. The polysilane was characterized by Gel Permeation Chromatography, FT-IR, ^{29}Si-CP-MAS NMR, and ^{13}C-CP-MAS NMR spectroscopic techniques.[33]

The molecular weight estimated by GPC, using styrene as standard and toluene as solvent, showed $M_n = 1400$, $M_w = 1955$.

The infrared spectrum of polysilane showed absorptions at 2952 and 2895 cm^{-1} (C—H stretching), 2089 cm^{-1} (Si—H stretching), 1447 cm^{-1} (C—H deformation), 1252 cm^{-1} (Si—CH$_3$ deformation), 863 cm^{-1} (CH$_3$ rocking), 777, and 685 cm^{-1} (Si—C stretching).

The ^{13}C-CP-MAS NMR spectrum of PS [shown in Figure 2(a)] exhibited only one resonance signal at −4.14 ppm, which was assigned to SiSiCH$_3$. The spectrum indicated that PS had only one type of carbon atom and also that it was attached to the Si atom.

In the ^{29}Si-CP-MAS NMR spectrum of PS [Figure 2(b)], the peak around −68.97 ppm was assigned to be due to the
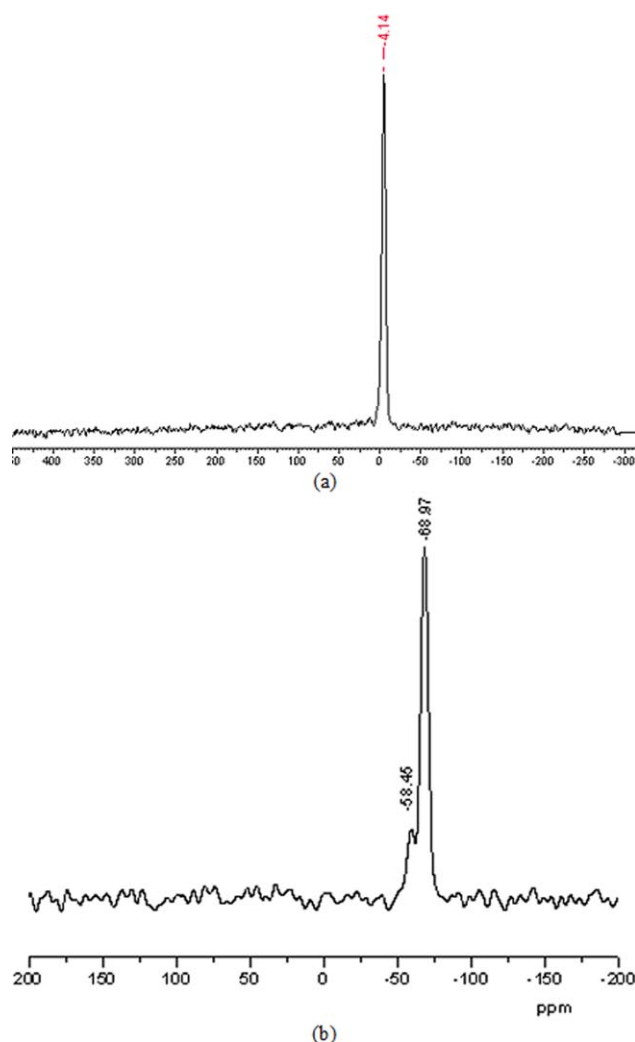
Figure 2. (a) ^{13}C CP-MAS NMR and (b) ^{29}Si CP-MAS NMR spectra of polysilane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resonance of silicon in $(CH_3)SiSi_3$ unit (branching unit). A small peak in close proximity to it around -58.45 ppm was corresponding to the $(CH_3)ClSiSi_2$ unit (linear unit).

The quantitative determination of chlorine in polysilane was done by modified Volhard's method.[34] The result showed that 10.45 mmol/g of chlorine was present in the polymer.

General Procedure for the Solid Phase Synthesis of Polypropyleneimine Dendrimer

Solid phase synthesis of PPI dendrimer was carried out on polysilane. The synthesis of the dendrimer was initiated by the conversion of chloride groups into aminoethyl groups by the reaction with excess ethylenediamine (Figure 1). The primary amino groups so obtained could function as the core and also as the linker that connected the polysilane support and the dendrimer.

FTIR spectrum showed peak at 3694 cm^{-1} due to stretching vibration of the primary amino group. The presence of amino group was confirmed by the Kaiser Ninhydrin test. The amount
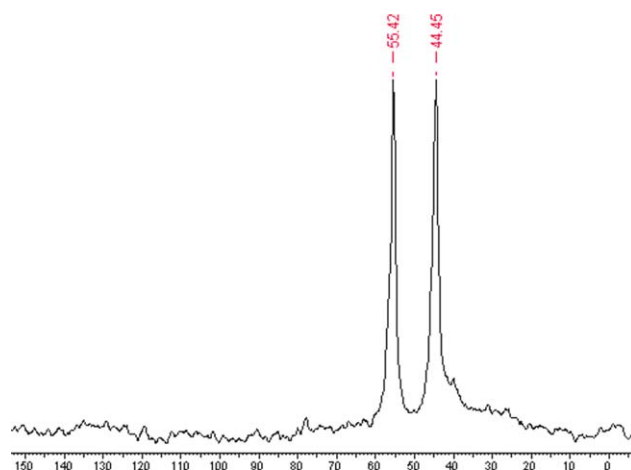

Figure 3. ^{13}C CP-MAS NMR spectrum of aminoethyl polysilane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of amino groups on the resin was estimated to be 9.87 mmol/g of the polymer. It indicated that all the chloride groups were not converted into aminoethyl groups.

The ^{13}C-CP-MAS NMR spectrum of aminoethylpolysilane (Figure 3) gave two major peaks at 55.42 ppm and 44.45 ppm. The peak at 55.42 ppm was due to the resonance of Si—NH—CH_2 and the peak at 44.45 ppm was obtained due to the resonance of Si—NH—CH_2—CH_2—NH_2.

PPI dendrimer was synthesized on aminoethylpolysilane support. The reaction proceeded through double Michael addition of acrylonitrile to the amino groups of the polysilane support followed by the reduction of the nitrile groups to amino groups using LiAlH$_4$ (Figure 1).

The progress of the reaction was monitored by FTIR spectroscopy and Kaiser Ninhydrin test. Amino groups were estimated for each generation and the values are listed in Table I. From the result we can conclude that in each step of the dendrimer synthesis, the conversions were almost complete. During the synthesis of PPI dendrimer, the reaction proceeded with almost complete transformation in each generation.

The ^{13}C-NMR spectrum of PS-PPIG2.5 dendrimer (Figure 4) showed peak around 114.09 ppm which was assigned to be due to the carbon in CN group. It confirmed the product formation. The peaks around 75–65 ppm were due to the carbon atoms which were adjacent to the branching nitrogen atom. Peaks between 33 and 26 ppm were due to the carbon atom which lies in between two carbon atom linked to the nitrogen

Table I. Amino Group Equivalent in Each Generation of the Dendrimer

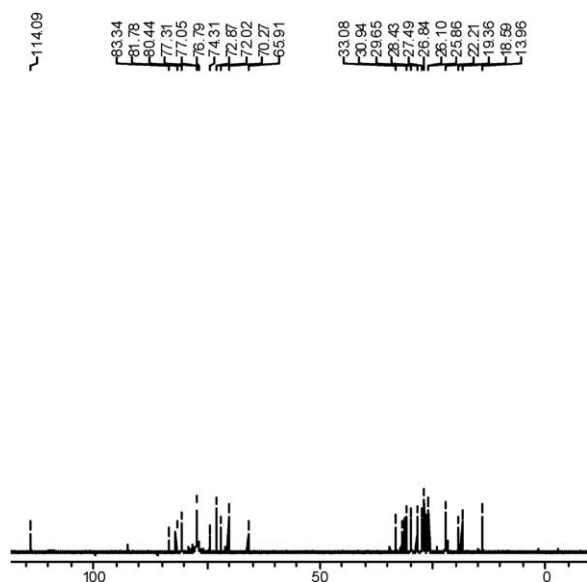| Generation	Amino groups/g
One	9.89 mmol
Two	9.88 mmol
Three	9.87 mmol

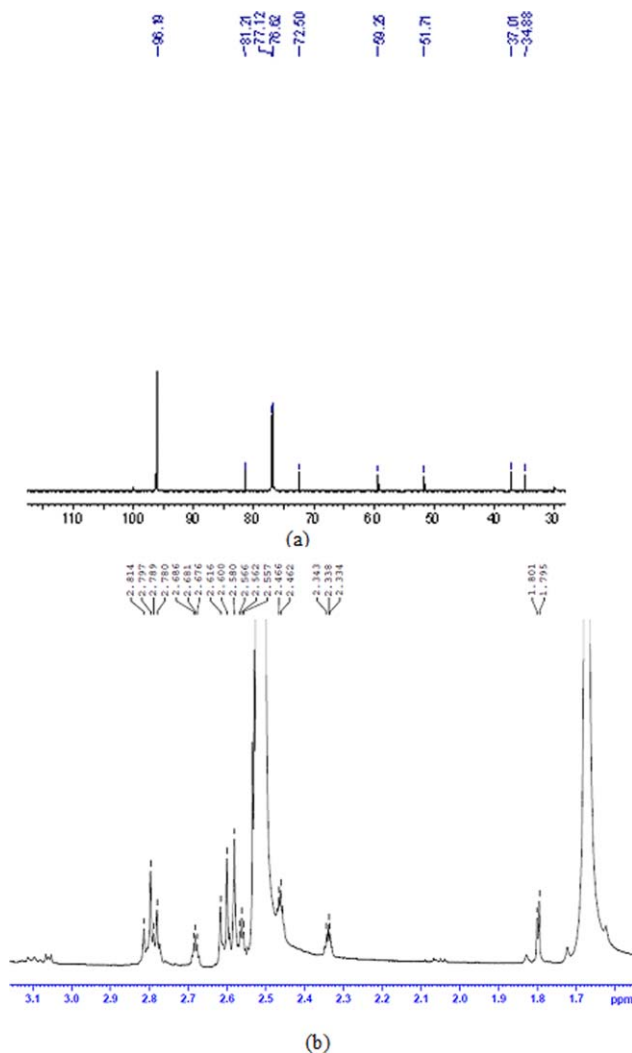**Figure 4.** ^{13}C-NMR spectrum of PS-PPIG 2.5 in DMSO-d$_6$.

Figure 5. (a) ^{13}C-NMR and (b) ^{1}H-NMR spectra of PS-PPIG3 in DMSO-d$_6$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
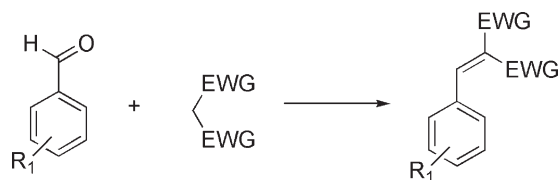

Figure 6. General scheme for Knoevenagel condensation reaction.

atoms. Peaks obtained around 19–18 ppm indicated the presence of carbon atoms which were attached to the nitrile group.

The ^{13}C-NMR spectrum of PS-PPIG3 dendrimer [Figure 5(a)] showed the absence of peak around 114 ppm, indicating complete reduction of nitrile groups. Peaks obtained at 37 and 34 ppm were due to the carbon atoms which were adjacent to the primary amino group.

The proton NMR spectrum of PS-PPIG3 dendrimer [Figure 5(b)] indicated the presence of different types of hydrogen atoms in the compound. Peaks around 2.81–2.33 ppm indicated the presence of H-atoms connected to carbon which were linked to the branching nitrogen. Peaks around 1.80–1.79 ppm indicated the presence of protons connected to carbon which lay in between two carbon atoms which were connected directly to the branching nitrogen.

From the spectral data it was obvious that all the nitrile groups in the PS-PPIG2.5 dendrimer were reduced to amino groups and the structure of PS-PPIG3 dendrimer is as shown in Figure 1.

Catalytic Activity Study of PS-PPIG3 Dendrimer
The PS-PPIG3 dendrimer possessed high concentration of terminal amino groups. Hence it could act as a catalyst in a base catalyzed reaction. The amino groups in the dendrimer were considered as the catalytic sites and polysilane as solid support. The amount of catalyst was estimated in terms of the amino group capacity with respect to the substrates.

The Knoevenagel Condensation Reaction. The catalytic activity of PS-PPIG3 dendrimer was studied by taking Knoevenagel condensation reaction (Figure 6). The reaction involved the condensation of carbonyl compounds and compounds containing active methylene group in the presence of a base.

Optimization of Reaction Conditions. In order to quantify the catalytic performance of PS-PPIG3 dendrimer, reaction between

Table II. Optimization of Reaction Conditions

Entry	Reaction time (min)	Mol % of catalyst	Yield (%)
1	5	3	87
2	10	3	94
3	15	1	90
4	15	2	98
5	15	3	100

A total of 0.05 mol aldehyde, 0.05 mol compound with active methylene group, temp: 30°C, solvent: ethyl acetate.

Table III. Knoevenagel Condensation Reaction with Different Substrates

Entry	Carbonyl compound	Active methylene compound	Temperature (°C)	Yield (%)
1	Benzaldehyde	Malononitrile	30	100
2	Anisaldehyde	Malononitrile	30	100
3	4-Chlorobenzaldehyde	Malononitrile	30	100
4	4- Hydroxybenzaldehyde	Malononitrile	30	100
5	4-(Dimethylamino)benzaldehyde	Malononitrile	30	98
6	Benzaldehyde	Ethylcyanoacetate	50	97
7	Anisaldehyde	Ethylcyanoacetate	50	98
8	4-Chlorobenzaldehyde	Ethylcyanoacetate	50	100
9	4- Hydroxybenzaldehyde	Ethylcyanoacetate	50	97
10	4-(Dimethylamino)benzaldehyde	Ethylcyanoacetate	50	95

Reaction condition: 0.05mol aldehyde, 0.05mol compound with active methylene group, solvent: ethyl acetate, 3 mol % PS-PPIG3 dendrimer and time: 15 min.

benzaldehyde and malononitrile was carried out under various reaction conditions.

Initially, the reaction time was optimized. The reactions of equimolar concentrations of the substrates in the presence of 3 mol % of PS-PPIG3 dendrimer in ethyl acetate at different time intervals were conducted. It was seen that the reaction was completed within 15 min. under specified reaction conditions and it was chosen as the optimum reaction time. Secondly the amount of catalyst was optimized by conducting the same reaction in the presence of different mol % of PS-PPIG3 dendrimer, by keeping the reaction time interval as 15 min. The observations are presented in Table II. From the data obtained, the optimum amount of catalyst for the Knoevenagel condensation reaction under given conditions was taken as 3 mol %.

The catalytic activity of the PS-PPIG3 dendrimer was established by conducting the reaction with diverse sets of substrates under optimized reaction conditions, which are entered in Table III.

The products were known compounds and identified by comparing the spectral data (FTIR, ^{1}HNMR spectra, and mass spectra by LCMS) and melting points with those reported. All the reactions were analyzed by HPLC for yield and purity of the products.

Recycling of Catalyst. Reuse of the catalyst was studied by conducting the Knoevenagel condensation of benzaldehyde and malononitrile. As can be seen from the Table IV, the catalyst separated after the reaction was used for the same reaction in the next cycle. The reaction proceeded smoothly for the three

Table IV. Recycling Experiments Using PS-PPIG3 Dendrimer

No. of cycles	Yield (%)
1	100
2	98
3	97
4	92

A total of 0.05 mol of substrates, solvent-ethyl acetate, 3 mol % PS-PPIG3 dendrimer, temp: 30°C and time: 15 min.

cycles. But the yield gradually decreased in successive cycles and the yield dropped considerably in the fourth cycle.

Since the dendrimers have homogeneous nature, they can easily get solvated; therefore, the catalytic sites, that is, the NH_2 groups will be easily available for accelerating the reaction. The PS-PPIG3 dendrimer gave high yield for all the substrates. In addition to that, the heterogenization of dendrimer provides easy separation of the reaction products and reusability of the catalyst. Hence it can be considered as a good catalyst for Knoevenagel condensation reaction, in comparison with earlier reports[7,15,22,28] since they required more quantity of catalyst, prolonged reaction time, and gave low yields.

CONCLUSIONS

The application of PS-PPIG3 dendrimer as an organocatalyst was investigated by selecting Knoevenagel condensation reaction as a model reaction. The reaction conditions were optimized to get maximum yield. The catalytic activity of the PS-PPIG3 dendrimer was generalized by conducting the Knoevenagel condensation reaction with diverse sets of substrates. It was found that the PS-PPIG3 dendrimer showed excellent catalytic activity and could be reused. Immobilization of homogeneous catalysts on a solid support is one of the promising ways to prepare well defined catalytic systems. They can combine the advantages of both homogeneous and heterogeneous catalysts. The PS-PPIG3 dendrimer, which is an organocatalyst, can help in the elimination of toxic transition metal based catalysts in a synthetically important reaction like Knoevenagel condensation reaction.

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