Radical Addition-Coupling Polymerization with Various Nitroso Compounds

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ABSTRACT: Four nitroso esters were prepared by oxidation of 4,4-dimethyl dihydro-1,3-oxazine or 4,4-dimethyl-2-oxazoline with two equiv of *m*-chloroperoxybenzoic acid. All of them can be applied in radical addition-coupling polymerization to produce periodic polymer together with introduction of ester group at side chain. Compared with 2-methyl-2-nitrosopropane, 2-nitroso-2-methyl-4-acetoxypentane and 2-methyl-2-nitrosopropyl hexanoate present good stability at high temperature up to 70 °C and can result polymer with high molecular weight. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 810–815

KEYWORDS: atom transfer radical polymerization; functionalization of polymers; nitroso ester; radical addition-coupling polymerization; step-growth polymerization

INTRODUCTION Radical addition-coupling polymerization (RACP) has been proposed for synthesis of periodic polymer with regular monomer sequence.[1–3] As shown in Scheme 1, the polymerization involves consecutive addition of carbon-centered radical to N═O of C-nitroso compound followed by cross-coupling of carbon-centered radical and *in situ* formed nitroxyl radical, which produces copolymers with high molecular weight and unimodal molecular weight distribution from saturated and unsaturated monomers. The key step of RACP is the formation of intermediate nitroxyl radical, which is stable enough to take cross-coupling reaction with relatively active carbon-centered radical based on persistent radical effect.[4] The N═O double bond plays an essential role in RACP. 2-Methyl-2-nitrosopropane (MNP) as a simple and easily-made or commercially available nitroso compound is capable of trapping radical efficiently. But its low boiling point and stability limits its application in RACP at relative high temperature. Other commericially available nitroso compounds, such as nitrosobenzene (PhNO), are not suitable for RACP in the presence of Cu(I)/ligand, because the reaction of nitrosobenzene with Cu(I) complexes of the tetradentate ligand tris(2-dimethylaminoethyl)amine (Me_6Tren) has been reported.[5] Therefore, exploring the suitable nitroso compound is an important issue in RACP.

Nitroso compound is not so stable during preparation and storage, because it is subjected to be further oxidized to nitro compound or photodecompose to carbon-centered radical and nitric oxide. Methods for the preparation of C-nitroso compounds have been tentatively reviewed.[6,7] For the synthesis of aliphatic nitroso alkanes, oxidation of amine without α-hydrogen under mild condition is an easy method. For one-pot synthesis of aliphatic nitroso compounds containing ester group, oxidation of 4,4-dimethyl dihydro-1,3-oxazine or 4,4-dimethyl 2-oxazoline with *m*-chloroperoxybenzoic acid (MCPBA) is a convenient method.[8,9]

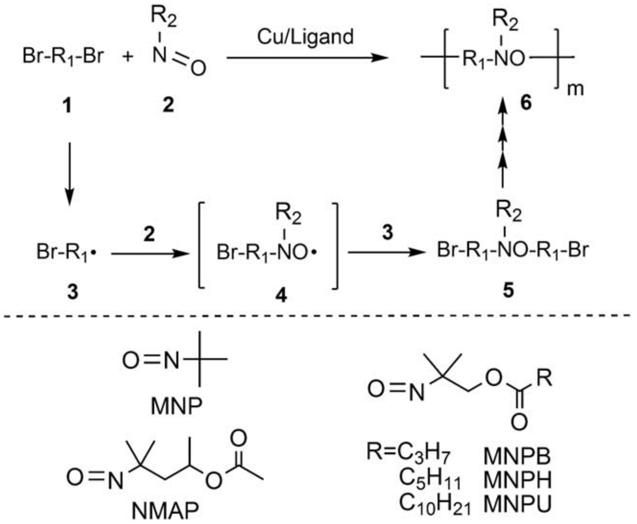
With respect to various dibromides successfully used in RACP, only MNP as nitroso compound has been used efficiently in RACP.[1–3] As an important component in RACP, screening on suitable nitroso compound for RACP at different temperature in various solvents and for different dibromides will broaden the versatility of this synthetic method. In this article, we report synthsis of some aliphatic nitroso esters and their application in RACP. Using nitroso ester, not only the RACP at various temperatures can be explored but also the possibility of incorporation of functional group at the side chain of the polymer can be realized as well.

RESULTS AND DISCUSSION

Synthesis of Nitroso Esters

Two methods are used to prepare aliphatic nitroso ester. As illustrated in Scheme 2, dihydrooxazine was first prepared by acid-catalyzed reaction of diol and acetonitrile,[10] which

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Mechanism of radical addition-coupling polymerization and the structure of nitroso esters.

was further oxidized by 2 equiv. of MCPBA.[8] The colorless crystals of the dimer can be obtained upon standing of its petroleum ether saturated solution at −20 °C. The nitroso ester, 2-nitroso-2-methyl-4-acetoxypentane (NMAP), was characterized by NMR, Elem. Anal (EA), and mass spectrum (MS) (see Supporting Information). The nitroso compound usually forms dimer in both solid state and solution, while in the ^{1}H NMR spectrum of NMAP, only one group of peaks were found, which suggested no dimer was formed in the solution. Combined with the results of EA and MS, it is clear that the nitroso ester was prepared.

The other method is oxidation of 2-oxazoline with 2 equiv. of MCPBA,[9] which was prepared by acid-catalyzed reaction between aliphatic carboxylic acid and 2-amino-2-methyl-1-propanol, as illustrated in Scheme 3.[11] Several nitroso esters, such as 2-methyl-2-nitrosopropyl butanoate (MNPB), 2-methyl-2-nitrosopropyl hexanoate (MNPH), 2-methyl-2-nitrosopropyl undecanoate (MNPU), were prepared by this method with various carboxylic acids. The nitroso esters were characterized by NMR, Elem. Anal, and mass spectrum. The ^{1}H NMR spectrum of MNPH and the assignment were presented in Figure 1. It is clear that both monomer and dimer can be detected in the ^{1}H NMR spectra. As the element analysis result fits well with the theoretic value, it is convinced that nitroso compound instead of nitro compound is obtained. The mass spectra also proved the formation of monomer and dimer of this compound.

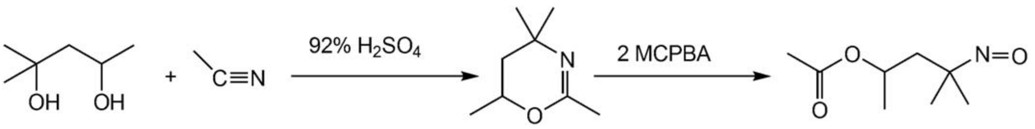
RACP Using Nitroso Esters

Equivalent dimethyl 2,13-dibromotetradecanedioate (DMDBT) and nitroso compound were polymerized in the presence of Cu/PMDETA for 1 h. The polymerization temperature varies from 25 to 70 °C. MNP was also used as the control. Figure 2 is the GPC curves of the polymer prepared by RACP using MNP as nitroso compound. At 25 °C, polymer with high number-average molecular weight (M_n) can be obtained. The M_n slightly increased when the polymerization temperature increased from 25 to 60 °C. When the temperature is further increased to 70 °C, the M_n greatly decreased. The main reason is that MNP is volatile and easy to photodecompose to *tert*-butyl radical and nitric oxide.[12]

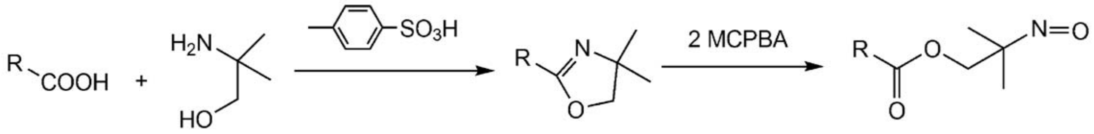
The nitroso esters prepared in this article were applied in RACP at different temperatures. Figure 3 is the GPC curves of polymers prepared by RACP using NMAP at different temperatures. It can be found that as the temperature increased from 25 to 50 °C, the M_n of polymer increased from 3.49×10^4 g/mol to 7.01×10^4 g/mol; and remained almost constant as the temperature increased from 50 to 70 °C. The polydispersity indexes of the polymers are around 1.5. This suggests that NMAP is better than MNP for high temperature polymerization and results polymer with high M_n.

The other three nitroso esters are also applied in RACP and the results are summarized in Table 1. The monomer conversion for all polymerizations using DMDBT and various nitroso esters is higher than 95%, which indicates these nitroso esters are efficient in RACP. For MNPB, the M_n of the polymer decreased with the polymerization temperature. For MNPH, the lowest M_n was obtained at 60 °C and the highest one at 70 °C, For MNPU, the M_n of polymer obtained at 25 °C is higher than those obtained at 50–70 °C. Among the three nitroso esters, MNPH can be applied to produce the polymer with the highest M_n at various temperatures. The possible reason is related to the chain length of the carboxyl unit. The short chain of carboxyl unit, such as MNPB, might result low stability of MNPB at high temperature, which leads to low M_n of polymer; the long chain analogs, such as MNPU, might lead to the low mobility and activity of nitroso ester, which also results low M_n at various temperatures.

The ^{1}H NMR spectrum and its assignment of polymer prepared by RACP between DMDBT and MNAP at 70 °C were illustrated in Figure 4. The ester group of NMAP can be detected in the spectrum in addition to the ester of dibromide. The molar ratio of two monomer units was calculated by ^{1}H NMR spectra (see Supporting Information). For all the polymers prepared by nitroso esters, the molar ratio of two units is close to 1:1. This indicates the obtained polymers have the regular alternative monomer sequence as reported in our previous paper.[1,3] Only the molar ratio of two units of polymer prepared by MNP at 70 °C is slightly different from 1:1. If MNP volatilized or decomposed, the real monomer



SCHEME 2 Synthesis route of NMAP.



SCHEME 3 Synthesis route of 2-methyl-2-nitrosopropyl alkyl ester.

ratio [DMDBT]:[MNP] will be higher than 1:1. The RACP follows the step-growth polymerization mechanism, and the M_n of the polymer is affected by the monomer ratio. As reported in our previous paper, the less amount of MNP than dibromide leads to low M_n of polymer.[1,3] As a result, the polymer composition in terms of [DMDBT]:[MNP] is higher than 1:1, which is evidenced by the 1.06:1 for polymer obtained by MNP at 70 °C.

The NMAP and MNPH exhibit better performance than MNP at high temperature in RACP. The reason can be explained in two aspects. On one hand, the relatively high boiling point and stability of NMAP and MNPH prevent them from volatilization and decomposition even at high temperature, which enable the concentration of nitroso compound to remain the same as the feed ratio. On the other hand, the equilibrium between monomer and dimer shifts to monomer if the temperature increases. More nitroso compound exists in monomer state in solution at higher temperature if the monomer of nitroso compound is stable. As the dibromide is the same, the higher M_n of polymer prepared by NMAP and MNPH at 70 °C suggests that they are stable enough to achieve high efficient concentration of monomeric nitroso compound at 70 °C.

The other dibromide, 1,4-bis(1-bromoethyl)benzene (BBEB), was also used in RACP with MNPH. As shown in Table 1, polymer can be obtained at 25 and 70 °C. In this case, the functional group was introduced at the side chain of polymer using nitroso ester as monomer.

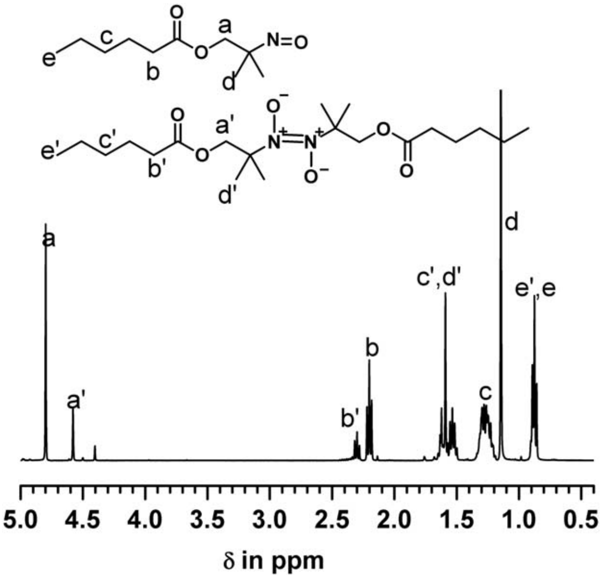


FIGURE 1 ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of MNPH.

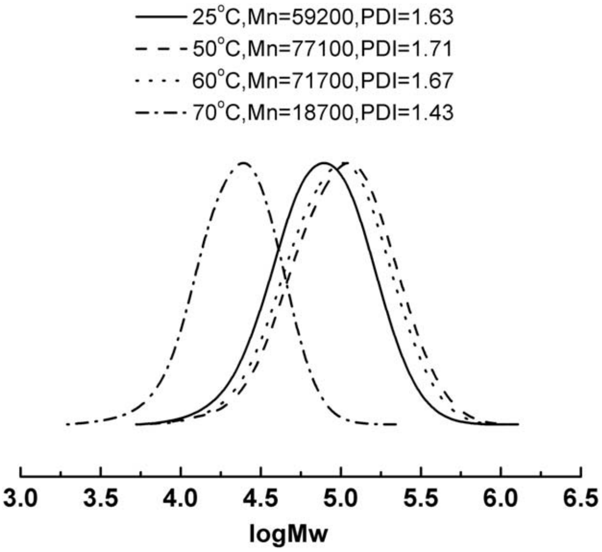


FIGURE 2 GPC curves of polymer prepared by RACP between DMDBT and MNP.

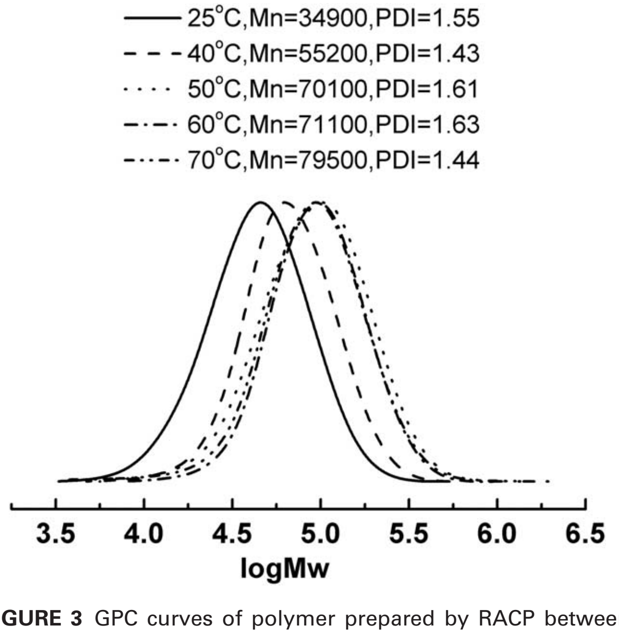


FIGURE 3 GPC curves of polymer prepared by RACP between DMDBT and NMAP.

TABLE 1 Polymer Prepared by Radical Addition-Coupling Polymerization Between Dibromo Monomers and Nitroso Esters Under Different Temperatures

				Polymer			
Run[a]	Nitroso Compound	Dibromide	Temp.[b] (°C)	Yield (%)[c]	M_n (10^3)[d]	PDI[d]	[Dibromide]/[Nitroso][e]
1	MNP	DMDBT	25	99.7	59.2	1.63	1.00
2			50	98.6	77.1	1.71	–
3			60	97.2	71.7	1.67	–
4			70	99.0	18.7	1.43	1.06
5	NMAP	DMDBT	25	97.9	34.9	1.55	–
6			40	97.9	55.2	1.43	–
7			50	98.3	70.1	1.61	–
8			60	99.1	71.1	1.63	–
9			70	98.5	79.5	1.44	1.00
10	MNPB	DMDBT	25	98.3	59.1	1.62	1.01
11			50	98.3	31.7	1.52	–
12			60	97.2	10.4	1.42	–
13			70	97.4	10.4	1.49	1.01
14	MNPH	DMDBT	25	98.1	71.3	1.74	–
15			50	98.0	77.5	1.85	–
16			60	97.4	59.8	1.63	–
17			70	98.2	83.9	1.80	1.00
18		BBEB[f]	25	99.1	9.4	1.92	0.99
19			70	–	7.2	2.22	–
20	MNPU	DMDBT	25	97.6	17.1	1.41	1.01
21			50	97.2	11.9	1.42	–
22			60	96.9	11.7	1.40	–
23			70	97.2	13.3	1.43	1.00

[a] [Nitroso compound]$_0$/[dibromide]$_0$/[Cu]$_0$/[PMDETA]$_0$ = 1.05/1/2/2.2, 1 h, V_{THF} = 0.3 mL.

[b] Polymerization temperature.

[c] Polymer yield calculated by the integrity area of original GPC curve of crude polymer.

[d] Number-averaged molecular weight (M_n in 10^3 g/mol) and polydispersity index (PDI) of polymer measured by gel permeation chromatography.

[e] Mole ratio of dibromo monomer unit to nitroso compound unit of polymer determined by ^{1}H NMR.

[f] M_n and PDI of polymers were measured without further purification.

EXPERIMENTAL

Materials

(±)−2-Methyl-2,4-pentanediol (98%, Alfa Aesar), *m*-chloroperoxybenzoic acid (70–75%, Alfa Aesar), 2-amino-2-methyl-1-propanol (>97%, Fluka), butyric acid (>99%, Alfa Aesar), hexanoic acid (>98%, Alfa Aesar), undecanoic acid (98%, Alfa Aesar), copper powder (3.25–4.75 μm, 99.9%, alfa), and *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyl diethylenetriamine (PMDETA, 98%, Alfa). Tetrahydrofuran (THF) was distilled from sodium benzophenone. Synthesis of dimethyl 2,13-dibromotetradecanedioate (DMDBT) and 1,4-bis(1-bromoethyl)benzene (BBEB) was reported in our previous article.[1] 2-Methyl-2-nitrosopropane dimer (MNP) was synthesized according to procedures previously reported in the literature.[13] All other reagents were used as received without further purification.

Characterization Methods

Number average (M_n) and molecular weight distributions were determined by gel permeation chromatograph (GPC) on a PL GPC220 equipped with two PLgel 5 μm MIXED-C columns using polystyrene standards and THF as the eluent at a flow rate of 1.0 mL/min at 40 °C. ^{1}H NMR spectra were recorded at room temperature by a Bruker DMX 400 MHz spectrometer using tetramethylsilane as the internal standard and deuterated chloroform as the solvent. Elemental analyses were performed with Flash EA1112 (Thermo Finnigan). ESI-MS (*m*/*z*) was performed using a LCQ Deca XP Max (Thermo Finnigan).

Synthesis of Nitroso Compounds

2-Nitroso-2-Methyl-4-Acetoxypentane

2-Nitroso-2-methyl-4-acetoxypentane (NMAP) was synthesized according to published literature.[8,10] The yield of NMAP is 16.7%.

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 1.10 (6H, d, CH_3—C—CH_3), 1.21 (3H, d, CH_3—CH), 1.88 (3H, s, CH_3—C=O), 2.17, 2.81 (2H, dd, —CH_2—), 4.90 (1H, m, —CH—O). ^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm): 20.54

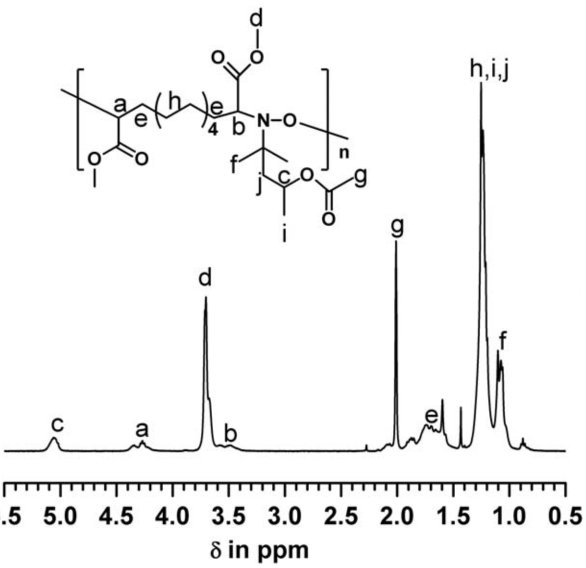


FIGURE 4 ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of polymer prepared by RACP between DMDBT and NMAP at 70 °C.

(CH$_3$—CH), 21.08 (CH$_3$—C═O), 21.30, 21.95 (CH$_3$—C—CH$_3$), 43.18 (—CH$_2$—), 67.36 (—C—), 97.92 (O—CH—CH$_3$), 170.29 (—C═O). ESI (m/z): 185.80 (100) [M+Na]$^+$, 368.55 (21.25) [2M+Na]$^+$, 165.63 (3.96) [M−NO+Na]$^+$. Anal. calcd. For $C_8H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.63; H, 8.75; N, 7.99.

2-Methyl-2-nitrosopropyl alkyl esters were synthesized according to the published procedure.[9,11] Undecanoic acid, hexanoic acid, and butyric acid were used.

2-Methyl-2-Nitrosopropyl Undecanoate

The yield of MNPU is 5.3%.

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 0.88 (3H, t, C$\boldsymbol{H}_3$—CH$_2$), 1.14 (6H, s, C$\boldsymbol{H}_3$—C—C$\boldsymbol{H}_3$), 1.25 (14H, m, CH$_3$— (C$\boldsymbol{H}_2$)$_7$—), 1.52 (2H, m, —C$\boldsymbol{H}_2$—CH$_2$—C═O), 2.20 (2H, t, —C$\boldsymbol{H}_2$—C═O), 4.79 (2H, s, —C$\boldsymbol{H}_2$—O). ESI (m/z): 293.89 (100) [M+Na]$^+$, 535.02 (47.87) [2M−NO+Na]$^+$, 564.19 (35.26) [2M+Na]$^+$, 241.02 (12.92) [M−NO]$^+$, 512.32 (11.93) [2M−NO]$^+$, 775.87 (9) [3M−2NO+Na]$^+$. Anal. calcd. for $C_{15}H_{29}NO_3$: C, 66.38; H, 10.77; N, 5.16. Found: C, 65.85; H, 10.85; N, 5.08.

2-Methyl-2-Nitrosopropyl Hexanoate

The yield of MNPH is 5.1%.

^{1}H NMR (monomer, 400 MHz, CDCl$_3$) δ (ppm): 0.88 (3H, t, C$\boldsymbol{H}_3$—CH$_2$), 1.15 (6H, s, C$\boldsymbol{H}_3$—C—C$\boldsymbol{H}_3$), 1.25 (6H, m, CH$_3$—(C$\boldsymbol{H}_2$)$_3$—), 2.20 (2H, t, —C$\boldsymbol{H}_2$—C═O), 4.80 (2H, s, —C$\boldsymbol{H}_2$—O). ^{1}H NMR (dimer, 400 MHz, CDCl$_3$) δ (ppm): 0.88 (3H, t, C$\boldsymbol{H}_3$—CH$_2$), 1.53 (6H, m, CH$_3$— (C$\boldsymbol{H}_2$)$_3$—), 1.59 (6H, s, C$\boldsymbol{H}_3$—C—C$\boldsymbol{H}_3$), 2.32 (2H, t, —C$\boldsymbol{H}_2$—C═O), 4.58 (2H, s, —C$\boldsymbol{H}_2$—O). ESI (m/z): 424.45 (100) [2M+Na]$^+$, 223.85 (87.19) [M+Na]$^+$, 394.95 (80.72) [2M−NO+Na]$^+$, 239.88 (8.85) [M+K]$^+$, 371.64 (5.95) [2M−NO]$^+$. Anal. calcd. for $C_{15}H_{29}NO_3$: C, 59.68; H, 9.52; N, 6.96. Found: C, 59.64; H, 9.50; N, 6.79.

2-Methyl-2-Nitrosopropyl Butyrate

The yield of MNPB is 4.6%.

^{1}H NMR (monomer, 400 MHz, CDCl$_3$) δ (ppm): 0.89 (3H, t, C$\boldsymbol{H}_3$—CH$_2$), 1.15 (6H, s, C$\boldsymbol{H}_3$—C—C$\boldsymbol{H}_3$), 1.56 (2H, m, CH$_3$—C$\boldsymbol{H}_2$—), 2.19 (2H, t, —C$\boldsymbol{H}_2$—C═O), 4.81 (2H, s, —C$\boldsymbol{H}_2$—O). ^{1}H NMR (dimer, 400 MHz, CDCl$_3$) δ (ppm): 0.94 (3H, t, C$\boldsymbol{H}_3$—CH$_2$), 1.59 (6H, s, C$\boldsymbol{H}_3$—C—C$\boldsymbol{H}_3$), 1.63 (2H, m, CH$_3$—C$\boldsymbol{H}_2$—), 2.29 (2H, t, —C$\boldsymbol{H}_2$—C═O), 4.58 (2H, s, —C$\boldsymbol{H}_2$—O). ESI (m/z): 195.86 (100) [M+Na]$^+$, 481.83 (89.69) [3M−2NO+Na]$^+$, 338.97 (70.92) [2M−NO+Na]$^+$, 368.76 (54.61) [2M+Na]$^+$. Anal. calcd. for $C_{15}H_{29}NO_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 52.70; H, 8.34; N, 7.64.

Radical Addition-Coupling Polymerization

Polymerization Procedure

In a typical procedure, nitroso compound (0.144 mmol), dibromo monomer (0.138 mmol), PMDETA (57 μL, 0.275 mol), and THF (0.3 mL) were added to a 10 mL Schlenk flask equipped with a stirring bar. After three freeze–pump–thaw cycles, copper powder (19.4 mg, 0.302 mmol) was added under N_2. The flask was reacted at 25 °C for 1 h. The mixture was diluted with THF and purified by passing through a neutral alumina column. The polymer solution was concentrated and dried under vacuum at 40 °C to yield polymer as a colorless tacky gum.

Purification of Polymer Prepared by RACP

To a solution (2%, m/m) of crude polymer in acetone in a 45 °C water bath, methanol/water (7/3, v/v) was added dropwise until the solution just became turbid. This turbid liquid was slowly cooled to room temperature and then kept at 4 °C over night. Oil-like product appeared at the bottom, which was separated and dried under vacuum at 45 °C to afford final product. Polymer yield was calculated based on the area corresponding to the fractions of monomer and polymer in the GPC curve of crude polymer before purification.

CONCLUSIONS

In summary, we report radical addition-coupling polymerization using various nitroso esters with dibromide at different temperatures. The nitroso esters can be polymerized at 70 °C and produce polymer with high molecular weight and regular monomer sequence in addition to introducing ester group at side-chain of polymer.

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