

First Example of Organocatalysis by Polystyrene-Supported PAMAM Dendrimers: Highly Efficient and Reusable Catalyst for Knoevenagel Condensations

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This paper describes the first use of polystyrene-supported poly(amidoamine) (PAMAM) dendrimers as heterogeneous basic organocatalysts for carbon–carbon bond formation. Polystyrene-supported PAMAM dendrimers of first, second and third generations have been used as reusable base catalysts in Knoevenagel condensations of carbonyl compounds with active methylene compounds. The reactions proceed in

short periods of time and with 100 % selectivity. This novel catalyst eliminates the use of aromatic and halogenated solvents, as well as complex purification processes. The catalysts can be recycled ten times.

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Introduction

In this golden age of organocatalysis, metal-free catalysts play important roles for reaction efficiency and environmental friendliness.^[1] Although many studies have used small molecules as organocatalysts, there are no limits to the molecular weight of the catalyst if the material has good catalytic properties.^[2] The main advantage organocatalysts offer is catalysis in the absence of transition metals, which are highly active catalysts in many reactions, but in many cases the metals leach out from the catalyst and thereby contaminate the valuable final products. On the other hand, the main disadvantage of organocatalysts is that the final separation of catalysts from products is difficult and time consuming.

Attaching the organocatalyst to an insoluble polymer matrix changes this situation. Separation of polymer-supported catalyst from the reaction mixture is very easy and involves simple filtration and washing. In many cases the catalysts can be reused several times without loss of efficiency. This simplified procedure makes organic chemistry more straightforward, cost effective and environmentally friendly. Most of the earlier reports on polymer-supported catalysts were concerned with phase-transfer catalysts and acid catalysts. Recently there have been several publications on polymer-supported base catalysts.^[3]

In this article we report the use of a polymer-supported base catalyst for Knoevenagel condensations between carbonyl compounds and molecules containing active methylene groups. As a carbon–carbon bond-forming reaction, the Knoevenagel condensation has found widespread application in the synthesis of polymerizable monomers with advantageous optical and electrical properties, natural products and pharmaceutically important molecules.^[4] A large number of catalysts are used for this reaction, from conventional catalysts such as piperidine to ionic liquids and carbon nanotubes containing nitrogen.^[5] A number of examples of supported catalysts used for Knoevenagel condensation can also be found in the literature,^[6] but many of them exhibit several drawbacks. Some are time consuming, some contain metals, some need special laboratory techniques and inert atmospheres, some necessitate the use of halogenated or aromatic solvents, etc. Here we report the use of polystyrene-supported poly(amidoamine) (PAMAM) dendrimers as highly efficient and environmentally friendly base catalysts for Knoevenagel condensations. Dendrimers are highly symmetric molecules, which have attracted the curiosity of many scientists from the time of their discovery and have found widespread applications.^[7] Dendrimer-based catalysis is an emerging area, attracting the attention of many research groups, and a large number of papers are published every year.^[8] Literature examples involving the synthesis and applications of organocatalysts based on polymer-supported dendrimers, however, are few in comparison with those concerning homogeneous dendrimer-based catalysts. Recently, Portnoy and co-workers reported a polymer-supported aryl ether dendrimer-based organocatalyst for aldol reactions.^[9] Kapoor et al. showed that PAMAM dendri-

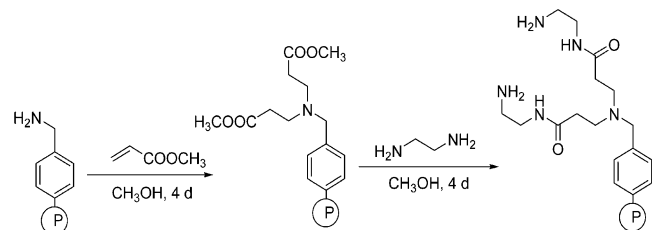
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mers attached to silica supports can act as base catalysts for Knoevenagel condensations,^[10] but the catalytic activity was checked only for one set of substrates and the reactions required longer periods of time and high temperatures in order to provide good yields. To the best of our knowledge, the use of polymer-supported PAMAM dendrimers as recyclable base catalysts has not been reported yet. The catalysts described in this manuscript eliminate many of the problems faced by conventional catalysts used in Knoevenagel condensations. Moreover, the catalysis can be performed even in water, and the catalyst can be recycled many times without loss of activity, offering a greener route to Knoevenagel condensation products.

Results and Discussion

First-, second- and third-generation PAMAM dendrimers were prepared on amino methyl polystyrene (1% DVB crosslinked, 100–200 micron, 1.0 mmol amino groups per gram) by the literature procedure,^[11,12] with suitable modification. The reaction scheme is shown in Scheme 1. The formation of dendrimers was confirmed by amino group estimation, FTIR spectroscopy and solid-state ¹³C NMR spectroscopy. The FTIR spectra clearly indicate the appearance and disappearance of the primary amino groups, as well as the changes in C=O stretching associated with the conversion of a methyl ester into an amide. The solid-state NMR spectra of the polymer before and after the dendrimer synthesis were compared, and a new peak at $\delta = 174$ ppm, due to the amide carbon atom present in the spectrum of the resin carrying the dendrimer, was observed. As an additional confirmation, the same synthesis was performed with nitrated aminomethyl polystyrene as support. After the completion of the synthesis, the dendrimer was cleaved from the polymer support photolytically and analyzed by MALDI-TOF MS. The MALDI-TOF MS showed only one peak at 1615 D ($[M]^+$ peak). All these results confirmed the formation of third-generation PAMAM dendrimer on the polymer beads without any defects. Thermal analysis of the dendronized polymer showed that the polymer was stable up to 250 °C without significant degradation. The structure of the third-generation catalyst is shown in Figure 1.



Scheme 1. Schematic representation of solid-phase dendrimer synthesis.

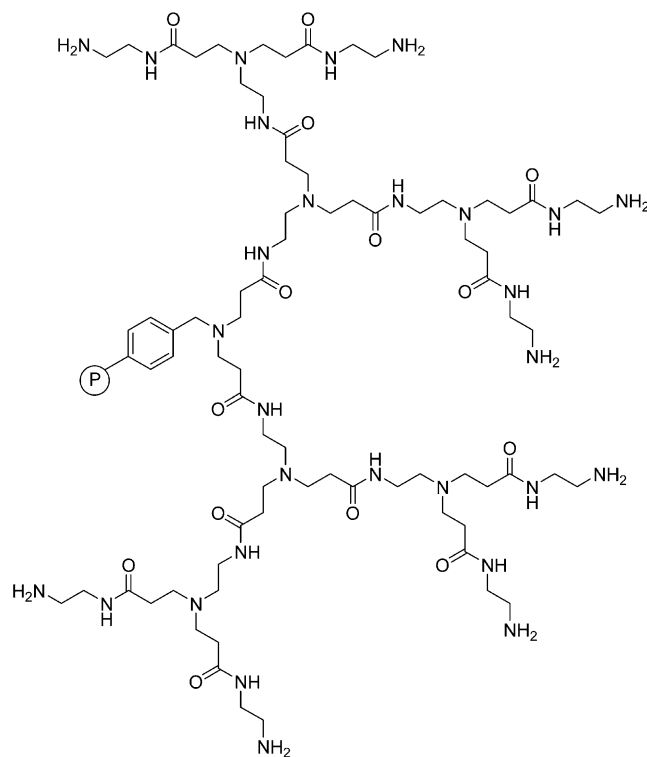


Figure 1. Third-generation PAMAM dendrimer supported on polystyrene.

In order to study the catalytic nature of the polymer-supported dendrimer, the model reaction between benzaldehyde and malononitrile was carried out in various solvents. The results are summarized in Table 1.

Table 1. Effect of solvents on the Knoevenagel condensation catalyzed by the polystyrene-supported dendrimer.

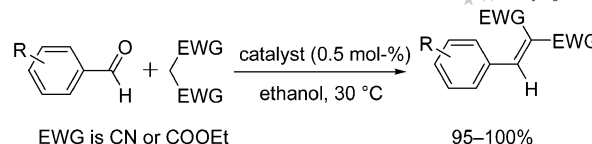
Entry	Solvent	Time [min]	Yield [%] ^[a,b]
1	ethanol	15	100
2	methanol	15	100
3	water	90	98
4	benzene	360	70
5	THF	480	75
6	CH ₃ CN	600	70
7	CH ₃ Cl	600	70

[a] Reaction conditions: benzaldehyde (5 mmol), malononitrile (5 mmol), catalyst (G3PAMAM on PS, 0.5 mol-%), solvent (5 mL), room temperature (30 °C). [b] Isolated yield of product.

The reaction proceeded very well in polar solvents, including in water. Normally, polystyrene-supported catalysts favour nonpolar solvents. The opposite behaviour observed here is because of the dendritic branches on the polymer surface, which are highly polar and make the polymer-supported system as a whole more compatible to polar solvents. The preference for polar solvents in catalysis by dendrimer catalysts carrying polar surface groups was reported previously.^[13] In a previous report, Kobayashi showed that systems based on polystyrene containing polar sulfonic acid groups can act as highly efficient catalysts in water even if strongly hydrophobic groups are attached to the benzene

ring of the polystyrene.^[14] This enables the Knoevenagel condensation to be carried out in a greener fashion, whereas many conventional Knoevenagel condensations demand solvents such as benzene, toluene, acetonitrile etc. in the presence of other catalysts.

In a second step, the amount of catalyst was optimized. It was found that only 0.5 mol-% of the catalyst was required to drive the reaction to completion within a very short time. The speed of the reaction with this catalyst in relation to others may be due to the local concentration of a large number of catalytic sites within a very small volume due to the dendritic backbone. A speculative mechanism of the reaction includes the formation of imines from the amino group of the dendrimer and carbonyl compounds, and these then react with the active methylene compound to give the corresponding olefins. The product obtained after the completion of the reaction and evaporation of the solvent is of high purity and needs no further purification. This is an added advantage over other catalysts used in the same reaction, where column chromatography is necessary for the purification of products. The reaction proceeded smoothly at room temperature when malononitrile was used as the active methylene compound, but for other active methylene compounds a slightly higher temperature was needed (50 °C). The general reaction scheme is given in Scheme 2.



Scheme 2. Knoevenagel condensations catalyzed by polystyrene-supported PAMAM dendrimers.

The results are summarized in Table 2. Substrates such as benzoin and benzil also gave condensation products, but required more time for the completion of reaction. This may be due to the steric hindrance offered by the two phenyl groups close to the carbonyl group. Benzophenone did not give the product even after prolonged reaction times under similar conditions. The carbonyl group flanked between two benzene rings is prevented from interacting with the dendrimer surface groups, and this prevents the reaction of benzophenone. Similar selectivities of dendrimer-based catalysts for smaller substrates have been reported in the literature.^[15] When ethyl cyanoacetate was used for condensations, only the *E* isomers of the products were formed, except in the case of acetophenone, in which the formation of two isomers was confirmed by GC–MS, which showed two well-separated GC peaks having the same molecular mass.

Table 2. Knoevenagel condensations catalyzed by polystyrene-supported PAMAM dendrimers.

Entry	Carbonyl compound	Active methylene compound	<i>T</i> [°C]	Time [min]	Yield [%] ^[a,b]
1	C ₆ H ₅ CHO	CH ₂ (CN) ₂	30	15	100
2	4-CH ₃ OC ₆ H ₄ CHO	CH ₂ (CN) ₂	30	15	100
3	4-ClC ₆ H ₄ CHO	CH ₂ (CN) ₂	30	20	99
4	4-(CH ₃) ₂ NC ₆ H ₄ CHO	CH ₂ (CN) ₂	30	20	100
5	2-OHC ₆ H ₄ CHO	CH ₂ (CN) ₂	30	20	98
6	4-OHC ₆ H ₄ CHO	CH ₂ (CN) ₂	30	15	99
7	3-NO ₂ C ₆ H ₄ CHO	CH ₂ (CN) ₂	30	15	99
8	4-NO ₂ C ₆ H ₄ CHO	CH ₂ (CN) ₂	30	15	100
9	4-OH,3-CH ₃ OC ₆ H ₃ CHO	CH ₂ (CN) ₂	30	20	100
10	3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO	CH ₂ (CN) ₂	30	20	99
11	furfural	CH ₂ (CN) ₂	30	10	99
12	cyclohexanone	CH ₂ (CN) ₂	50	15	99
13	C ₆ H ₅ COCH ₃	CH ₂ (CN) ₂	50	30	98
14	C ₆ H ₅ COCHOHC ₆ H ₅	CH ₂ (CN) ₂	50	90	98
15	C ₆ H ₅ COCOC ₆ H ₅	CH ₂ (CN) ₂	50	120	100
16	C ₆ H ₅ CHO	CNCH ₂ CO ₂ Et	50	15	99
17	4-CH ₃ OC ₆ H ₄ CHO	CNCH ₂ CO ₂ Et	50	15	99
18	4-ClC ₆ H ₄ CHO	CNCH ₂ CO ₂ Et	50	20	98
19	4-(CH ₃) ₂ NC ₆ H ₄ CHO	CNCH ₂ CO ₂ Et	50	15	100
20	2-OHC ₆ H ₄ CHO	CNCH ₂ CO ₂ Et	50	20	99
21	4-OHC ₆ H ₄ CHO	CNCH ₂ CO ₂ Et	50	15	100
22	3-NO ₂ C ₆ H ₄ CHO	CNCH ₂ CO ₂ Et	50	20	100
23	4-NO ₂ C ₆ H ₄ CHO	CNCH ₂ CO ₂ Et	50	20	100
24	4-OH,3-CH ₃ OC ₆ H ₃ CHO	CNCH ₂ CO ₂ Et	50	20	100
25	3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO	CNCH ₂ CO ₂ Et	50	20	100
26	furfural	CNCH ₂ CO ₂ Et	50	15	98
27	cyclohexanone	CNCH ₂ CO ₂ Et	50	20	98
28	C ₆ H ₅ COCH ₃	CNCH ₂ CO ₂ Et	50	45	95
29	C ₆ H ₅ CHO	CH ₂ (CO ₂ Et) ₂	50	60	95
30	4-CH ₃ OC ₆ H ₄ CHO	CH ₂ (CO ₂ Et) ₂	50	60	97

[a] Reaction conditions: carbonyl compound (5 mmol), active methylene compound (5 mmol), catalyst (G3PAMAM on PS, 0.5 mol-%), ethanol (5 mL). [b] Isolated yield of product.

An investigation into the effect of the generation of the dendrimer on the catalytic activity showed that the zero- and first-generation dendrimers gave products after long reaction times and that the yields were low. With second-generation dendrimer the product formation was observed within a relatively small interval of time and the yields were good, but with many aldehydes and ketones the reactions were not so efficient as with the third-generation dendrimer. Even if the loadings of the lower-generation dendrimers were increased, it was difficult to obtain results similar to those obtained with the third-generation dendrimer. The variation of the ease of the reaction with the generation of dendrimer is considered to be a dendrimer effect; similar behaviour has been observed with other dendrimer-based catalysts.^[16] The results are summarized in Table 3.

Table 3. Effect of generation of dendrimer on catalysis.

Entry	Generation	Catalyst [mol-%]	Time [min]	Yield ^[a,b] [%]
1	0	0.5	60	20
2	1	0.5	60	42
3	2	0.5	30	91
4	2	1.0	30	96
5	3	0.5	15	100

[a] Reaction conditions: benzaldehyde (5 mmol), malononitrile (5 mmol), ethanol (5 mL), room temperature (30 °C). [b] Isolated yield of product.

To gain better insight into the effect of the generation of dendrimer on catalysis, the reaction between benzaldehyde and malononitrile was carried out in the presence of various generations of dendrimers in such a way that the equivalence of amino groups was the same in all cases. The results are summarized in Table 4 (Entries 1–4).

Table 4. Effect of dendronization on catalysis.

Entry	Generation	Amino groups [equiv.]	Time [min]	Yield ^[a,b] [%]
1	0	0.2	60	40
2	1	0.2	45	52
3	2	0.2	25	93
4	3	0.2	15	100
5	0	0.2	15	nil
6	1	0.2	15	nil
7	2	0.2	15	70

[a] Reaction conditions: benzaldehyde (5 mmol), malononitrile (5 mmol), ethanol (5 mL), room temperature (30 °C). [b] Isolated yield of product.

As shown in Table 4, the third-generation catalyst gave better results under identical reaction conditions. From these experiments it is possible to assume that catalytic species situated at the periphery of a dendrimer exhibit cooperative interaction that can play a decisive role in catalysis. Because of this cooperative effect the dendronized catalyst is more effective than individual catalyst of same quantity.

The catalytic efficiency of the immobilized third-generation dendrimer was compared with that of unsupported first-generation PAMAM dendrimer. Since both the supported third-generation dendrimer and unsupported first-generation dendrimer have the same number of peripheral

amino groups, a comparable result should be expected. The unsupported dendrimer required only half the time (7 min) required by the supported dendrimer (15 min) for completion of the reaction between benzaldehyde and malononitrile under similar conditions. In the case of unsupported catalyst, however, removal and recycling of the catalyst was difficult and required chromatographic separation. The advantage of easy removal and multiple recycling of the supported catalyst might compensate for the longer reaction time.

The possibility of recycling the catalyst was studied. For this purpose, the used catalyst was washed extensively with ethyl acetate and dried under vacuum at room temperature. The colour of the polymer-supported catalyst had turned to light brown from yellow after the first run, but the catalytic activity remained the same for the subsequent runs. FTIR measurements showed that the catalyst did not undergo any chemical change. The catalyst showed no substantial reduction in activity even after the tenth run. The result of recycling is given in Table 5.

Table 5. Recycling of the catalyst.

Entry	No. of recycling runs	Time [min]	Yield ^[a,b] [%]
1	1	15	100
2	2	15	100
3	5	15	100
4	7	20	99
5	10	20	97

[a] Reaction conditions: benzaldehyde (5 mmol), malononitrile (5 mmol), catalyst (G3PAMAM on PS, 0.5 mol-%), ethanol (5 mL), room temperature (30 °C). [b] Isolated yield of product.

Conclusions

It is concluded that polystyrene-supported PAMAM dendrimer is a very active and reusable basic organocatalyst capable of promoting Knoevenagel condensations in an environmentally friendly way with high efficiency.

Experimental Section

General Information: Chloromethyl polystyrene (1% DVB crosslinked, 100–200 mesh, 1.1 mmol Cl atoms per gram) was obtained from Thermax India Ltd. as a gift sample and was washed with methanol, dioxane and acetone (2 × 20 mL) and dried under vacuum. Aminomethyl polystyrene was prepared by the standard procedure, and the amount of amino group was estimated to be 1.0 mmol g⁻¹. Benzaldehyde, anisaldehyde, salicylaldehyde and methyl acrylate were purified by the standard procedures. All other chemicals were used as received. Absolute ethanol obtained from s.d. fine India Ltd. was used as received. All other solvents were purified by standard procedures prior to use. FTIR measurements were done with a JASCO FTIR spectrometer as KBr pellets. Solid state CP-MAS ¹³C-NMR spectra were recorded with a Bruker 400 MHz instrument with a spinning rate of 7 K (results obtained from NMR research centre, IISc, Bangalore, India). ¹H NMR spectra were recorded with a Bruker 300 MHz or 400 MHz instrument with TMS as internal standard in CDCl₃, CD₃OD or (CD₃)₂SO as

solvent (results obtained from NMR research centre, IISc. Bangalore, India). GC–MS was performed with a Varian 1200L single quadrupole GC–MS with capillary column. MALDI TOF MS was carried out with a Shimadzu Kratos compact analytical MALDI TOF MS with use of an Nd-YAG laser with an operating wavelength of 354 nm (results obtained from RGCB, Thiruvananthapuram, Kerala, India). The matrix used was α -cyano-4-hydroxycinnamic acid. Angiotensin II and insulin were used as internal standards. Melting point determination and TG-DTA analysis were carried out with Perkin–Elmer Diamond model TG/DTA system with platinum as a standard.

Preparation of Nitrated Chloromethyl Polystyrene:^[17] A 250-mL beaker was charged with fuming nitric acid (50 mL) and cooled to 0 °C in an ice–salt bath. Chloromethyl polystyrene (5 g) was added to the nitric acid in small lots with stirring. The addition was very slow, so that the temperature was not allowed to rise above 5 °C. After completion of the addition of the polymer, the temperature was maintained at 0–5 °C for 1 h with constant stirring. The temperature was slowly brought up to room temperature over a period of 2–3 hours. The reaction mixture was heated slowly to 50 °C. It was poured over crushed ice. The polymer beads were recovered by filtration and washed with water (5 × 20 mL), dioxane (3 × 20 mL) and methanol (3 × 20 mL) and dried under vacuum. Yield 6.5 g.

Preparation of Aminomethyl Polystyrene:^[18] A 250-mL round-bottomed flask fitted with a condenser was charged with dry DMF (75 mL). Chloromethyl polystyrene or nitrated chloromethyl polystyrene (5 g) was added, followed by potassium phthalimide (1.7 g, 8.9 mmol). The reaction mixture was kept at 50 °C for 24 h with constant stirring. The polymer beads were filtered, washed with dry DMF (3 × 20 mL), methanol (3 × 20 mL), water (5 × 20 mL) and methanol (3 × 20 mL) and dried under vacuum. Yield 5.8 g.

A 250 mL round-bottomed flask fitted with a condenser was charged with absolute ethanol (50 mL). The phthalimidomethyl polystyrene prepared as described above (5.8 g) was added to the round-bottomed flask, followed by hydrazine hydrate (1 mL). The reaction mixture was heated at reflux with stirring for 24 h. The polymer beads were recovered by filtration and washed with ethanol (3 × 20 mL), aqueous KOH (5%, 3 × 20 mL), water (5 × 20 mL) and ethanol (3 × 20 mL). The polymer beads were dried under vacuum. Yield 5.25 g.

Estimation of Amino Groups: The polystyrene resin bearing the amino groups (200 mg) was suspended in HCl (0.01 M, 40 mL) for 24 h with occasional stirring. The resin was filtered and washed well with distilled water. The filtrate and washings were collected. The unreacted HCl was determined by titration against a standard Na₂CO₃ solution with use of methyl orange indicator. A blank titration was also carried out. From these values, the amount of amino groups per gram of the resin was calculated.

Solid-Phase Synthesis of PAMAM Dendrimers: First-, second- and third-generation^[19] PAMAM dendrimers were synthesized on the aminomethyl polystyrene (1% DVB crosslinked, 100–200 mesh, 1 mmol NH₂ per gram). PAMAM dendrimers were synthesized by a reported procedure with minor modification. The resin (1 g, 1 mmol –NH₂ groups) was added in portions at room temperature with stirring to methyl acrylate (22 mL, 250 mmol) and methanol (20 mL) in a 100-mL round-bottomed flask. The reaction mixture was stirred at room temperature under nitrogen for 5 d. After the reaction, excess reactants and solvent were removed under vacuum. The polymer was washed well with methanol, dichloromethane and acetone (3 × 20 mL). It was dried under vacuum for 24 h. FTIR spectra showed a band at 1735 cm^{–1} due to the C=O stretching

vibration of the ester group, whereas bands due to the stretching vibration of the amino groups had completely disappeared.

In the second step, the resin obtained as above was subjected to transamination as follows. The resin was added in small fractions with stirring to a mixture of ethylenediamine (16 mL, 250 mmol) and methanol (20 mL) in a round-bottomed flask, cooled to 0 °C in an ice–salt bath. The reaction mixture was stirred at 0 °C for 1 h, the temperature was allowed to rise to room temperature (30 °C), and the mixture was stirred at room temperature for 4 d to ensure complete reaction. It was filtered under vacuum, was washed well with methanol, acetone and diethyl ether (2 × 20 mL) and was dried under vacuum for 24 h. The FTIR spectrum showed the appearance of bands due to primary amino groups and a shift in the band at 1735 to 1660 cm^{–1} due to the conversion of ester to amide. Estimation of amino groups showed that the number of amino groups had been doubled relative to the starting polymer. Repetition of the above steps gave second- and third-generation PAMAM dendrimers attached to the polymer beads. After the synthesis, the polymer-supported dendrimers were characterized by FTIR and solid-state ¹³C NMR spectroscopy.

In addition, to confirm the growth and homogeneity of the dendrimer, the synthesis was performed on nitrated aminomethyl polystyrene and the dendrimers were cleaved photolytically from the support in methanol. The third-generation dendrimer was characterized by ¹H NMR and MALDI-TOF MS without further purification. The single peak at 1615 D (M⁺ ion) confirms the formation of G3 PAMAM dendrimer on the polymer without considerable defects. The dendronised resin prepared in this manner was used for further studies. From the estimation of amino groups, and CHN analysis it was estimated that the resin contained 0.260 mmol dendrimer per gram of the resin (Table 6).

Table 6. Estimation of amino groups.

Entry	Generation	Amount of amino groups [mmol g ^{–1}]
1	0	1.0
2	1	1.61
3	2	1.88
4	3	2.08

General Procedure for Knoevenagel Condensation: A 10-mL round-bottomed flask was charged with the carbonyl compound (5 mmol), active methylene compound (5 mmol), polymer-supported catalyst (96 mg, 0.5 mol-% of the substrates) and absolute ethanol (5 mL). The reaction mixture was stirred at the requisite temperature. The formation of the product was monitored by TLC. After completion of the reaction, the reaction mixture was filtered. The catalyst was washed several times with ethyl acetate. The washings were collected and combined with the filtrate. The products were isolated by removing the solvent by evaporation. In general, no further purification method was required. All the products were previously reported and were characterized by melting point determination (see characterization data; literature values of melting points are in brackets) and with FTIR and ¹H NMR spectroscopy. In the case of liquid products, GC/MS was used for characterization and yield determination. Selected data for typical compounds are given below.

2-[(4-Dimethylaminophenyl)methylene]malononitrile: Orange crystals (986.2 mg, 100%). M.p. 180 °C (ref.^[5] 180–181 °C). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.8 (d, J = 9.0 Hz, 2 H, phenyl), 7.4 (s, 1 H, CH), 6.6 (d, J = 9.0 Hz, 2 H, phenyl), 3.1 (s, 6 H,

CH₃) ppm. FTIR (KBr): $\tilde{\nu}$ =2200 (CN), 1614 (C=C) cm⁻¹. See Table, Entry 4.

2-(2-Hydroxy-1,2-diphenylethylidene)malononitrile: Colourless crystals (1301.45 mg, 100%). M.p. 133 °C. ¹H NMR (400 MHz, [D₆] DMSO, 25 °C): δ = 7.9 (s, 2 H, phenyl), 7.5–7.2 (m, 8 H, phenyl), 3.3 (s, 1 H, CH), 2.5 (s, 1 H, OH) ppm. FTIR (KBr): $\tilde{\nu}$ = 3413 (OH), 2216 (CN), 1599 (C=C) cm⁻¹. See Table, Entry 15.

Ethyl (E)-2-Cyano-3-(4-hydroxyphenyl)prop-2-enoate: Yellow crystals (1086.1 mg, 100%). M.p. 168–169 °C (ref.^[5] 169–170 °C). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 8.2 (s, 1 H, CH), 7.9 (d, *J* = 8.0 Hz, 2 H, phenyl), 7.0 (d, *J* = 8.0 Hz, 2 H, phenyl), 4.4 (q, *J* = 7.0 Hz, 2 H, CH₂), 1.4 (t, *J* = 7.0 Hz, 3 H, CH₃) ppm. FTIR (KBr): $\tilde{\nu}$ = 3353 (OH), 2227 (CN), 1608 (C=C), 1174 (C–C–O), 1030 (O–C–C) cm⁻¹. See Table, Entry 21.

Diethyl 2-(4-Methoxybenzylidene)malonate: Colourless liquid (1349.75 mg, 97%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.6 (s, 1 H, CH), 7.3 (d, *J* = 8.0 Hz, 2 H, phenyl), 6.8 (d, *J* = 8.0 Hz, 2 H, phenyl), 4.4 (q, *J* = 7.0 Hz, 2 H, CH₂), 4.3 (q, *J* = 7.0 Hz, 2 H, CH₂), 3.8 (s, 3 H, OCH₃), 1.4 (t, *J* = 7.0 Hz, 3 H, CH₃), 1.3 (t, *J* = 7.0 Hz, 3 H, CH₃) ppm. FTIR (KBr): $\tilde{\nu}$ = 1728 (C=O), 1283 (C–C–O), 1112 (O–C–C) cm⁻¹. See Table, Entry 30.

Supporting Information (see footnote on the first page of this article): Characterization data for all the olefins prepared and MALDI-TOF-MS spectrum of the third-generation dendrimer.

Acknowledgments

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