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Catalyst-free click cascade functionalization of unsaturated-bond-containing polymers using masked-ketene-tethering nitrile *N*-oxide

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ABSTRACT

We developed a facile protocol for grafting-onto and cross-linking unsaturated-bond-containing common polymers via the formation of masked-ketene-functionalized polymers. The protocol utilizes a cascade functionalization agent **1** that has nitrile *N*-oxide and masked ketene functionalities. Through the model ligation reactions using **1**, it turned out that the **1** facilitates the catalyst-free click introduction of masked ketene moieties to the unsaturated bonds such as C≡N and C=C bonds, capable of undergoing catalyst-free ligation with not only a nucleophilic amine but also a neutral alcohol with low nucleophilicity. On the basis of these results, the catalyst-free grafting reactions of PEG onto EPDM and PAN using **1** were performed to afford the corresponding graft copolymers in excellent conversion yields. In addition, it was also revealed that heating of both PAN and NR with masked ketene moieties at 250 °C for 1 h without catalyst enables the efficient conversion to give the respective cross-linked polymers.

1. Introduction

Among various modification or functionalization methods of polymers, the stepwise protocol using a cascade functionalization tool is beneficial owing to the remarkable versatility of functional groups and a high functionalization ratio. However, it is inferior to direct methods in terms of the number of reactions employed. A masked-ketene-functionalized polymer (MKP) [1–10] is a potential reactive polymers that can be used for the post-modification of processed materials toward the development of advanced materials. The MKP skeleton includes ketene equivalents, such as Meldrum's acid derivatives and benzodioxinones, to generate a ketene functionality by external stimuli, *e.g.*, heating [11,12] and photoirradiation [13]. The resulting ketene is highly reactive to various nucleophiles and provides the corresponding adducts without any catalyst [14–16]. The ketene gradually dimerizes in the absence of nucleophiles to give cyclobutadione [17]. Therefore, MKP exhibits dual reactivity to produce both polymers functionalized with nucleophiles and cross-linked polymers by self-reaction. In light of Yağci's [18–20] and Hawker's pioneering reports [21] of the synthesis of MKP based on the polymerization of masked-ketene-containing monomers for general materials applications, we developed a new protocol to directly form MKPs from common polymers using nitrile *N*-oxide agents.

Recently, we reported a new cascade functionalization agent for common polymers, consisting of an ambident agent having both nitrile *N*-oxide and epoxide functionalities [22]. This agent enables the easy molecular integration of various nucleophiles onto C=C-, C≡C-, and C≡N-containing polymers in the presence of an appropriate catalyst. Building on our previous reports [23–32], in this study, we describe a convenient protocol to introduce a masked ketene moiety to unsaturated-bond-containing common polymers via a catalyst-free click reaction. Central to this method is the use of a new ambident agent that possesses both nitrile *N*-oxide and masked ketene functionalities (Fig. 1). Heating of the resulting MKPs enables both a catalyst-free grafting-onto reaction with a nucleophilic polymer and a catalyst-free cross-linking reaction.

2. Experimental section

2.1. Materials

For NMR analyses, deuterated solvents with trimethylsilane by Across Organics Inc. were used. Wako Gel® C-400HG (Wako Chemical Inc.) was used for silica gel chromatography. Meldrum's acid was purchased from Wako Chemical Inc. All compounds given below bear the same formula numbers as used in the main body. Compounds unlabeled in the main body are labeled with letters

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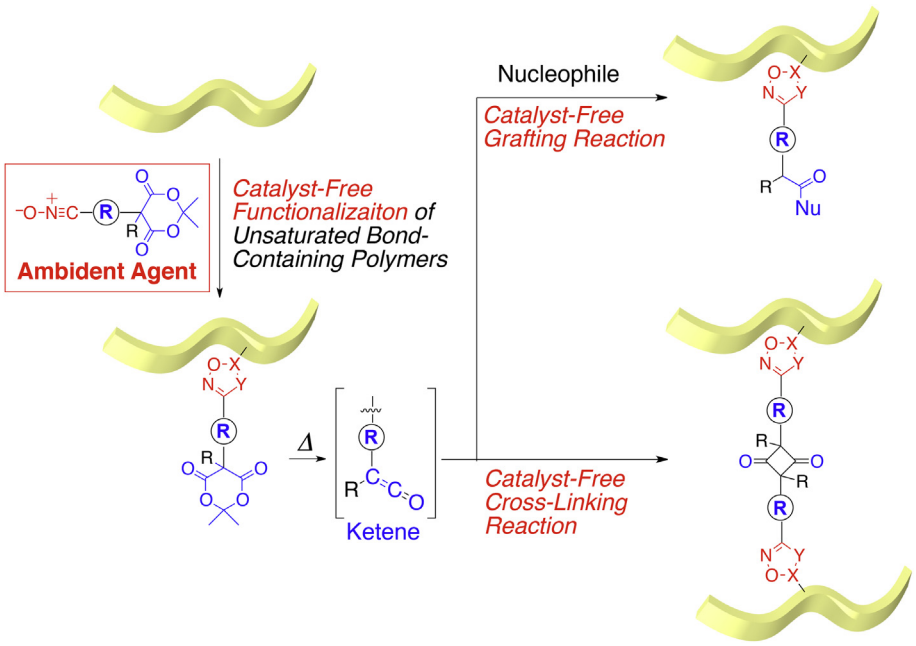


Fig. 1. Synthetic strategy for MKP and its subsequent modification to enable grafting and cross-linking using an ambident agent having nitrile *N*-oxide and masked ketene functionalities.

[**A**–**E**]. Compound **A** was prepared according to the literature [33]. Other reagents and solvents commercially available were used without further purification unless otherwise noted.

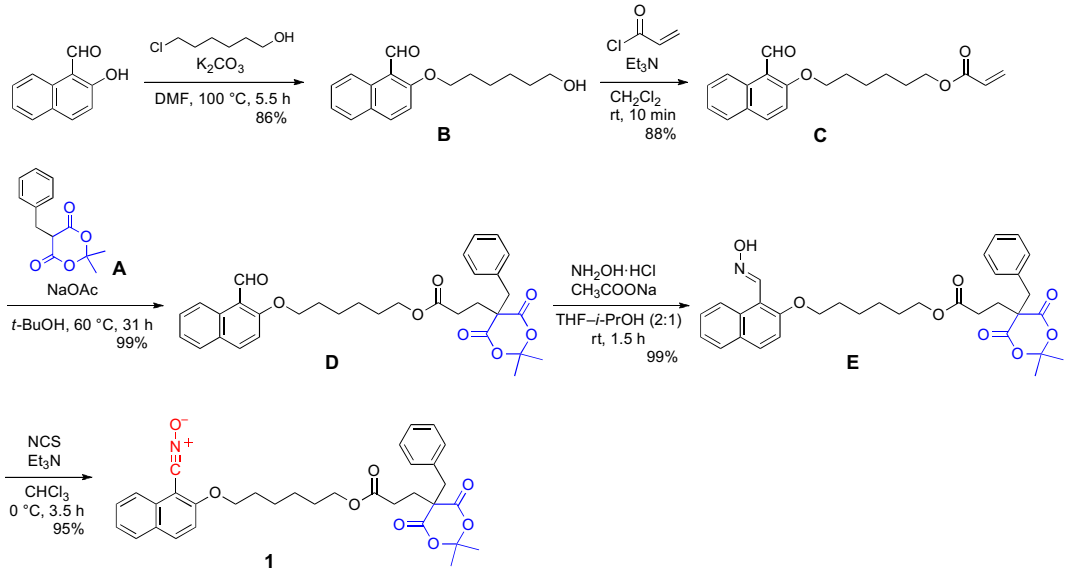
2.2. Characterization

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL AL-400 spectrometers using tetramethylsilane as an internal standard. MALDI–TOF MS spectra were measured with a Shimadzu AXIMA-CFR mass spectrometer using a dithranol matrix. Melting points were measured with a Stuart Scientific SMP3. SEC analyses were carried out on JASCO PU-2080 plus pump with a JASCO UV-1570 (UV detector) and JASCO RI-1530 (RI detector) equipped with a consecutive linear polystyrene gel columns TOSO TSK gel GMHXL and G5000HXL at 30 °C. TGAs were carried out on a Shimadzu TGA-50 instrument at N_2 atmosphere (flow rate of 50 mL/min) to determine 5% weight decomposition temperature (T_{d5}) at which 5% weight loss was observed. DSC analyses were carried out with a Shimadzu DSC-60 instrument at N_2 atmosphere (flow rate of 50 mL/min) with liquid N_2 as a refrigerant to determine glass transition temperature (T_g).

2.3. Synthesis of new cascade functionalization agent *1*

2.3.1. Synthesis of alcohol *B*

2-Hydroxy-1-naphthaldehyde (5.00 g, 29.0 mmol) was dissolved in DMF (146 mL) at room temperature. K_2CO_3 (4.81 g, 35.0 mmol) and 6-chlorohexanol (4.50 mL, 32.0 mmol) were



Scheme 1. Synthetic pathway of **1**.

added into the solution and the mixture was stirred at 100 °C for 5.5 h, and cooled to room temperature. The mixture was diluted with CH_2Cl_2 and washed with water. The products were extracted with CH_2Cl_2 (200 mL, 3 times). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude was purified by a flash column chromatography on silica gel (hexane:ethyl acetate = 1:1) to afford the product (**B**) as bright brown solids (2.8 g, 69% yield); m.p. 81.1–83.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 10.93 (s, 1H), 9.28 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.62 (dd, J = 8.6, 7.1 Hz, 1H), 7.42 (dd, J = 8.0, 7.1 Hz, 1H), 7.28 (d, J = 9.0 Hz, 1H), 4.24 (t, J = 6.4 Hz, 2H), 3.68 (t, J = 6.4 Hz, 2H), 1.95–1.44 (m, 8H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 192.2, 163.5, 137.5, 131.5, 128.4, 128.2, 124.9, 124.7, 119.0, 116.2, 113.5, 69.7, 62.8, 42.6, 39.3, 25.9, 25.5 ppm; IR (NaCl) υ 3416 (O–H), 2936 (C–H(aromatic)), 2865 (C–H(aliphatic)), 2800 (C–H, aldehyde), 1669 (C=O(ether)), 1513 (CH_2(alkane)), 1246 (C–O, as, Ar-O-R) cm^{-1}; MALDI–TOF MS (m/z) calc'd for $C_{17}H_{20}O_3Na$ $[M + Na]^+$, 295.13; found, 294.49.

2.3.2. Synthesis of acrylate *C*

To a solution of alcohol **B** (3.00 g, 11 mmol) and acryloyl chloride (1.80 mL, 22 mmol) in CH_2Cl_2 (15 mL) was added dropwise Et_3N (3.06 mL, 22 mmol) by dropping at 0 °C. The solution was stirred at room temperature for 10 min. The reaction was quenched by the addition of sat. aq. $NaHCO_3$. The products were extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude was purified by a flash column chromatography on silica gel (hexane:ethyl acetate = 1:1) to give the product **C** as bright yellow solids (2.37 g, 88% yield); m.p. 41.8–42.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 10.93 (s, 1H), 9.28 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.62 (dd, J = 8.6, 7.1 Hz, 1H), 7.42 (dd, J = 8.0, 7.1 Hz, 1H), 7.28 (d, J = 9.0 Hz, 1H), 6.43 (d, J = 9.0 Hz, 1H), 6.38 (dd, J = 12.0 Hz, 1H), 5.82 (d, J = 9.0 Hz, 1H), 4.24–4.17 (m, 4H), 1.93–1.48 (m, 8H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 192.6, 166.8, 164.0, 138.1, 132.0, 131.1, 130.3, 129.3, 129.0, 127.3, 125.4, 117.1, 117.1, 113.9, 69.8, 64.9, 29.7, 29.0, 28.2, 26.2 ppm; IR (NaCl) υ 2940 (C–H(aromatic)), 2865 (C–H(aliphatic)), 2800 (C–H, aldehyde), 1730 (C=O(ester conjugated with C=C)), 1671 (C=O(aldehyde conjugated with aromatic)), 1512 (CH_2(alkane)), 1246–1153 (C–O, as, Ar-O-R) cm^{-1}; MALDI–TOF MS (m/z) calc'd for $C_{20}H_{22}O_4Na$ $[M + Na]^+$, 349.14; found, 348.69.

2.3.3. Synthesis of aldehyde *D*

Compound **C** (2.41 g, 7.39 mmol) and Meldrum's acid derivative (**A**) (4.31 g, 18.4 mmol) were dissolved in *t*-BuOH (15 mL). Sodium acetate trihydrate (5.03 g, 37.0 mmol) was added to the mixture and the mixture was stirred at 60 °C for 31 h. The mixture was cooled to room temperature, and poured into EtOAc. The solution was washed with water and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over by $MgSO_4$, filtered, and concentrated *in vacuo*. The crude was purified by a flash column chromatography on silica gel (hexane:EtOAc = 5:3) to give **D** as bright yellow solids (4.12 g, 99% yield); m.p. 107.0–107.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 10.93 (s, 1H), 9.28 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.62 (dd, J = 8.6, 7.1 Hz, 1H), 7.42 (dd, J = 8.0, 7.1 Hz, 1H), 7.30–7.17 (m, 6H), 4.24 (t, J = 6.3 Hz, 2H), 4.11 (t, J = 6.8 Hz, 2H), 3.34 (s, 2H), 2.50 (t, J = 7.3 Hz, 2H), 2.38 (t, J = 7.3 Hz, 2H), 1.94–1.46 (m, 11H), 0.67 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 192.2, 171.5, 168.5, 163.8, 137.7, 135.1, 130.5, 130.5, 129.0, 129.0, 128.4, 128.1, 125.1, 124.9, 113.6, 133.6, 133.6, 106.2, 69.5, 65.0, 56.6, 43.8, 30.1, 29.5, 29.4, 28.9, 28.6, 27.9, 25.9, 25.8 ppm; IR (NaCl) υ 2941 (C–H(aromatic)), 2868 (C–H(aliphatic)), 2798 (C–H, aldehyde), 1770, 1733 (C=O(ester)), 1673 (C=O(aldehyde conjugated with aromatic)), 1512 (CH_2(alkane)), 1269-1155 (C–O, as, Ar-O-R) cm^{-1}; MALDI–TOF MS (m/z) calc'd for $C_{33}H_{36}O_8Na^+$ $[M + Na]^+$, 583.23; found, 583.11.

2.3.4. Synthesis of oxime *E*

Compound **D** (2.0 g, 3.57 mmol) was dissolved in a mixed solvent of THF and *i*-PrOH (2:1, 30.6 mL). A solution of hydroxylammonium chloride (281.1 mg, 3.92 mmol) and sodium acetate trihydrate (542.1 mg, 3.92 mmol) in water (5.1 mL) was added dropwise into the solution of **D** at 0 °C during stirring for 30 min. The mixture was warmed to room temperature and stirred for 1 h. The mixture was diluted with EtOAc (30 mL), and washed with water three times. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give **E** as yellow solids (2.03 g, 99% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.88 (s, 1H), 8.77 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.51 (dd, J = 8.8, 7.1 Hz, 1H), 7.38 (dd, J = 8.0, 7.1 Hz, 1H), 7.27–7.17 (m, 6H), 4.17–4.09 (m, 4H), 3.34 (s, 2H), 2.49 (t, J = 8.9 Hz, 2H), 2.37 (t, J = 8.9 Hz, 2H), 1.88–1.46 (m, 11H), 0.65 (s, 3H) ppm; ^{13}C NMR δ (100 MHz, $CDCl_3$, 298K) δ 171.5, 168.6, 156.5, 148.0, 135.1, 132.2, 131.8, 130.6, 129.2, 129.1, 128.5, 125.7, 125.7, 124.2, 114.7, 114.0, 106.3, 106.3 69.6, 65.1, 56.6, 43.8, 30.2, 29.5, 29.4, 28.9, 28.6, 28.0, 26.0, 25.8 ppm; IR (NaCl) υ 3445 (O–H), 2940 (C–H (aromatic)), 2868 (C–H (aliphatic)), 1770, 1733 (C=O(ester)), 1652 (C=N), 1270 (C–O, as, Ar-O-R) cm^{-1}; MALDI–TOF MS (m/z) calc'd for $C_{33}H_{37}NO_8Na^+$ $[M + Na]^+$, 598.24; found, 597.39.

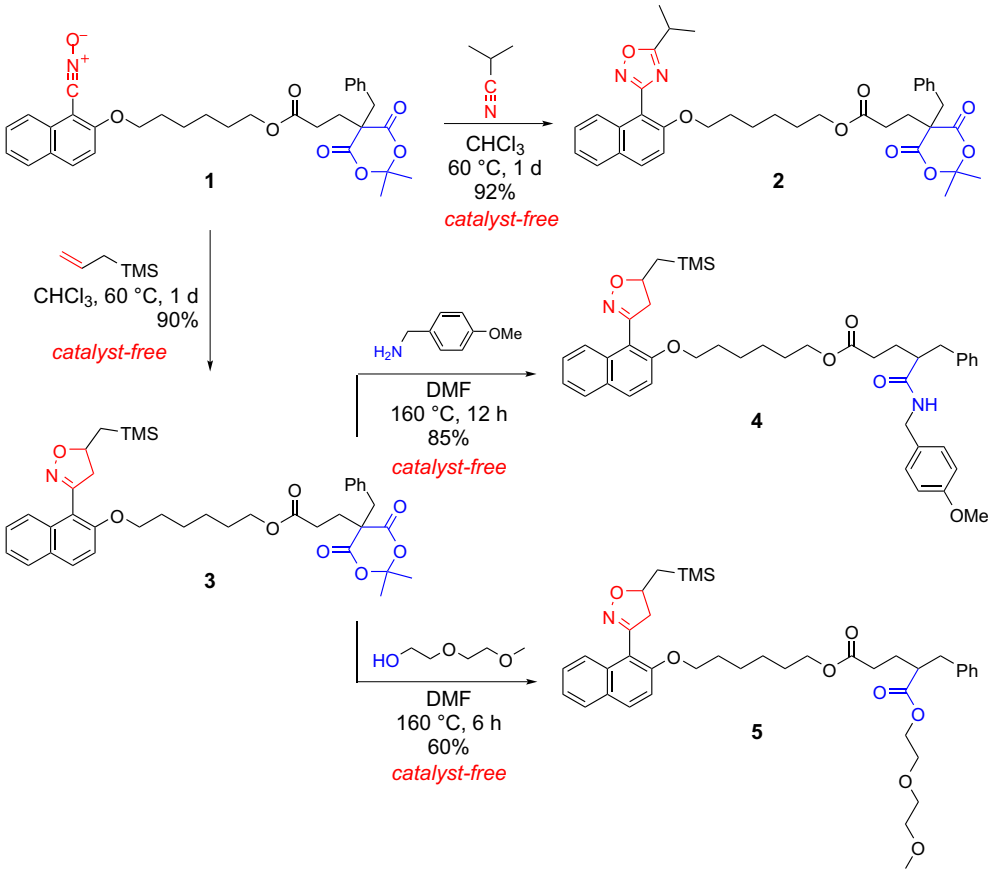
2.3.5. Synthesis of cascade functionalization agent *1*

Compound **E** (2.03 g, 3.53 mmol) was dissolved in $CHCl_3$ (35 mL) at 0 °C. Et_3N (690 μL) was added to the mixture. *N*-Chlorosuccinimide (577.9 mg, 4.24 mmol) was portionwised into the solution, and the mixture was continually stirred at 0 °C for 3.5 h. The reaction was quenched by pouring into water (30 mL). The products were extracted with $CHCl_3$. The combined organic layer was washed with water 2 times, brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to obtain **1** as a bright yellow oil (1.92 g, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.98 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 7.60 (dd, J = 8.9, 7.1 Hz, 1H), 7.43 (dd, J = 8.3, 7.0 Hz, 1H), 7.27–7.17 (m, 6H), 4.22 (t, J = 6.6 Hz, 2H), 4.11 (t, J = 6.8 Hz, 2H), 3.34 (s, 2H), 2.50 (t, J = 8.8 Hz, 2H), 2.38 (t, J = 8.1 Hz, 2H), 1.93–1.47 (m, 11H), 0.67 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 171.5, 168.6, 161.0, 135.2, 132.9, 130.6, 130.6, 129.1, 128.9, 128.5, 128.1, 128.1, 125.1, 124.1, 113.4, 106.2, 106.2, 69.6, 65.1, 56.6, 43.8, 30.2, 29.5, 29.2, 28.9, 28.6, 28.6, 25.8, 25.8 ppm; IR (NaCl) υ 2941 (C–H(aromatic)), 2868 (C–H(aliphatic)), 2292 (C≡N), 1771, 1739 (C=O(ester)), 1274 (C–O, as, Ar-O-R) cm^{-1}; MALDI–TOF MS (m/z) calc'd for $C_{33}H_{35}NO_8Na^+$ $[M + Na]^+$, 596.23; found, 595.38 .

2.4. Synthesis of model compounds obtained by using cascade functionalization agent *1*

2.4.1. Synthesis of oxadiazole *2*

Compound **1** (50 mg, 87.2 μmol) was dissolved in $CHCl_3$ (0.5 mL). Isobutyronitrile (78.3 μL, 872 μmol) was added to the mixture. The mixture was stirred at 60 °C for 1 d, cooled to room temperature, and concentrated *in vacuo* to give **2** (56.0 mg, 92% yield) as an yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.95 (d, J = 9.2 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.44 (dd, J = 8.1, 7.0 Hz, 1H), 7.39–7.17 (m, 7H), 4.13 (t, J = 6.5 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H), 3.41–3.34 (m, 1H), 3.34 (s, 2H), 2.49 (t, J = 8.7 Hz, 2H), 2.36 (t, J = 8.7 Hz, 2H), 1.75–1.36 (m, 17H), 0.65 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 183.6, 171.3, 168.4, 165.4, 155.9, 135.0, 133.2, 132.2, 132.2, 130.4, 128.9, 128.7, 128.0, 127.5, 127.4, 124.1, 114.4, 110.8, 106.1, 69.5, 65.0, 56.5, 43.6, 35.3, 30.0, 30.0, 29.4,



Scheme 2. Catalyst-free ligation between unsaturated bond and nucleophile using **1**.

29.1, 28.8, 28.5, 27.6, 25.6, 20.3 ppm; IR (NaCl) υ 2938 (C–H(aromatic)), 2867 (C–H(aliphatic)), 1772, 1738 (C=O(ester)), 1271 (C–O, as, Ar-O-R), 1624 (C=N) cm^{-1}; MALDI–TOF MS (m/z) calc'd for $C_{37}H_{42}N_2O_8Na^+$ $[M + Na]^+$, 665.28; found, 665.41.

2.4.2. Synthesis of isoxazoline **3**

Compound **1** (50 mg, 87.2 μmol) was dissolved in $CHCl_3$ (0.5 mL). Allytrimethysilane (141.3 μL) was added to the mixture. The mixture was stirred at 60 °C for 1 d, cooled to room temperature, and concentrated *in vacuo* to give **3** as a mixture of the target product (**3**) (59.3 mg, 90% yield) and the regio-isomer (10%). **3**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.04 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.48 (dd, J = 8.8, 7.3 Hz, 1H), 7.43 (dd, J = 8.0, 7.3 Hz, 1H), 7.27–7.17 (m, 6H), 5.29–4.87 (m, 1H), 4.16–4.07 (m, 4H), 3.42 (dd, J = 9.4, 9.3 Hz, 2H), 3.33 (s, 2H), 2.99 (dd, J = 9.4, 9.3 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 2.37 (t, J = 7.2 Hz, 2H), 1.86–1.39 (m, 12H), 1.14 (dd, J = 8.9, 8.8 Hz, 1H), 0.67 (s, 3H), 0.12 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 172.2, 169.4, 156.2, 155.8, 135.9, 133.6, 132.1, 131.4, 131.4, 129.9, 129.9, 128.9, 128.3, 125.4, 124.9, 114.8, 114.7, 107.1, 80.6, 70.1, 65.9, 57.4, 47.2, 44.6, 36.2, 30.3, 29.7, 26.8, 26.8, 26.7, 26.7, 25.1, 25.1, 0.0 ppm; IR (NaCl) υ 2940 (C–H(aromatic)), 2859 (C–H(aliphatic)), 1769, 1742 (C=O(ester)), 1270 (C–O, as, Ar-O-R) cm^{-1}; MALDI–TOF MS (m/z) calc'd for $C_{39}H_{49}NO_8SiNa^+$ $[M + Na]^+$, 710.31; found; T_{d5} 248 °C.

2.4.3. Synthesis of **4**

Isoxazoline **3** (40 mg, 58.2 μmol) was dissolved in DMF (116 μL). 4-Methoxybenzylamine (76.0 μL, 582 μmol) was added to the mixture. The mixture was refluxed for 12 h, cooled to room temperature, and concentrated *in vacuo*. The crude was purified by a flash column chromatography on silica gel (CH_2Cl_2:MeOH = 10:1) in to give **4** as a bright yellow oil (35.7 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.02 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.47 (dd, J = 7.0, 8.6 Hz, 1H), 7.36 (dd, J = 7.0, 8.2 Hz, 1H), 7.27–7.13 (m, 6H), 6.87 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 4.93–4.88 (m, 1H), 4.33 (d, J = 6.2 Hz, 2H), 4.30 (d, J = 6.2 Hz, 2H), 4.13 (t, J = 6.7 Hz, 2H), 4.05 (t, J = 4.2 Hz, 2H), 3.77 (s, 3H), 3.41 (dddd, J = 2.5, 2.5, 2.4, 2.4 Hz, 1H), 3.01–2.90 (m, 3H), 2.75 (d, J = 6.2 Hz, 2H), 2.72 (d, J = 6.2 Hz, 2H), 2.42–2.36 (m, 2H), 2.32–2.23 (m, 1H), 2.06–2.02 (m, 2H), 1.84–0.86 (m, 10H), 0.11 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 174.7, 174.3, 154.4, 137.7, 137.0, 135.0, 132.1, 130.1, 130.0, 129.9, 129.9, 129.4, 129.4, 129.0, 128.3, 127.3, 125.4, 125.0, 114.8, 114.8, 80.6, 70.2, 65.4, 56.5, 54.4, 50.0, 47.0, 43.8, 40.1, 32.9, 30.7, 30.4, 29.5, 28.9, 26.8, 25.1, 0.0 ppm; IR (NaCl) υ 3300 (N–H), 2931 (C–H(aromatic)), 2849 (C–H(aliphatic)), 1733 (C=O(ester)), 1646 (C=O(amide)), 1248 (C–O) cm^{-1}; MALDI–TOF MS (m/z) calc'd for $C_{43}H_{54}N_2O_6SiNa^+$ $[M + Na]^+$, 745.37; found, 745.29.

2.4.4. Synthesis of **5**

Isoxazoline **3** (25 mg, 36.4 μmol) was dissolved in DMF (374 μL). Diethylene glycol monomethyl ether (42.8 μL, 364 μmol) was added to the mixture. The mixture was refluxed for 8 h, cooled to room temperature, and concentrated *in vacuo*. The crude was purified by a flash column chromatography on silica gel (CH_2Cl_2) in to give **5** as a bright yellow oil (15.4 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.04 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.48 (dd, J = 8.3, 7.3 Hz, 1H), 7.36 (dd, J = 8.3, 7.3 Hz, 1H), 7.26–7.15 (m, 6H), 4.95–4.87 (m, 1H), 4.18 (t, J = 4.6 Hz, 2H), 4.13 (t, J = 6.4 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 3.59–3.50 (m, 9H), 3.36 (s, 3H), 3.01–2.95 (m, 1H), 2.78 (t, J = 6.1 Hz, 2H), 2.38–2.30 (m, 1H), 1.85–0.88 (m, 12H), 0.12 (s, 9H), ppm; ^{13}C NMR (100 MHz,

$CDCl_3$, 298 K) δ 175.7, 173.9, 156.2, 155.8, 139.8, 133.6, 132.0, 129.9, 129.9, 129.4, 129.0, 128.3, 127.4, 125.4, 125.0, 114.8, 114.5, 80.6, 72.8, 71.4, 70.2, 70.0, 65.4, 64.4, 60.1, 47.6, 47.0, 39.3, 32.8, 30.7, 30.7, 30.4, 29.6, 27.8, 26.8, 0.0 ppm; IR (NaCl) υ 2924 (C–H(aromatic)), 2849 (C–H(aliphatic)), 1733 (C=O(ester)), 1248 (C–O, as, Ar-O-R) cm^{-1}; MALDI–TOF MS (m/z) calc'd for $C_{40}H_{55}NO_8SiNa^+$ $[M + Na]^+$, 728.36; found, 728.18.

2.5. Typical procedure for polymer modification using **1**

2.5.1. Typical procedure for modification of PAN with **1** under solution reaction (Table 1, entry 2)

A solution of PAN (M_w 150,000) (50 mg, 943.4 μmol) and **1** (54.0 mg, 94.2 μmol) in DMF (2.0 mL) was stirred at 60 °C for 3 d. The mixture was cooled to room temperature, and precipitated into H_2O, washed again with $CHCl_3$. The precipitates were collected by filtration and dried *in vacuo* to give the Meldrum's acid-functionalized PAN (99% yield, 35% conversion) as a white solid; ^1H NMR (400 MHz, DMSO, 298 K) δ 8.03–7.03 (m), 4.12–4.39 (m), 3.32 (m), 3.25–3.13 (m), 2.65 (s), 2.44–2.02 (m), 1.67–1.23 (m), 0.70 (s) ppm; IR (KBr) υ 2243 (C≡N), 1735 (C=O(ester)), 1453 (H– C≡N), 1270 (C–O, as, Ar-O-R) cm^{-1}; T_{d5} 287 °C; T_g 105 °C.

2.5.2. Typical procedure for modification of NR with **1** under solution reaction (entry 4)

NR (M_w 1,250,000) (50 mg, 0.735 mmol) was dissolved in $CHCl_3$ (0.5 mL) overnight. Compound **1** (42.1 mg, 74 μmol) was added to the mixture. The solution was stirred at 60 °C for 3 d. The solution was cooled to room temperature, and poured into MeOH to give precipitates. The precipitates were collected by filtration and dried *in vacuo* to give the Meldrum's acid-functionalized NR (99% yield, 16% conversion); ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.08–7.19 (m), 5.12 (s), 4.22–4.11 (m), 3.34 (s), 2.47–1.25 (m), 0.66 (s) ppm; IR (NaCl) υ 1737 (C=O(ester)), 1270 (C–O, as, Ar-O-R) cm^{-1}; T_{d5} 213 °C; T_g –23 °C.

2.5.3. Typical procedure for modification of NR with **1** under solid-state reaction (entry 7)

NR (M_w 1,250,000) (50 mg, 735 μmol) and **1** (42.1 mg, 74 μmol) were ground in a mortar at 70 °C for 2 h. The mixture was cooled to room temperature, and dissolved with $CHCl_3$, and poured into MeOH to give precipitates. The precipitates were collected by filtration and dried *in vacuo* to give the Meldrum's acid-functionalized NR (99% yield, 37% conversion) as a yellow solid; ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.08–7.19 (m), 5.12 (s), 4.22–4.11 (m), 3.34 (s), 2.47–1.25 (m), 0.66 (s) ppm; IR (KBr) υ 1737 (C=O(ester)), 1270 (C–O, as, Ar-O-R) cm^{-1}; T_{d5} 213 °C; T_g –23 °C.

2.5.4. Typical procedure for modification of NBR with **1** under solid-state reaction (entry 8)

NBR (acrylonitrile: 33%, 50 mg, 930.7 μmol) and **1** (53.4 mg, 93.7 μmol) were ground in a mortar at 70 °C for 2 h. The mixture was cooled to room temperature, and dissolved with $CHCl_3$, and poured into MeOH to give precipitates. The precipitates were collected by filtration and dried *in vacuo* to give the Meldrum's acid-functionalized NBR (99% yield, 85% conversion) as an yellow solid; ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.97–7.18 (m), 5.54–5.41 (m), 5.11–4.97 (m), 4.15–4.09 (m), 3.66–3.49 (m), 3.33 (s), 2.59–1.16 (m), 0.66 (s) ppm; IR (KBr) υ 2235 (C≡N), 1739 (C=O(ester)), 1267 (C–O, as, Ar-O-R) cm^{-1}; T_{d5} 332 °C; T_g –3.4 °C.

2.5.5. Typical procedure for modification of EPDM with **1** under solid-state reaction (entry 9)

EPDM (ENB: 10%, 50 mg, 115 μmol) and **1** (38.2 mg, 115 μmol) were ground in a mortar at 70 °C for 2 h. The mixture was cooled to room temperature, and dissolved with $CHCl_3$, and poured into MeOH to give precipitates. The precipitates were collected by filtration and dried *in vacuo* to give the Meldrum's acid-functionalized EPDM (99% yield, 64% conversion) as an yellow rubber; ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.07–7.17 (m), 5.25–5.02 (m), 4.22–4.11 (m), 3.34 (s), 2.47–0.83 (m), 0.66 (s) ppm; IR (KBr) υ 1735 (C=O(ester)), 1261 (C–O, as, Ar-O-R) cm^{-1}; T_{d5} 309 °C; T_g –17 °C.

2.6. Typical procedure for grafting-onto reaction

2.6.1. Typical procedure for grafting reaction of PEG onto EPDM

Meldrum's acid-functionalized EPDM (25 mg, 19.8 μmol, 64% conversion) was dissolved in mesitylene (632 μL). To the solution was added MeOPEGOH (M_n 350) (63.4 μL, 19 μmol) and $CaSO_4$ (63.2 mg). The mixture was stirred at room temperature for 1 h and heated at 160 °C for 9 h. The solution was cooled to room temperature, and poured into water to give precipitates. The precipitates were collected by filtration, and the filtrate was washed with H_2O and MeOH and dried *in vacuo* to give the PEG-grafted EPDM (99% yield, 98% conversion of Meldrum's acid); ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.14–6.95 (m), 5.25–5.02 (m), 4.34–4.23 (m), 3.92–3.46 (m), 2.45–0.88 (m) ppm; IR (KBr) υ 1260 (C–O, as, Ar-O-R), cm^{-1}; T_{d5} 217 °C; T_g –18 °C.

2.6.2. Typical procedure for one-pot grafting reaction of PEG onto PAN

A mixture of PAN (50 mg, 943.4 μmol), **1** (54.1 mg, 94.3 μmol), MeOPEGOH (M_n 350, 330.2 μL, 943.4 μmol), and $CaSO_4$ (100 mg) in DMF (1.0 mL) was stirred at room temperature for 1 h. The mixture was warmed to 60 °C and stirred for 1 d. The reaction temperature was elevated to 160 °C and stirred for 12 h. The mixture was cooled to room temperature, filtered, and poured into water to give precipitates. The precipitates were collected by filtration and the filtrate was washed with H_2O and $CHCl_3$ and dried *in vacuo* to give the PEG-grafted PAN (249.2 mg, 99% yield, 27% conversion for the 1,3-dipolar cycloaddition, 97% conversion for the grafting reaction); ^1H NMR (400 MHz, DMSO, 298 K) δ 8.31–7.17 (m), 4.12–4.03 (m), 3.59 (s), 3.48–3.12 (m), 2.75 (s), 2.44–2.02 (m), 1.67–1.23 (m) ppm; IR (KBr) υ 2243 (C≡N), 1600 (C=O(ester)), 1453 (H–C≡N), 1270 (C–O, as, Ar-O-R) cm^{-1}; T_{d5} 292 °C; T_g 133 °C.

2.7. Typical procedure for cross-linking reaction of Meldrum's acid-functionalized polymer: synthesis of cross-linked NR

NR with 16% Meldrum's acid functionality (15.0 mg, 0.1 mmol) was dissolved in $CHCl_3$. The mixture was placed to Teflon plate and heated at 40 °C to give a self-standing film. The film was heated at 250 °C for 1 h under N_2 to give the cross-linked polymer. The cross-linked polymer was purified by swelling in toluene to remove the unreacted materials, and gently dried at room temperature for 1 d to give the corresponding cross-linked NR (11.4 mg). To evaluate the cross-linking efficiency, the cross-linked polymer was immersed into toluene overnight to give the swollen gel (swelling ratio: 1300%). The cross-linking density (ν, mol/cm^3) was calculated by the modified Flory–Rehner equation [34] to evaluate that the interchain reaction efficiency of Meldrum's acid moieties on the cross-linking reaction was 25%: By the following Flory–Rehner equation, the cross-linking density (ν) was calculated to be 1.31×10^{-5} mol/cm^3.

$$\nu = -\frac{g}{V}\left[\frac{\ln(1-V_R)+V_R+\mu V_R^2}{g^{2/3}V_R^{2/3}-V_R/2}\right],$$

where ν, V, g, μ, and V_R are cross-linking density (mol/cm^3), molar volume of the solvent (toluene: 106.3 cm^3/mol), volume fraction of

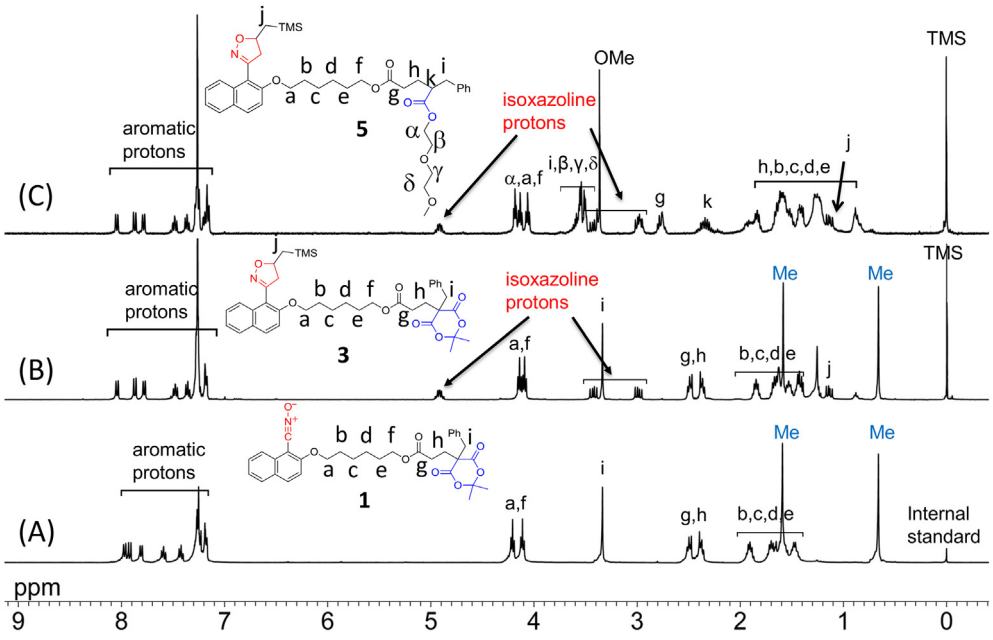


Fig. 2. ^{1}H NMR spectra of (A) **1**, (B) **3**, and (C) **5** (400 MHz, $CDCl_3$, 298 K).

cross-linked gel (1.003), interaction parameter between polymer and solvent (natural rubber–toluene: 0.39), and volume fraction of polymer in the gel (6.19×10^{-2}), respectively. Therefore, the interchain reaction efficiency of Meldrum's acid moieties on the cross-linking reaction would be described with the following equation:

$$\text{interchain reaction efficiency (\%)} = \frac{[\text{observed cross-linking density (mol/cm}^3)] \times [\text{sample volume (cm}^3)]}{[\text{expected mol of cross-linking point as 100\% efficiency (mol)}]} \times [\text{yield}]$$

3. Results and discussion

3.1. Model study of *1*

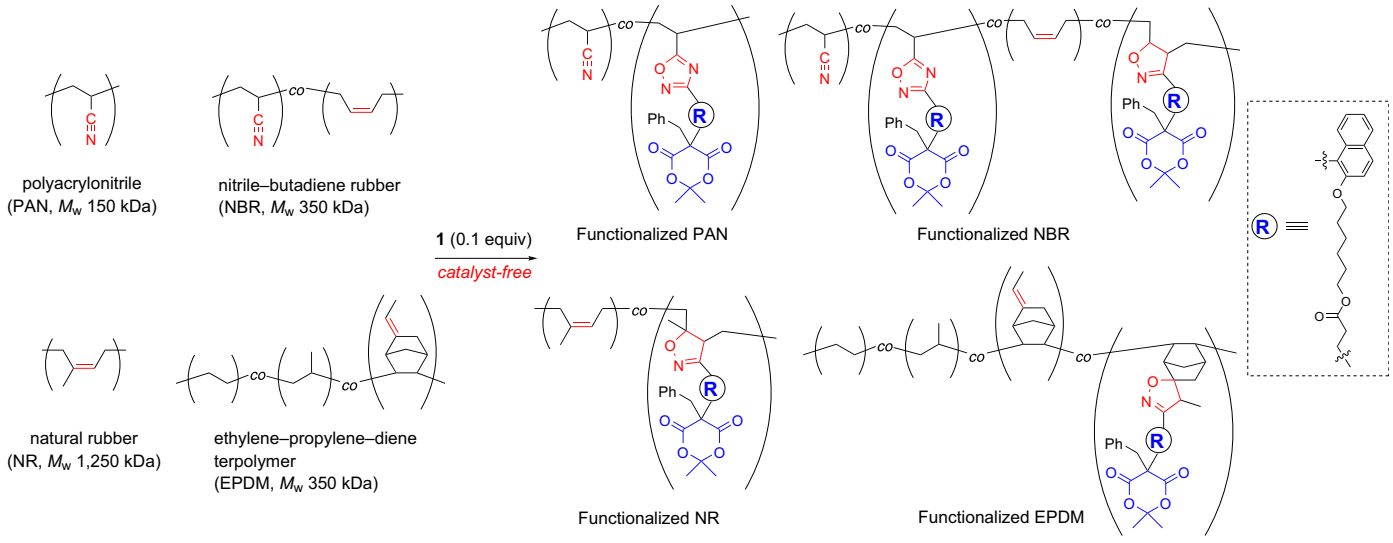
Before investigating the utility of **1** as an attachment tool for common polymers, we performed model ligation reactions to evaluate its reactivity toward the 1,3-dipolar cycloaddition reaction of C=C and C≡N groups and the subsequent nucleophilic substitution to the thermally generated ketene moiety, as shown in Scheme 2.

The treatment of **1** with isobutyronitrile or allyltrimethylsilane at 60 °C without a catalyst produced the corresponding heteroaromatics **2** and **3** in high yields, indicating adequate reactivity of the nitrile *N*-oxide moiety of **1** to C≡N and C=C bonds. The subsequent catalyst-free nucleophilic attack at the thermally generated ketene of **3** was examined using an amine and an alcohol. Since the gradual weight loss of **3** (attributed to the elimination of acetone and CO_2 from the masked ketene moiety [35]) was observed at around 160 °C by thermogravimetric analysis (TGA), we conducted the nucleophilic modification at this temperature. As a result, refluxing a mixture of **3** and the nucleophiles in DMF produced the corresponding adducts **4** and **5** in high yields without a catalyst. It should be noted that **1** enables catalyst-free ligation between the unsaturated bond and not only a nucleophilic amine but also a neutral alcohol with low nucleophilicity. Fig. 2 shows ^{1}H NMR spectra of (A) **1**, (B) **3**, and (C) **5**. In the spectrum (B), the appearance of the signals originating from the isoxazoline skeleton protons and TMS protons afforded the direct evidence for the formation of **3**. In the spectrum (C), the characteristic signals of diethylene glycol monomethyl ether (α, β, γ, δ, and OMe) along with the disappearance of signals of geminal dimethyl protons of Meldrum's acid moiety support the formation of **5**. The ratio of ^{1}H NMR integrals of TMS protons, the isoxazoline protons, and the protons from the alcohol as a nucleophile clearly indicates that the cascade functionalization agent **1** served as a molecular glue to mediate successfully the ligation reaction between allyltrimethylsilane and diethylene glycol monomethyl ether.

3.2. Synthesis of functionalized polymers

On the basis of these results, we next investigated the reactions of various unsaturated-bond-containing polymers with **1** (Scheme 3). The results are summarized in Table 1.

The reaction in DMF using 0.1 equiv of **1** per repeating unit of polyacrylonitrile (PAN) at 60 °C for 24 h resulted in the formation of oxadiazole-containing polymer (Table 1, entries 1 and 2). Increasing the reaction time increased the conversion percentage for the cycloaddition reaction but only up to a maximum of 35% (entry 2).



Scheme 3. Catalyst-free functionalization of unsaturated-bond-containing polymers using **1**.

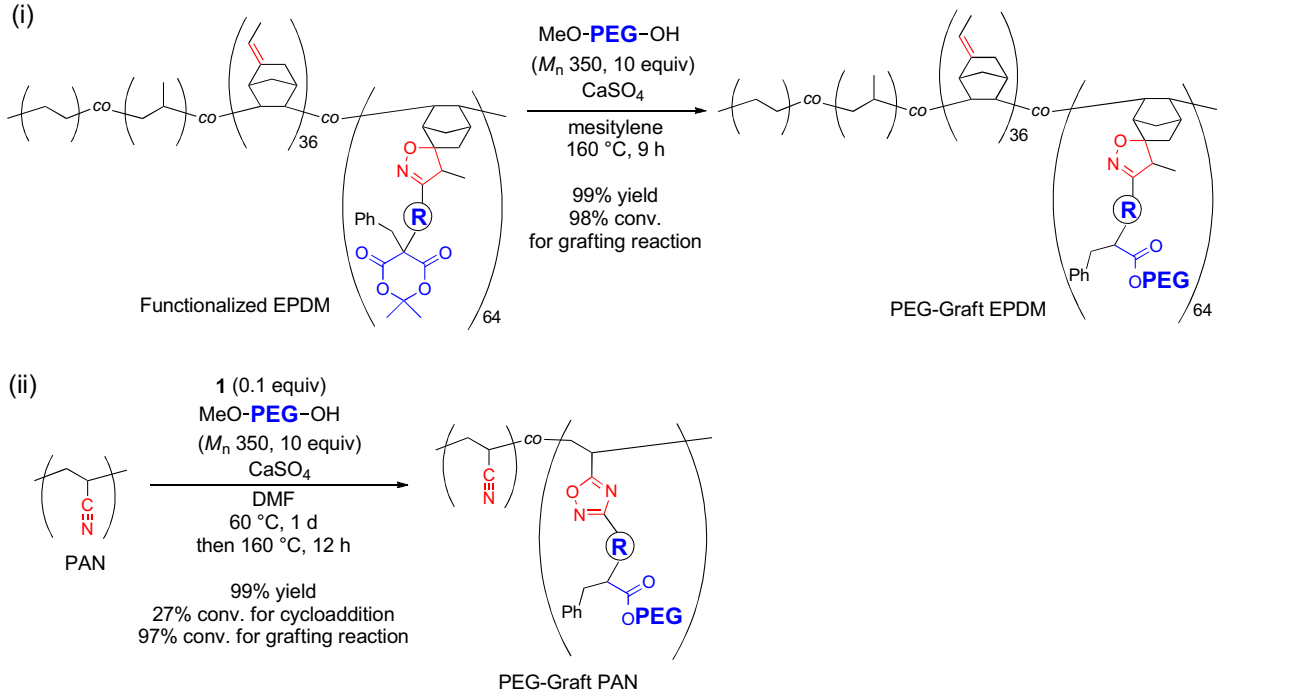
Table 1
Functionalization of various polymers with **1**.

Entry	Polymer	Reaction media	Temp. (°C)	Time (h)	Conversion for cycloaddition[a] (%)	Functionalization ratio of polymer (%)
1[b]	PAN	DMF	60	24	25	2.5
2[b]	PAN	DMF	60	72	35	3.5
3[b]	NR	$CHCl_3$	60	24	12	1.2
4[b]	NR	$CHCl_3$	60	72	16	1.6
5[b]	NR	–[c]	rt	2	21	2.1
6[b]	NR	–[c]	rt	72	59	5.9
7[b]	NR	–[c]	70	2	37	3.7
8[b]	NBR	–[c]	70	2	Olefin: 90, CN: 76	Olefin: 9.0, CN: 7.6
9[d]	EPDM	–[c]	70	2	64	64

[a] Estimated by ^{1}H NMR.
[b] Reaction was performed by using 0.1 equiv of **1**.
[c] Reaction was performed in the solid state.
[d] 1.0 equiv of **1** was used.

The cycloaddition of **1** to natural rubber (NR) in $CHCl_3$ gave the corresponding functionalized NR in low conversion yields (entries 3 and 4), probably because of the low reactivity (caused by steric hindrance) of the trisubstituted internal olefin in NR [22]. Through considerable effort, it was found that the solvent-free press-grinding of a mixture of NR and **1** enabled a more rapid cycloaddition reaction with higher conversion of NR (21%) than in the solution reactions (entries 3 and 4), even when the reaction is performed at room temperature (entry 5).

In addition, a prolonged reaction time at room temperature or an elevated reaction temperature (70 °C) increased the conversion yields (entry 6: 59%, entry 7: 37%). The reactions of two commercially available elastomers, acrylonitrile-butadiene rubber (NBR) and ethylene–propylene–diene terpolymer (EPDM), gave the corresponding modified polymers in high conversion yields (entries 8 and 9). Such high conversion yields are probably



Scheme 4. (i) Catalyst-free grafting of PEG (M_n 350) onto masked-ketene-functionalized EPDM and (ii) one-pot grafting of PEG onto PAN.

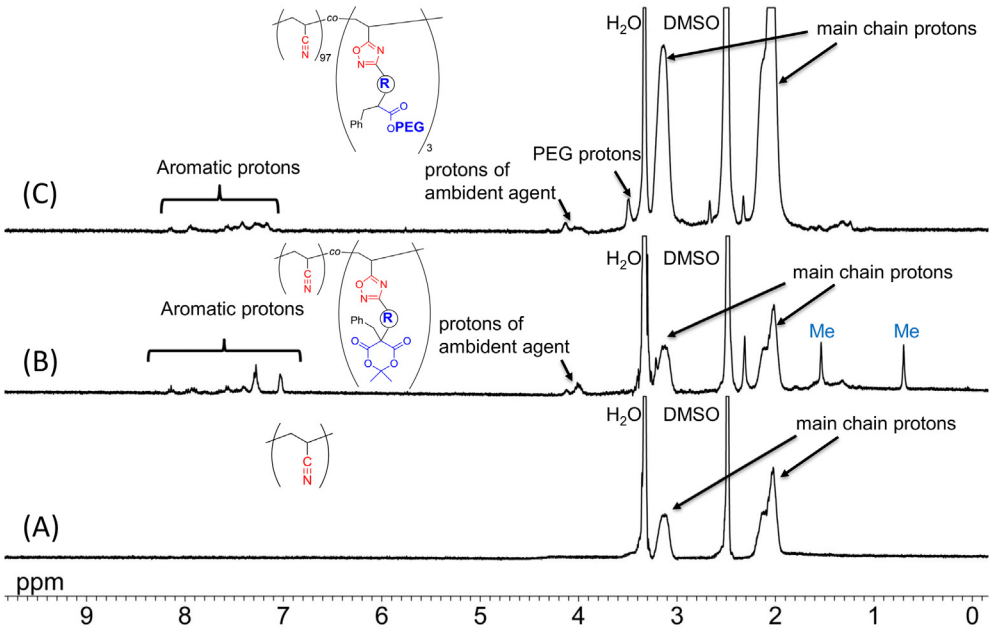


Fig. 3. ^{1}H NMR spectra of (a) PAN, (b) functionalized PAN with 3% functionalization ratio, and (c) PEG-grafted PAN (400 MHz, DMSO-d_6, 298 K).

attributed to the higher reactivity of the disubstituted olefin in NBR and the *exo*-olefin in EPDM to the nitrile *N*-oxide of **1** in comparison with the trisubstituted olefin in NR.

Having produced several masked-ketene-containing polymers, we demonstrated the grafting reaction using monomethyl-terminated polyethylene glycol (Scheme 4). We attempted the treatment of masked-ketene-functionalized EPDM (64% conversion) with 10 equiv of PEG in mesitylene at 160 °C for 9 h. The corresponding PEG-grafted EPDM was obtained with 50% grafting conversion. On the other hand, when $CaSO_4$ was added to the reaction mixture as a dehydrating agent, the grafting-onto reaction produced PEG-grafted EPDM in an excellent conversion yield (98%).

The structure of PEG-grafted EPDM was determined by ^{1}H NMR, IR spectral analysis, and SEC. Fig. 3 shows ^{1}H NMR spectra of (a) PAN, (b) functionalized PAN with 3% functionalization ratio, and (c) PEG-grafted PAN. In the spectrum (c), the signals originating from PAN, the skeleton of **1**, and PEG along with disappearance of the protons attributed to the Meldrum's acid moieties are in good accordance with the formation of PEG-grafted PAN. From the integral ratio between the protons from **1** and the main chain protons of PAN, we determined that the conversion for cycloaddition reaction was 27%. In addition, we determined the conversion for grafting reaction of PEG was 97%, which was calculated from the integral ratio between the protons from **1** and the protons of PEG considering the number average molecular weight of PEG (M_n 350). It is noted that the conversion for the cycloaddition during the one-pot grafting reaction is in a good agreement with that in the absence of MeO–PEG–OH (Table 1, entry 1, 25%), emphasizing that the 1,3-dipolar cycloaddition of nitrile *N*-oxide and nucleophilic substitution of PEG to the thermally generated ketene are not competitive.

The SEC profiles of EPDM and PEG-grafted EPDM are shown in Fig. 4. PEG-grafted EPDM appeared as a monomodal peak at an elution time later than that of unreacted EPDM. This result indicates a distinct structural change in EPDM, and it is consistent with a stronger interaction between the polar graft chains on the polymer and the SEC stationary phase.

In addition, we examined a one-pot grafting reaction of PEG onto PAN. The step-by-step heating of a mixture of PAN, 0.1 equiv of **1**, and PEG (60 °C, 1 d then 160 °C) without a catalyst was performed and the latter process at 160 °C was monitored by using the SEC profiles (Fig. 5). As a result, we found that the SEC change finished in 12 h, indicating the completion of the addition reaction of PEG to the polymer backbone. The longer reaction time of grafting reaction than that from **3** to **5** (6 h, Scheme 1) could be probably attributed to the steric repulsion between PEG as a nucleophile and PAN as a trunk polymer.

Finally, we investigated the catalyst-free thermal cross-linking of MKPs (Scheme 5). The cross-linking reactions of both PAN and NR with masked ketene moieties efficiently proceeded at 250 °C (1 h) to give the respective cross-linked polymers as a solvent-insoluble part. In the case of cross-linked NR, the density of the network chain, cross-linking ratio, and efficiency of the cross-linking reaction were estimated by a modified Flory–Rehner equation [34], based on the swelling ratio of the insoluble polymer in toluene. As a result, it turned out that the interchain reaction efficiency of Meldrum's acid moieties on functionalized NR was 25%.

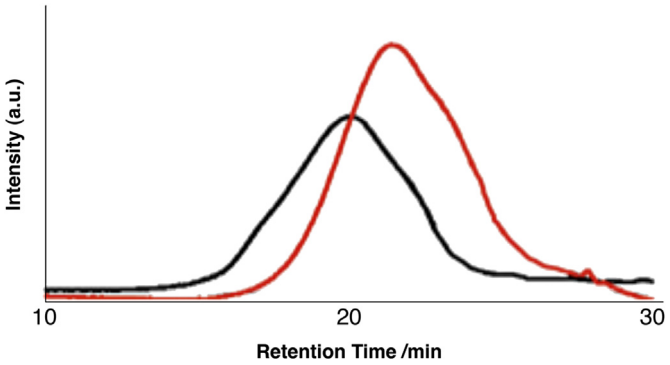


Fig. 4. SEC profiles of EPDM (black line) and PEG-grafted EPDM (red line) (eluent: DMF, 303 K). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

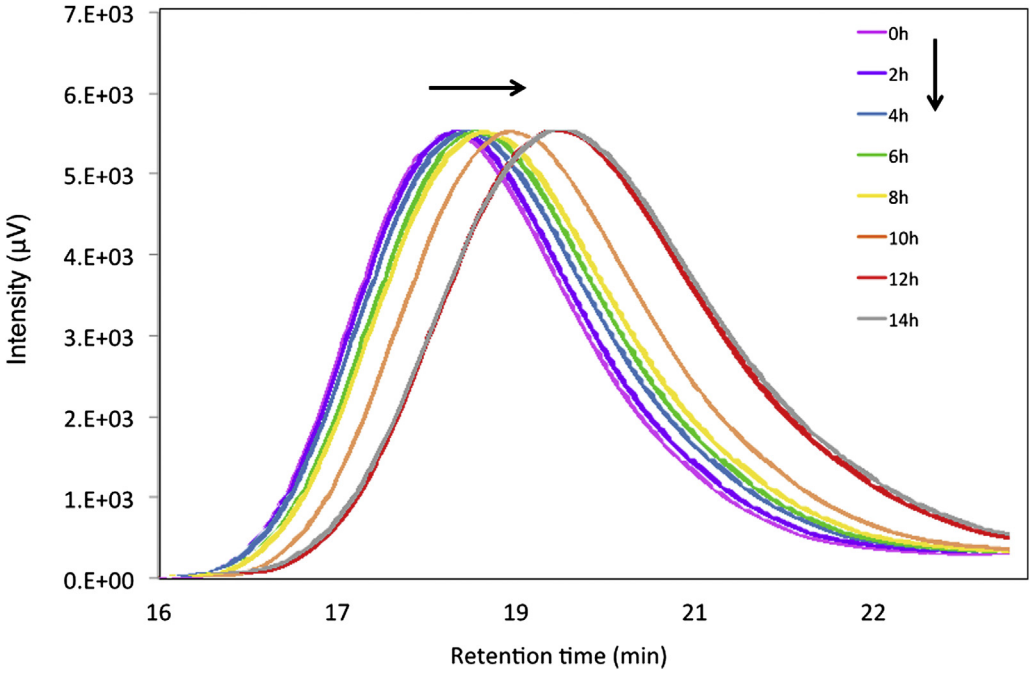
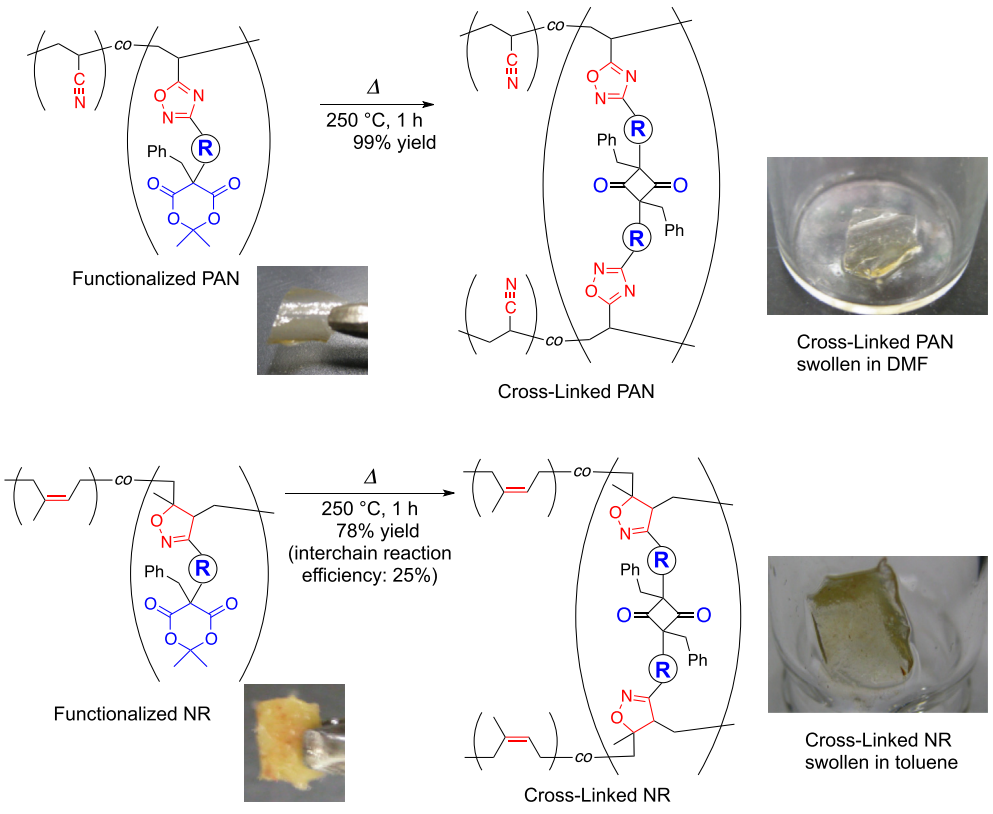


Fig. 5. Time-dependent SEC change of PEG-Graft PAN during the one-pot grafting reaction of PEG onto PAN using **1** at 160 °C (eluent: DMF, 303 K).



Scheme 5. Catalyst-free cross-linking of MKPs.

4. Conclusion

We have designed and developed a facile and widely applicable protocol for obtaining MKPs from unsaturated-bond-containing polymers via a catalyst-free click reaction and its subsequent modification to enable grafting and cross-linking. In this protocol, the cascade functionalization agent possessing both nitrile *N*-oxide and masked ketene functionalities serves as a molecular glue to mediate the ligation reaction between unsaturated bonds and nucleophiles. The agent proved capable of catalyst-free click introduction of masked ketene moieties to the unsaturated bond-containing common polymers to give the MKPs. Heating of the resulting MKPs in the presence

of nucleophiles afforded the corresponding adducts in high yields without a catalyst. On the other hand, heating of the MKPs in the absence of nucleophile resulted in the formation of cross-linked polymer based on the interchain dimerization reaction of Meldrum's acid moieties to give cyclobutadiones at the cross-linking points. The outcome would have broad applications not only to post-modification and surface modification of highly processed plastics made from common polymers but also supramolecular chemistry, because we have previously reported effective synthesis of rotaxane and polyrotaxane exploiting a cycloaddition of stable nitrile *N*-oxide [29–32]. Further investigations using the ambident agent along this line are currently underway.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.polymer.2013.06.020.

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