

Solvent-Free Cyanoethylation of Selected Alcohols Using Amberlyst A-21 Polymer Resin

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ABSTRACT: Solvent-free cyanoethylation of selected alcohols with acrylonitrile (AN) using a weakly basic polymer resin, Amberlyst A-21 (AA-21) was studied at 75°C. The conversion of primary alcohols, 1-octadecanol, hexane-1,6-diol, pentaerythritol, but-2-yne-1,4-diol, *N*-methyldiethanolamine, triethanolamine and diethanolamine is higher than secondary alcohols, isopropanol and glycerol in the presence of polymer resin. Of various alcohols, but-2-yne-1,4-diol gave the product in high conversion (87%) in cyanoethylation with a polymer resin/AN weight ratio of 0.04. The polymer resin showed recycling ability only in two cycles to produce cyanoethylated product from diethanolamine. In case of 1-octadecanol, hexane-1,6-diol, and *N*-methyldiethanolamine with AN under similar conditions, no recycling ability was observed. Thermally treated polymer resin at 75°C afforded the product in lower conversion (55%) whereas the same product was obtained in 69% when fresh polymer resin was used in cyanoethylation of 1-octadecanol. No catalytic effect was observed for polymer resin treated at 100°C. Fourier transform infrared (FTIR) spectra showed CN stretching at 2248 cm⁻¹ for the polymer resin collected after the reaction which was caused by the AN binding on polymer resin during the reaction. As per thermogravimetric curves, 5% weight loss was observed at 201°C for recovered resin and at 161°C for polymer resin treated at 100°C. Scanning electron microscope images confirmed the AN binding on polymer beads after catalytic activity. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

In the last few decades, there is an immense progress on the use of polymer based homogeneous and heterogeneous catalysts in organic synthesis.^{1–9} The use of polymeric heterogeneous catalysts increases the manufacturing flexibility and reduces the operational costs. They are environmentally friendly because of their recycling ability. These catalysts are generally, in the form of beads, colloids, fiber, or hollow fiber and immobilized on inorganic supports.¹⁰ Recently, polymer-based heterogeneous catalysts based on nano-porous polymers, such as covalent organic frameworks and porous organic polymers have received much attention due to their facile role in organic catalysis and asymmetric transformations.¹¹

The cyanoethylation of alcohols is an important C–O bond forming reaction. In general, the cyanoethylated products are produced by homogeneous catalysis using alkali hydroxides and alkoxides and also by heterogeneous catalysts such as anion exchange resins, alkaline earth oxides, alkali hydroxide sup-

ported metal hydrotalcites and rare-earth-modified layered double hydroxides.^{12–14} However, the cyanoethylation also produces byproducts such as acrylonitrile (AN) oligomer or polymer along with cyanoethylated products. To minimize unwanted AN polymerization in the reaction mixture, the experimental conditions were adjusted by lowering the temperature, catalyst addition, and maintaining inert atmosphere during the reaction but which undoubtedly increase the operational costs.¹⁵ Polymer-supported phase transfer catalysts are known to lower the activation energy¹⁶ with cooperative effect of anchored active sites on polymer chain and also provides the hydrophobic microenvironment by diffusion of the reagents. In addition to this, insoluble polymer networks have been used as scavengers¹⁷ for organic transformations.¹⁸ Therefore, a variety of organic molecules and modified polymers can be produced by means of cyanoethylation in the presence of polymer^{19,12} and inorganic-based^{20–22} catalysts for various applications, for example in making drug intermediates and in improving polymer properties,^{23–25} respectively.

Polymer based insoluble heterogeneous catalyst, i.e., Amberlyst A-21 (AA-21), a weakly basic resin with $N(\text{CH}_3)_2$ functional group^{26,27} is a commercially available inexpensive resin⁷ and has been used as a reusable polymer catalyst.²⁸ In the past decades, the AA-21 has been explored as heterogeneous solid base for various applications such as selective removal of chromates²⁹ from solution by varying pH, temperature, and concentration, adsorption of palladium(II) complexes from HCl-NaCl solutions,³⁰ removal of azo dye³¹ and ring cleavage³² of 2-nitrocycloalkanoes to produce methyl omega-nitroalkanoates. Furthermore, it has been used for the Henry reaction,^{33–35} the Michael reaction,¹⁹ and transesterification.³⁶ It has also been used in the synthesis of semipermeable membrane microcapsules.³⁷ In addition to this, modified AA-21 with copper(I) iodide has been used for the Huisgen cycloaddition reactions.^{28,38} In this article, we report for the first time, a solvent-free cyanoethylation of alcohols with AN using the AA-21 polymer resin as a heterogeneous catalyst. The catalytic activity of the polymer resin was tested thoroughly before and after the reaction.

EXPERIMENTAL

Materials

Polymer resin, AA-21 (opaque spherical beads, particle size, harmonic mean size: 0.490 – 0.690 mm with uniformity coefficient ≤ 1.80 , surface area: $35 \text{ m}^2 \text{ g}^{-1}$, total pore volume: 0.10 cc g^{-1} (Nitrogen BET) from Aldrich), AN (Ranbaxy Labs), 1-octadecanol (Aldrich), hexane-1,6-diol (AVRA), pentaerythritol (2,2-bis(hydroxymethyl)1,3-propanediol) (Aldrich), but-2-yne-1,4-diol (Aldrich), *N*-methyl-diethanolamine (Aldrich), triethanolamine (Aldrich), diethanolamine (Qualigens), isopropanol (sd fine Chem) and glycerol (Qualigens) were used as received without any further purification.

Characterization Techniques

The FTIR spectroscopy (Thermo Nicolet Nexus 670 spectrometer) was used to identify the functional groups of the cyanoethylated products and to understand the changes of the AA-21 catalyst before and after the reaction. The spectra were measured at a resolution of 4 cm^{-1} using KBr optics at room temperature and a minimum of 32 scans were signal averaged.

The proton nuclear magnetic resonance (^1H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded for cyanoethylated products on AVANCE-300 or INOVA-500 spectrometer in CDCl_3 or in a mixture of CDCl_3 and dimethyl sulfoxide- d_6 ($\text{DMSO-}d_6$) depends on the solubility of the products with tetramethylsilane as an internal standard. Mass spectra were recorded on FINNGAN LCQ Advance Max in methanol for AA-21 catalyzed products.

Gas chromatography (GC) was used to stabilize the reaction conditions and to study the cyanoethylation kinetics. GC profiles were obtained from GC-SHIMADZU-2010 and Agilent Technologier 7890 A using DB-1 WAX and HP-1 column, respectively. The high-resolution mass spectrometry (HRMS) (QSTARXL mass spectrometer) was used to obtain accurate mass of the synthesized compounds. Methanol was used as a solvent for the HRMS measurements.

Thermogravimetric (TG) analyses were performed to understand the thermal decomposition of the AA-21 resin before and

after the reaction. TG curves were obtained from TGA Q-500 thermal analyzer, TA instruments at heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere.

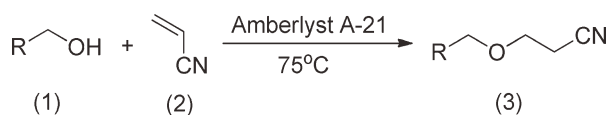
The scanning electron microscope (SEM) analysis was conducted to study the surface morphology of AA-21 resin before and after the catalytic activity. SEM images were taken using Hitachi S-3000 N under high pressure. The surfaces of the AA-21 beads were coated with gold by vacuum evaporation method.

Polymer Resin Catalyzed Cyanoethylation

A mixture of polymer resin, AA-21 (0.3 g), 1-octadecanol (1.0 g), and AN (1.21 g) was stirred in a two-necked round bottom flask equipped with water condenser at 75°C for 4.5 h and the progress of the reaction was monitored by thin layer chromatography. The resulting mixture was filtered to separate the polymer beads. The excess of AN was removed under vacuum at room temperature. The crude product was purified by column chromatography on silica gel (Acme's, 60–120 mesh) using ethyl acetate and *n*-hexane mixture as eluent to afford the pure 3-octadecyloxypropanenitrile. All products were characterized by FTIR, ^1H NMR, and mass spectroscopy methods and a few selected products were characterized by ^{13}C NMR and HRMS.*

Kinetic studies were performed for 1-octadecanol and hexane-1,6-diol. A typical procedure is as follows. A mixture of polymer

* **3a** 3-octadecyloxypropanenitrile ^1H NMR (CDCl_3 , 300 MHz): δ 0.88 (m, 4H), δ 1.25 (s, 26H), δ 1.56, 3.62 (t, each 2H, $J = 6.6 \text{ Hz}$, $-\text{CH}_2-$), δ 2.55, 3.45 (t, each 2H, $J = 6.4 \text{ Hz}$, $-\text{CH}_2-$). ESIMS: m/z : 346 ($\text{M}^+ + \text{Na}^+$). IR (KBr, cm^{-1}): ν 1125 (C–O–C), 2250 ($-\text{CN}$). ^{13}C NMR (CDCl_3 , 75 MHz): δ 14.17, 18.79, 22.60, 25.89, 29.70, 31.71, 38.58, 65.08, 71.54, 117.82. **3b** 1,4-butane-di(4-oxa,pentanenitrile) ^1H NMR (CDCl_3 , 300 MHz): δ 1.34–1.38 (p, 4H), δ 1.56, 2.53, 3.44, 3.59 (t, each 4H, $J = 6.0 \text{ Hz}$, $-\text{CH}_2-$). ESIMS: m/z : 247 ($\text{M}^+ + \text{Na}^+$). IR (neat, cm^{-1}): ν 1114 (C–O–C), 2250 ($-\text{CN}$). **3c** methane-tetra(4-oxa,pentanenitrile) ^1H NMR ($\text{DMSO-}d_6$, 300 MHz): δ 2.60, 3.67 (t, each 8H, $J = 5.8 \text{ Hz}$, $-\text{CH}_2-$), δ 3.48 (s, 8H, $-\text{CH}_2-$). ESIMS: m/z : 366 ($\text{M}^+ + \text{NH}_4^+$). IR (neat, cm^{-1}): ν 1109 (C–O–C), 2251 ($-\text{CN}$). ^{13}C NMR ($\text{DMSO-}d_6$, 75 MHz): δ 18.04, 45.03, 65.57, 68.29, 119.16. HRMS, m/z found 349.1875 (calc. for $\text{C}_{17}\text{H}_{25}\text{N}_4\text{O}_4$ ($\text{M}^+ + \text{H}$): 349.1873). **3d** 1, 2-ethene-di(4-oxa,pentanenitrile) ^1H NMR (CDCl_3 , 400 MHz): δ 2.58, 3.65 (t, each 4H, $J = 6.4 \text{ Hz}$, $-\text{CH}_2-$), δ 4.13 (d, 4H, $J = 4.3 \text{ Hz}$, $-\text{CH}_2-$), δ 5.73 (t, 2H, $J = 4.3 \text{ Hz}$, $-\text{CH}=\text{CH}$). ESIMS: m/z : 217 ($\text{M}^+ + \text{Na}^+$). IR (neat, cm^{-1}): ν 1103 (C–O–C), 2250 ($-\text{CN}$). **3e** acetylene-di(4-oxa,pentanenitrile) ^1H NMR (CDCl_3 , 300 MHz): δ 2.63, 3.75 (t, each 4H, $J = 6.0 \text{ Hz}$, $-\text{CH}_2-$), δ 4.26 (s, 4H, $-\text{CH}_2-$). ESIMS: m/z : 215 ($\text{M}^+ + \text{Na}^+$). IR (neat, cm^{-1}): ν 1097 (C–O–C), 2251 ($-\text{CN}$). ^{13}C NMR (CDCl_3 , 75 MHz): δ 18.16, 57.88, 63.82, 81.73, 117.56. HRMS, m/z found 215.0796 (calc. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_2\text{Na}$ ($\text{M}^+ + \text{Na}$): 215.0796). **3f** methylamine-di(4-oxa,hexanenitrile) ^1H NMR (CDCl_3 , 300 MHz): δ 2.36 (s, 3H, $\text{N}-\text{CH}_3$), δ 2.59, 3.68 (t, each 4H, $J = 6.2 \text{ Hz}$, $-\text{CH}_2-$), δ 2.67, 3.60 (t, each 4H, $J = 5.4 \text{ Hz}$, $-\text{CH}_2-$). IR (neat, cm^{-1}): ν 1118 (C–O–C), 2251 ($-\text{CN}$). **3g** amine-tri(4-oxa,hexanenitrile) ^1H NMR ($\text{DMSO-}d_6$, 500 MHz): δ 2.65, 3.72 (t, each 12H, $J = 5.9 \text{ Hz}$, $-\text{CH}_2-$). ESIMS: m/z : 309 ($\text{M}^+ + \text{H}^+$). IR (neat, cm^{-1}): ν 1118 (C–O–C), 2252 ($-\text{CN}$). **3h** 3-isopropoxypropanenitrile ^1H NMR (CDCl_3 , 300 MHz): δ 1.18 (d, 6H, $J = 6.2 \text{ Hz}$, $-\text{CH}_3$), δ 2.54 (t, 2H, $J = 6.4 \text{ Hz}$, $-\text{CH}_2-$), δ 3.62 (m, 3H, $-\text{CH}_2-$ and $-\text{CH}-$). IR (neat, cm^{-1}): ν 1130 (C–O–C), 2251 ($-\text{CN}$). **3i** 4-oxa,pentanenitrile-di(4-oxa,pentanenitrile) ^1H NMR (CDCl_3 , 300 MHz): δ 2.61, 3.72, 3.88 (t, 6H, 4H, 2H, respectively, $J = 6.0 \text{ Hz}$, $-\text{CH}_2-$), δ 3.62 (m, 5H, $-\text{CH}_2-$ and $-\text{CH}-$). ESIMS: m/z : 274 ($\text{M}^+ + \text{Na}^+$). IR (neat, cm^{-1}): ν 1115 (C–O–C), 2251 ($-\text{CN}$).



Scheme 1. Cyanoethylation.

resin, AA-21 (2.25 g), 1-octadecanol (7.5 g), and AN (8.9 g) was stirred in a two-necked round bottom flask equipped with water condenser at 75°C. The constant stirring (350 rpm) was maintained throughout the study. Every 30 min, the samples were collected through the septum using a 0.5 mL syringe. The samples were analyzed by GC. The pseudo first-order rate constants (k_{obs}) were obtained by plotting the $\log(a \div (a-x))$ against time up to 200 min, where a , initial percentage of concentration of 1-octadecanol and x , percentage of concentration of 1-octadecanol at that time. The slope of the straight line was determined and multiplied with 2.303 to obtain k_{obs} values.

RESULTS AND DISCUSSION

Polymer Resin Catalytic Activity

The cyanoethylation (Scheme 1) of various primary alcohols (mono-, di-, tri- and tetra-alcohols) with various functionalities

such as tertiary amines, olefins, and alkynes proceeds in good yields under the influence of polymer resin in solvent-free conditions. The results are summarized in Table I. Among various primary alcohols, but-2-yne-1,4-diol gave the product **3e** in 87% yield with the polymer resin/AN weight ratio of 0.04. Triethanolamine gave the product **3g** in 60% yield when low quantity of AN was used (polymer resin/AN weight ratio of 0.21 for tri alcohols) at 75°C for 4.5 h. Indeed, secondary alcohols gave the product in low yield compared with the primary alcohols. The reactivity of the base polymer resin depends upon the acidic nature of the alcohols (primary alcohols are more acidic compare to the secondary).²⁰ In the case of glycerol, the corresponding product was obtained in poor yield in water (entry i, Table I) due to the poor solubility of AN in water and enhanced hydrogen bonding between glycerol and water and steric hindrance of the glycerol. Figure 1 shows the AN/polymer resin (w/w) ratio vs. conversion (%) curves of 1-octadecanol under solvent-free and in presence of tetrahydrofuran (THF). The maximum conversion was achieved to 69% under solvent-free conditions, whereas 16% conversion was observed in THF when the reaction was performed with AN/polymer resin weight ratio of 3.93. Further increase in AN concentration, the conversion

Table I. Cyanoethylation of Alcohols with AN (2) Over Amberlyst A-21

S. No.	Reactant (1)	AA-21/Reactant (w/w)	AA-21/AN (w/w)	Product (3)	Yield (%)	Melting point (°C)
a.		0.30	0.248		69	49-52
b.		0.30	0.074		80	- ^a
c.		0.30	0.062		56	42-44
d.		0.28	0.074		75	-
e.		0.30	0.037		87	-
f.		0.29	0.093		56	-
g.		0.30	0.207		60	-
h.		0.30	0.073		22	-
i. ^b		0.24	0.116		8	-

Reaction condition: temperature: 75°C and time: 4.5 h, ^aLiquid, ^bAdded 3 g water and time: 10 h.

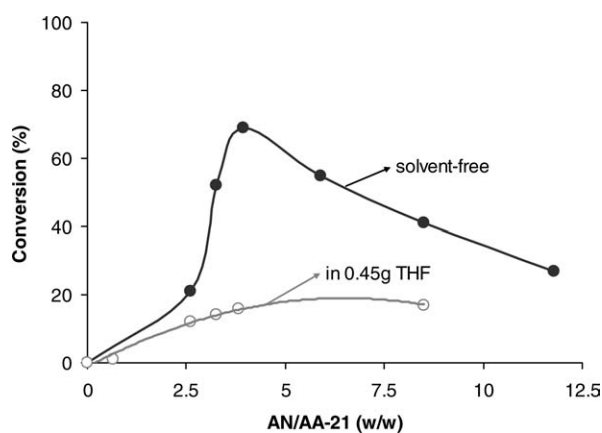
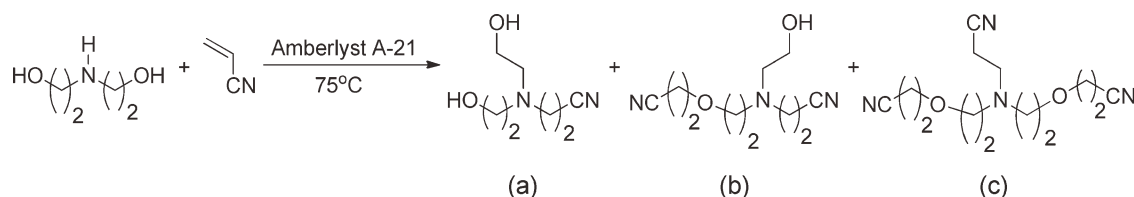


Figure 1. Cyanoethylation of 1-octadecanol with AN at 75°C for 4.5 h.



Scheme 2. Cyanoethylation of diethanolamine with AN, (a) aza- (b) aza- with mono-oxa- and (c) aza- with di-oxa-Michael product.

was decreased. In solvent-free cyanoethylation reaction, AN acts as reagent as well as solvent. At lower concentration of AN, the yield was lower due to the insufficient amount of the AN. On the other hand, higher concentration of the AN leads to the side reactions such as AN binding on polymer resin and formation of AN oligomer. By increasing the amount of the catalyst ranging from 0.3 g to 0.6 g in cyanoethylation of 1-octadecanol gave the desired product **3a** in 73% yield under identical conditions (entry a, Table I).

The rate of catalytic activity of the polymer resin was examined for 1-octadecanol and hexane-1,6-diol as shown in Figure 2. In case of hexane-1,6-diol, the conversion was higher compared to 1-octadecanol. Lower activity of the polymer resin is attributed to the presence of longer alkyl chain of 1-octadecanol. The conversion was increased when about 6% of cyanoethylated 1-octadecanol was found in reaction mixture. The pseudo first-order rate constants^{39,16} for cyanoethylation of 1-octadecanol and hexane-1,6-diol were 1.105×10^{-3} (coefficient of determination $R^2 = 0.67$) and 6.525×10^{-3} ($R^2 = 0.88$), respectively.

The catalyst could be easily separated by simple filtration and reused in cyanoethylation. After first cycle, the recovered polymer beads were washed with ethanol and dried at room temperature and then used in further cycles. For instance, treatment of diethanolamine (1.0 g) with AN (1.44 g) in the presence of 0.21 g of polymer resin gave a mixture of aza-[†] (22.6%, calculated by gas chromatography) and aza- with oxa-Michael products

[†]3-(bis(2-hydroxyethyl)amino)propanenitrile ¹H NMR (CDCl₃+DMSO-*d*₆, 300 MHz): δ 2.52, 2.88 (t, each 2H, $J = 6.7$ Hz, $-\text{CH}_2-$), δ 2.69, 3.62 (t, each 4H, $J = 4.5$ Hz, $-\text{CH}_2-$). IR (neat, cm^{-1}): ν 1144 (C—O—C), 2250 ($-\text{CN}$).

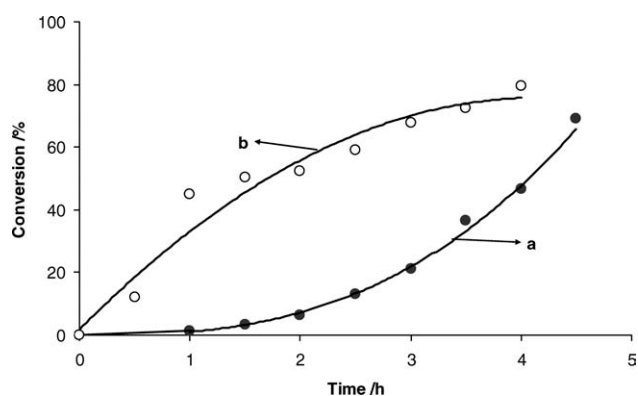


Figure 2. Rate of the reaction at 75°C, polymer resin 0.3 g per 1 g of reactant, and reactant:AN $\approx 1 : 6$ (mol/mol) of (a) 1-octadecanol and (b) hexane-1,6-diol.

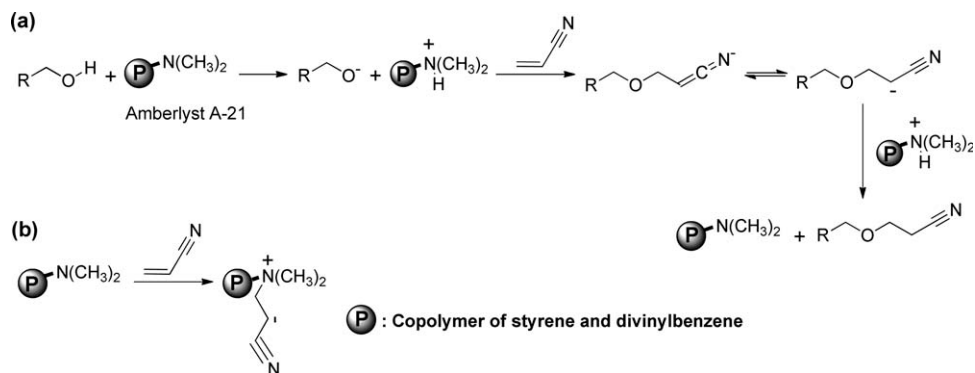
(mono-oxa[‡]: 66.3% and di-oxa[§]: 11%) in similar yields over two cycles as shown in Scheme 2. After second cycle, the polymer resin became inactive. The possible reaction mechanism in cyanoethylation of alcohols with AN in the presence of polymer resin is shown in Scheme 3(a). The reusability of the recovered catalyst in cyanoethylation of 1-octadecanol, hexane-1,6-diol, and *N*-methyl-diethanolamine with AN at 75°C was examined. Except diethanolamine, the recovered catalyst was found to be inactive for recycling. It could be due to the organic fouling by binding of AN on the surface and pores of the polymer resin spherical beads. The AN binding mechanism is shown in Scheme 3(b).

Regeneration of AA-21 by Thermal Treatment

The catalytic activity was tested by removing the moisture from polymer resin by vacuum at room temperature and by thermal treatment at 75 and 100°C (gradually increased the temperature with $10^\circ\text{C min}^{-1}$). After removing the moisture by vacuum, the catalyst activity (for similar weight of polymer resin) was similar as before, whereas thermally treated resin at 75°C for 10 min showed 55% conversion in cyanoethylation of 1-octadecanol. On the other hand, only 47% conversion was observed in

[‡]3-((2-(2-cyanoethoxy)ethyl)(2-hydroxyethyl)amino)propanenitrile ¹H NMR (CDCl₃+DMSO-*d*₆, 300 MHz): δ 2.53, 2.92 (t, each 2H, $J = 6.6$ Hz, $-\text{CH}_2-$), δ 2.62 to 2.69 (m, 4H, $-\text{CH}_2-$), δ 2.78 (t, 2H, $J = 5.2$ Hz), δ 3.51–3.59 (m, 4H, $-\text{CH}_2-$), δ 3.66 (t, 2H, $J = 6.2$ Hz, $-\text{CH}_2-$). IR (neat, cm^{-1}): ν 1116 (C—O—C), 2249 ($-\text{CN}$).

[§]4-azabutanenitrile-di(4-oxa,hexanenitrile) ¹H NMR (CDCl₃+DMSO-*d*₆, 500 MHz): δ 2.49, 2.96 (t, each 2H, $J = 6.4$ Hz, $-\text{CH}_2-$), δ 2.60, 3.68 (t, each 4H, $J = 6.0$ Hz, $-\text{CH}_2-$), δ 2.82, 3.60 (t, each 4H, $J = 5.0$ Hz, $-\text{CH}_2-$). IR (neat, cm^{-1}): ν 1114 (C—O—C), 2249 ($-\text{CN}$).



Scheme 3. A plausible reaction mechanisms of (a) polymer resin recycling and (b) AN binding on polymer resin.

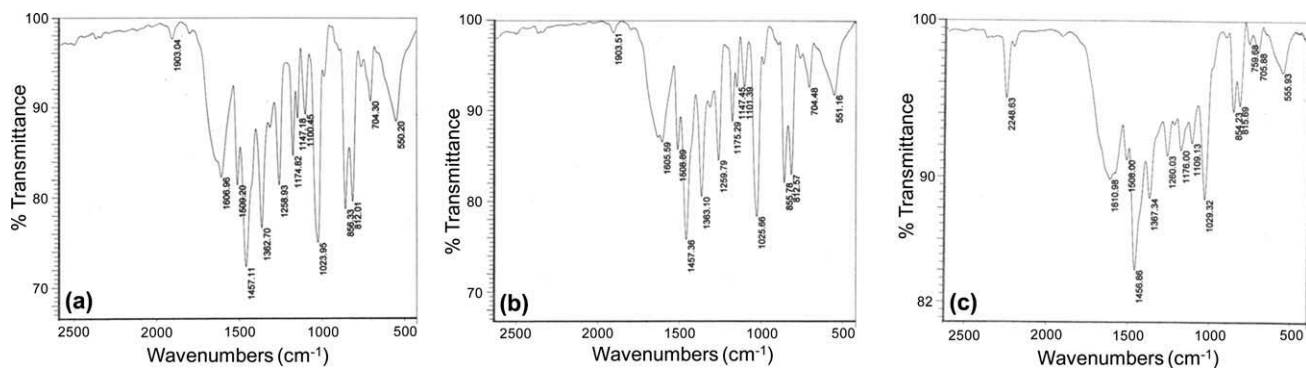


Figure 3. FTIR spectra of the polymer resin (a) fresh resin, (b) treated at 100°C and (c) after solvent-free reaction.

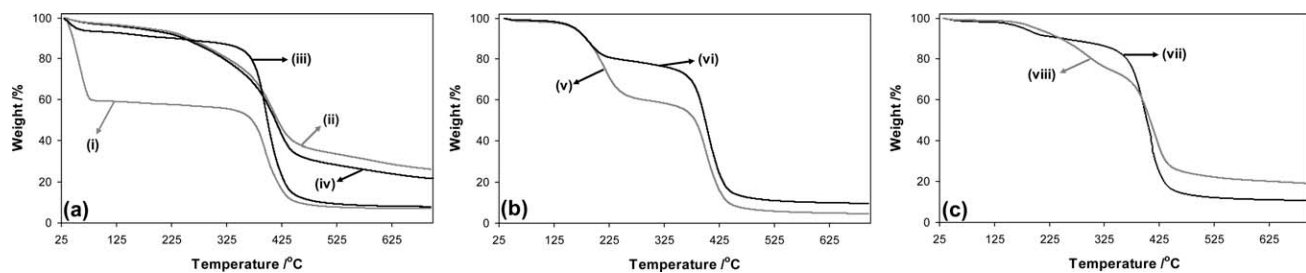


Figure 4. TG curves of the AA-21 catalyst (a) (i) fresh resin, (ii) dried by vacuum at RT, and (iii) and (iv) dried at 75 and 100°C, respectively, (b) after the reaction between diethanolamine and AN (v) 1st cycle and (vi) 2nd cycle and (c) after the reaction between 1-octadecanol and AN (vii) in THF and (viii) solvent-free.

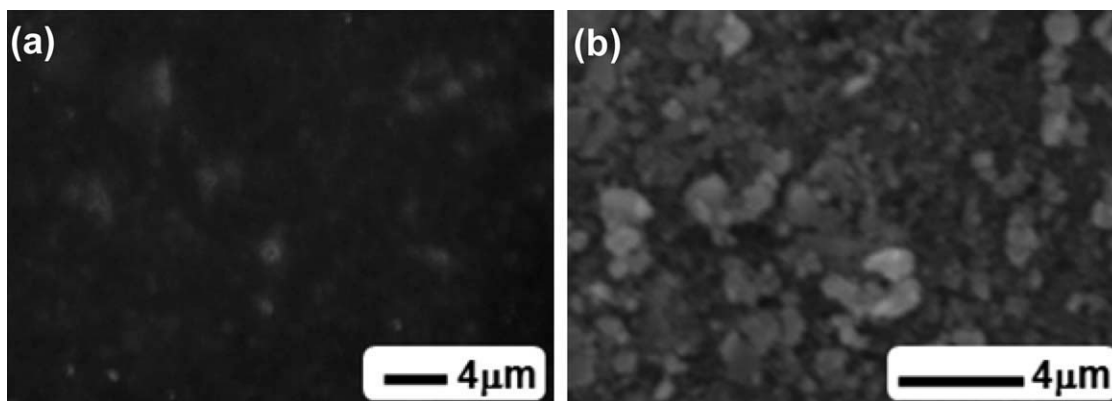


Figure 5. SEM images of the AA-21 catalyst (a) fresh resin and (b) after the reaction.

the same reaction using thermally treated resin at 75°C for 4 h. No catalytic activity was observed with the resin treated at 100°C.

Polymer Resin Characterization

The FTIR spectrum of polymer resin (Figure 3) showed the characteristic absorption for C—N—C stretching⁴⁰ at 1100 cm⁻¹, while a thermally treated polymer resin exhibited 1101 cm⁻¹ band for C—N—C stretching. Moreover, thermally treated resin showed about 4% decrease in transmittance region from 1607 to 812 cm⁻¹. The resin collected after the solvent-free reaction, the FTIR spectrum exhibited nitrile (—CN) stretching at 2248 cm⁻¹ and C—N—C stretching at 1109 cm⁻¹. This is due to the AN deposition on polymer resin. After the solvent-free reaction, the color of the polymer beads became yellow.

The TG analysis of the polymer resin was performed under nitrogen atmosphere with a fresh resin, thermally treated resin (at 75 and 100°C) and the resin after the reaction. Figure 4 shows the TG curves of the polymer resins. Fresh polymer resin was lost 40% of its weight at 100°C due to the loss of moisture compared with the polymer resin dried by vacuum and also the resin treated at 100°C for 10 min as shown in Figure 4(a). TG curves of the polymer resin, after the reaction between diethanolamine and AN, exhibited two stages weight loss as shown in Figure 4(b). The first stage weight loss was occurred due to the evaporation of the diethanolamine (boiling point: 217°C, Aldrich) which exists in polymer resin pores. The second stage could be due to the degradation of resin and AN binding. First stage weight loss was more in first cycle resin (40%) comparatively second cycle resin (20%). It indicates the AN binding in the bead pores and surface after recovery of the polymer beads from the second cycle. Figure 4(c) shows weight loss of the recovered polymer resins from solvent-free and THF media. In both cases, 5% weight loss was observed at 201°C for recovered resin from solvent-free condition and at 178°C for recovered resin from THF. The increased thermal stability of the polymer resin could be due to the AN binding on polymer beads.

The SEM images of the fresh and after first cycle resin surfaces are shown in Figure 5. The surface of the polymer resin, after the reaction, exhibited rough and lumps deposition on the surface compared to the fresh resin. This is due to the AN deposition on polymer resin after the reaction.

CONCLUSIONS

The cyanoethylation of selected alcohols with AN using polymer resin, AA-21 as a catalyst was studied in both solvent and solvent-free conditions. This method is compatible with various functionalities such as tertiary amines, olefins, and alkynes. After the reaction, acrylonitrile binding on polymer resin spherical beads was observed. Both AN binding with polymer resin and the reaction temperature $\geq 75^\circ\text{C}$ are the hindering factors for a catalytic activity of the polymer resin.

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