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Synthesis of Highly Reactive Polymer Nitrile *N*-Oxides for Effective Solvent-Free Grafting

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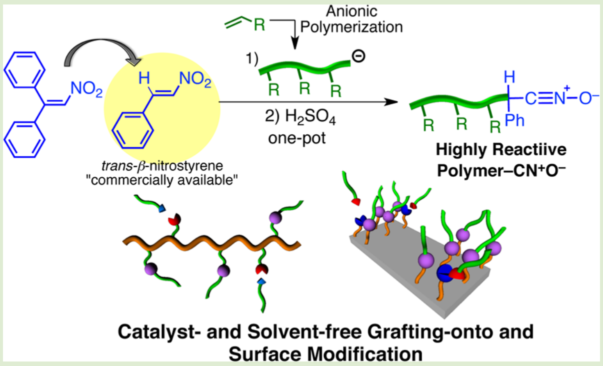
Supporting Information

ABSTRACT: A one-pot synthesis of polymer nitrile *N*-oxides was achieved via the Michael addition of living polymer anions derived from vinyl monomers to commercially available *trans-β*-nitrostyrene and subsequent dehydration with concd H_2SO_4. The polymer nitrile *N*-oxides are effective as grafting agents in catalyst- and solvent-free 1,3-dipolar cycloadditions to unsaturated-bond-containing polymers with high conversion and exhibit higher reactivity compared to that of nitrile *N*-oxides prepared from 1,1-diphenylnitroethene. Application to the preparation of a functional glass surface was demonstrated using P*t*BMA nitrile *N*-oxide as a grafting agent.



Grafting reactions have been employed for the modification of polymers, inorganic materials, and material surfaces to attach arbitrary functions and properties.[1] In recent years, click chemistry, particularly the copper(I)-catalyzed azide−alkyne cycloaddition (CuAAC), has been widely employed across multiple fields as a powerful chemical ligation technique.[2,3] Click chemistry is a useful method for the construction of highly sophisticated macromolecular architectures including graft polymers, because of its simple procedure, high efficiency, and easy purification characteristics. For example, Fréchet and co-workers have employed the CuAAC to construct dendronized linear polymers from poly(vinylacetylene),[4] while Gao and Matyjaszewski reported an effective grafting-onto method based on a combination of atom transfer radical polymerization and CuAAC for the synthesis of polymer brushes from alkyne-containing linear polymers.[5] Many other groups have also demonstrated the usefulness of the CuAAC for the synthesis of graft copolymers via simple click grafting-onto strategies.[6−12]

However, the requirement of a copper catalyst brings about some inevitable limitations to the usage of the CuAAC.[13] In addition, the explosiveness of azide at high temperatures also presents a potential danger.[14] Thus, metal-free click chemistry has mushroomed within the past few years as a safe and effective alternative. Several metal-free click reactions, such as strain-promoted azide−alkyne cycloadditions,[15] thiol−ene additions,[16] and Diels−Alder cycloadditions,[17] have been reported and exploited for material science, macromolecular synthesis, and surface modification.

Nitrile *N*-oxides are useful 1,3-dipoles that undergo efficient [2 + 3]cycloaddition to not only alkynes but also alkenes and nitriles to give heterocycles in the absence of any catalyst.[18] However, only a few attempts have so far been made to apply nitrile *N*-oxides to polymer science because of their chemical instability with respect to self-reactions.[19,20] In our previous work, we have focused on click chemistry exploiting kinetically stabilized nitrile *N*-oxide for polymer modification[21] and recently developed a one-pot synthesis of stable polymer nitrile *N*-oxides via the reaction of 1,1-diphenylnitroethene with living polymer anions.[22] Grafting of the polymer nitrile *N*-oxides onto several dipolarophile-containing polymers was also demonstrated. However, the two bulky phenyl groups at the polymer terminus, which have sufficient steric hindrance to stabilize the nitrile *N*-oxide, also vastly reduce the reactivity of the polymer nitrile *N*-oxides, leading to the requirement of high reaction temperatures. Recently, the commercial availability of *trans-β*-nitrostyrene was brought to our attention as an alternative to 1,1-diphenylnitroethene (synthesized from benzophenone imine via an aza-Henry reaction[23]) as a terminating agent for living polymer anions. Polymer nitrile *N*-oxides derived from *trans-β*-nitrostyrene should show higher reactivity, because there is only one phenyl group at the reactive polymer terminus (Figure 1). Herein, we describe the synthesis and characterization of stable polymer nitrile *N*-oxides from *trans-β*-nitrostyrene and their use in catalyst- and solvent-free grafting-onto reactions with common polymers and for the surface modification of a glass plate.

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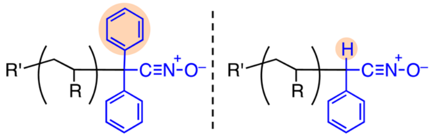
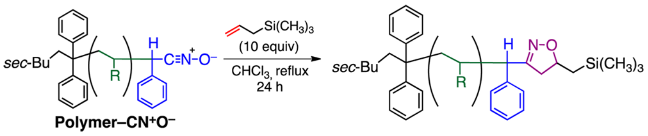


Figure 1. Two types of polymer nitrile *N*-oxides.

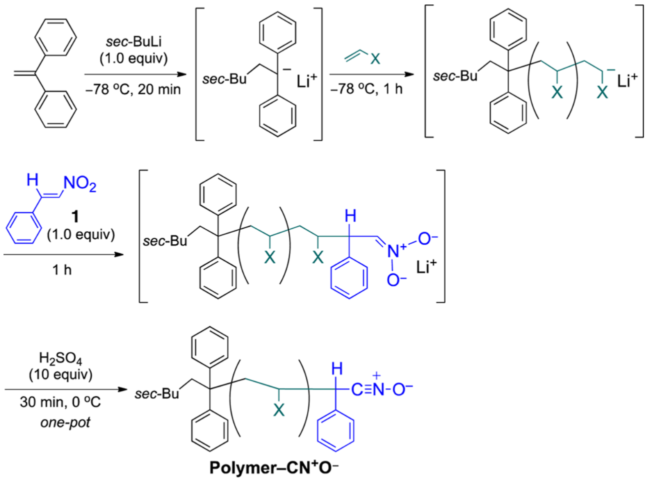
According to the method for the synthesis of aliphatic nitrile *N*-oxides,[22,24] several polymer nitrile *N*-oxides with controlled molecular weights and structures were prepared via anionic polymerization, as illustrated in Scheme 1. A solution of 1,1-diphenyl-3-methylpentyllithium was used as the initiator for the polymerization of vinyl monomers at −78 °C. The generated polymer anions reacted with *trans-β*-nitrostyrene via a Michael addition, and subsequent treatment with concd H_2SO_4 in one-pot afforded the corresponding polymer nitrile *N*-oxides (polymer−CN^+O^-s). Vinyl monomers including methyl methacrylate and *tert*-butyl methacrylates (MMA and *t*BMA) are available for this synthetic protocol to give the corresponding stable homopolymer-based nitrile *N*-oxides. PMMA−CN^+O^-s with controlled molecular weights, narrow polydispersities, and remarkable stability were prepared (entries 1−3, Table 1; see the Supporting Information for details of the thermal stability investigation).[25] Block copolymer anions, living poly(MMA-*b*-*t*BMA) and living poly(styrene-*b*-MMA) anions, were also prepared via sequential addition of vinyl monomers, which were terminated with *trans-β*-nitrostyrene and treated with concd H_2SO_4 in the same manner as described above to afford nitrile *N*-oxide-terminated copolymers. It is worth mentioning that the homopolystyrene nitrile *N*-oxide was unstable and decomposed spontaneously at room temperature, probably because of the occurrence of a side reaction involving intramolecular 1,3-dipolar cycloaddition with the neighboring benzene ring.[26] On the other hand, PS-*b*-PMMA−CN^+O^- containing a polystyrene segment was successfully synthesized and had significant stability because of the partial introduction of a PMMA segment at the connecting point of the nitrile *N*-oxide moiety. The PMMA−CN^+O^- derived from 1,1-diphenylnitroethene (**P3**) was also prepared as a control sample (M_n 2000, PDI 1.36).

Scheme 1. Catalyst-Free 1,3-Dipolar Cycloaddition of Polymer−CN^+O^-s to Allyltrimethylsilane to Give Isoxazolines



The generation of polymer−CN^+O^-s was directly confirmed by the presence of the characteristic IR absorption band of the nitrile *N*-oxide group around 2300 cm^{-1}.[25] Reaction of the polymer−CN^+O^-s with allyltrimethylsilane was performed via catalyst-free 1,3-dipolar cycloaddition to confirm their structures and determine the conversion of the living end of the PMMA to the nitrile *N*-oxide functional groups (Scheme 1). Based on integral ratio of the aromatic and TMS protons in the ^1H NMR spectra, it was found that approximately 100% terminal conversion was achieved for all of the polymer−CN^+O^-s. Analysis of the resulting isoxazoline-containing polymers via MALDI−TOF MS provided further evidence to support the excellent conversion.[25]

Table 1. Synthesis of Highly Reactive Polymer Nitrile *N*-Oxides

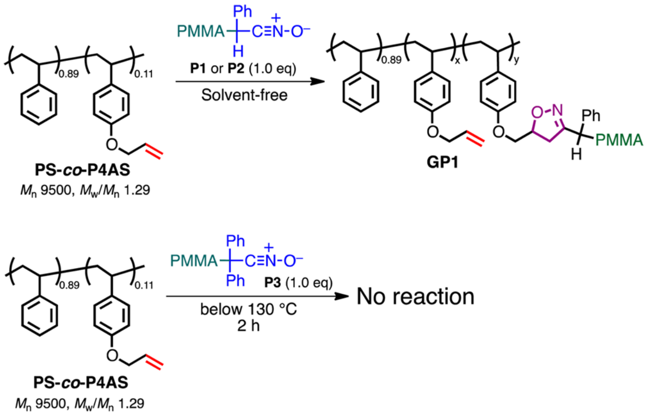


entry	polymer−CN^+O^-	[M]/[I]	M_n[a]	M_w/M_n[a]	yield (%)
1	PMMA−CN^+O^- (**P1**)	10	1600	1.24	94
2	PMMA−CN^+O^- (**P2**)	3	780[b]	[c]	85
3	PMMA−CN^+O^-	200	48000	1.28	93
4	P*t*BMA−CN^+O^-	10	3200	1.26	97
5	PMMA-*b*-P*t*BMA−CN^+O^-	MMA: 10 *t*BMA: 10	5600	1.81	80
6[d]	PS-*b*-PMMA−CN^+O^-	St: 10 MMA: 10	2400	1.45	88

[a] Absolute number-average molecular weights and polydispersity indices (M_w/M_n) were determined by SEC−MALS using $CHCl_3$ as the eluent. [b] Determined from ^1H NMR integrals. [c] N/A. [d] The polymerization was conducted by using *s*-BuLi as a initiator.

The PMMA−CN$^+$O$^-$s were then subjected to catalyst- and solvent-free click grafting onto poly(styrene-*co*-4-allyloxystyrene) (**PS-*co*-P4AS**) and the results are summarized in Table 2.

Table 2. Grafting Reactions of PMMA−CN$^+$O$^-$ onto PS-*co*-P4AS



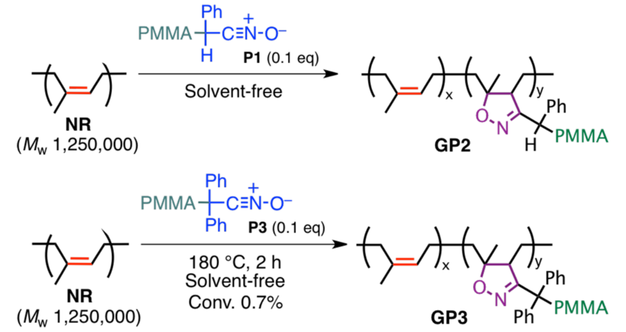
entry	PMMA−CN$^+$O$^-$	M_n	temp. (°C)	time (h)	conv.[a] (%)	yield (%)
1	**P3**	2000[b]	130	2	0[c]	95
2	**P1**	1600	100	2	21	98
3	**P1**	1600	130	2	67	90
4	**P1**	1600	130	6	86	93
5	**P1**	1600	160	2	39	96
6	**P2**	780	100	2	38	81
7	**P2**	780	130	2	54	100

[a] Determined from the ratio of ^{1}H NMR integrals. [b] PDI 1.36. [c] No reaction.

In the case of using PMMA−CN$^+$O$^-$ **P3**, no graft copolymer was obtained at 130 °C (entry 1, Table 2), and a high reaction temperature was necessary to achieve grafting reaction.[22] This result is attributed to the bulkiness of the reactive **P3** terminus, which has two phenyl groups and thus suppresses the reactivity. Conversely, the reaction of **P1**, which has a similar chain length to that of **P3**, with **PS-*co*-P4AS** (entries 2−5) proceeded even at a relatively low temperature of 100 °C, and the optimal temperature was found to be 130 °C (67% conv.). The high conversion for **P1** in the click grafting reaction at low temperature indicates its inherent high reactivity. In addition, the conversion was further improved to 86% after reaction at 130 °C for 6 h (entry 4). However, the conversion for the grafting reaction decreased at 160 °C (39%; entry 5). This phenomenon may be because of the simultaneous decomposition and cycloaddition of this PMMA−CN$^+$O$^-$ based on the results of the thermogravimetric analysis of **P1**.[25] The grafting reaction using **P2** with a short polymer chain was then investigated to evaluate the molecular weight dependence of the reactivity. Reaction of **P2** (M_n 780) with **PS-*co*-P4AS** at 100 and 130 °C afforded graft copolymers with 38% and 54% conversion, respectively, suggesting that the reactivity of the PMMA−CN$^+$O$^-$s is largely independent of their molecular weight.

On the basis of the above results, the grafting of the PMMA−CN$^+$O$^-$s onto natural rubber (NR) was investigated, as illustrated in Table 3. The reaction of **P3** proceeded with a low conversion because of the steric repulsion between the nitrile *N*-oxide and the trisubstituted internal olefin of NR (entry 1, Table 3). In addition, thermal cross-linking of NR was partly observed. On the other hand, the grafting reaction of **P1** onto NR proceeded smoothly (entries 2−5, Table 3). A conversion of 24.9% was obtained (entry 5), and the grafted NR was found to be partially soluble in acetone, which is a poor solvent for NR. This change in solubility made the separation of the grafted NR and free PMMA−CN$^+$O$^-$ difficult. Thus, it is indicated that the polymer dissolving in acetone might have a higher conversion than 24.9%. This result emphasizes that the higher reactivity of **P1** led to a significant improvement in the grafting reaction of NR. The moderate conversion of NR may be because of the steric problem of graft NR hindered by the grafted chains.

Table 3. Grafting Reaction of PMMA−CN$^+$O$^-$ onto NR



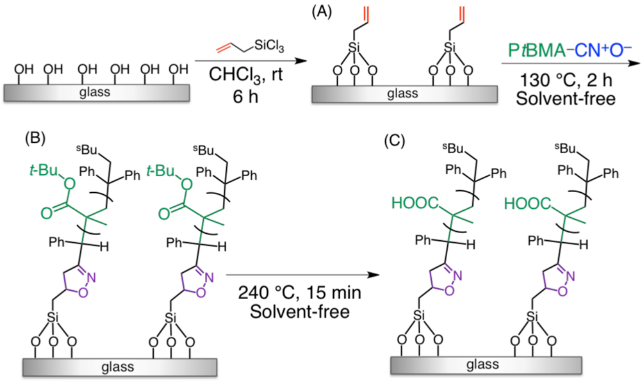
entry	PMMA−CN$^+$O$^-$	temp. (°C)	time (h)	conv.[a,b] (%)	yield[c] (%)
1	**P3**[d]	180	2	0.7	97
2[f]	**P1**[e]	130	6	11.4	100
3	**P1**[e]	140	6	8.7	100
4[f]	**P1**[e]	140	2	15.1	98
5[f]	**P1**[e]	140	6	24.9	49[g]

[a] Determined from the ratio of ^{1}H NMR integrals. [b] Based on the mole of nitrile *N*-oxide. [c] Based on the weight of NR and grafted PMMA. [d] M_n 2000, PDI 1.36. [e] M_n 1600, PDI 1.24. [f] Preheating at 160 °C for 1 h and then cooling to the reaction temperature in 15 min. [g] Partially dissolved in acetone.

The creation of functional surfaces has been attracted great interest for several applications such as biomaterials, stimuli-responsive materials, and organic−inorganic hybrid materials.[27] Polymer nitrile *N*-oxides as direct grafting agents can facilitate for the construction of polymer-bearing surfaces without the need to use any catalyst or solvent. To demonstrate this advantage of the polymer nitrile *N*-oxides, P*t*BMA−CN$^+$O$^-$ (**P4**, M_n 3200, PDI 1.26) was used in the catalyst- and solvent-free surface grafting onto a glass plate. **P4** was reacted with a glass plate bearing allyl-functional groups on the surface (**Allyl-GS**), as shown in Scheme 2. The surface grafting was performed by coating the surface with an excess of **P4** and heating at 130 °C for 2 h to give the poly(*tert*-butyl methacrylate)-modified glass surface (**P*t*BMA-GS**). The thermal decomposition behavior of P*t*BMA was examined via TGA,[25] and it was determined that the decomposition of the *tert*-butyl ester moieties occurs at approximately 235 °C.[28] Thus, the **P*t*BMA-GS** was heated at 240 °C to remove the *tert*-butyl ester moieties and afford a hydrophilic poly(methylacrylic acid)-modified glass surface (**PMAA-GS**).

Static water contact angle measurements were examined to confirm the surface properties of the modified glass, as shown in Figure 2. The static water contact angle of **Allyl-GS** was approximately 60° and decreased to 44° after the surface grafting reaction, suggesting that the cycloaddition of P*t*BMA−

Scheme 2. Preparation of PMAA-Modified Glass Surfaces via Catalyst- and Solvent-Free Grafting Reaction[a]



[a](A) **Allyl-GS**, (B) P*t*BMA**-GS**, and (C) **PMAA-GS**.

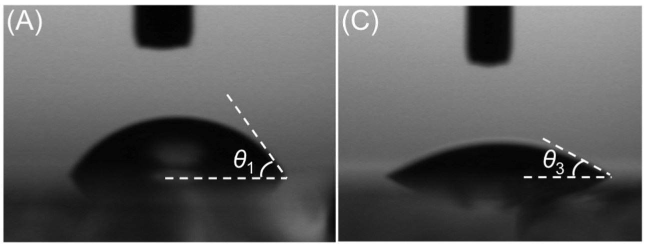


Figure 2. Water contact angles of **Allyl-GS** (A, θ_1 = 59.6°) and **PMAA-GS** (C, θ_3 = 32.0°). All angles were calculated by averaging the values for three different measurements.

CN^+O^- was achieved. After thermal decomposition of the ester groups in **P*t*BMA-GS**, the contact angle further decreased to 32°, indicating that the hydrophilic functionalization of the surface could be achieved via simple sequential click and ester decomposition reactions without the use of catalysts or solvents. In addition, when a basic buffer solution (pH = 10) was used, the contact angle of **PMAA−GS** was determined to be 24°, supporting the existence of carboxylic acid groups on the surface.[25]

In conclusion, a general and efficient method for the one-pot synthesis of polymer nitrile *N*-oxides was developed via the reaction of *trans-β*-nitrostyrene with living polymer anions. These polymer nitrile *N*-oxides prepared from *trans-β*-nitrostyrene have high reactivity for 1,3-dipolar cycloadditions to both pendant and internal olefin-containing polymers at relatively low temperatures. Moreover, the preparation of a functional surface via surface grafting of P*t*BMA nitrile *N*-oxide was achieved through sequential catalyst- and solvent-free click and ester decomposition reactions. Extension of this research to the preparation of polymers with precise structures and supramolecules[29] is currently underway.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, ^{1}H NMR, FT−IR, and MALDI−TOF MS spectra; detailed results of the thermal decomposition study of P*t*BMA−CN^+O^-. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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