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Synthesis of Thermal Degradable Poly(alkoxyamine) through a Novel Nitroxide Radical Coupling Step Growth Polymerization Mechanism

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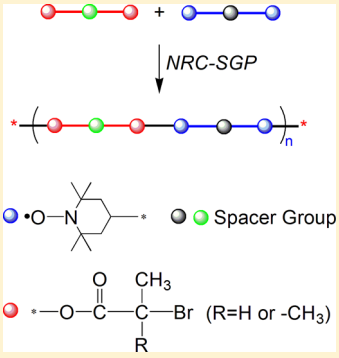
Supporting Information

ABSTRACT: The thermal degradable poly(alkoxyamine) was synthesized through a novel nitroxide radical coupling step growth polymerization (NRC-SGP) mechanism. The monomers of 1,4-phenylene bis(2-bromo-2-methylpropanoate) (monomer **1**) and 1,4-phenylene bis(2-bromopropanoate) (monomer **1′**) with two bromide groups and 1,6-di(4-(2,2,6,6-tetramethylpiperidine-1-oxyl))-hexa-2,4-diyne (monomer **2**) with two nitroxide radicals were first designed and synthesized. Then the NRC-SGP mechanism was investigated in detail by optimizing the factors such as polymerization time, temperature, solvents, catalysts, ligand, monomer concentration, and structures connected to halogen groups. The results showed that the termination by disproportionation was the major side reaction in the NRC-SGP mechanism, and the lower temperature (25 °C) would favor an important contribution. The proper combination of all factors could lead to an ideal NRC-SGP procedure. Finally, the thermal stability of formed poly(alkoxyamine) was monitored by TG, DSC and SEC instruments, and the results showed that the poly(alkoxyamine) would suffer a severe thermal degradation at the elevated temperature above 140 °C.



INTRODUCTION

The step growth polymerization mechanism has been widely used in polymer industry, and various bulk materials have been manufactured, such as the polyether, polyamide, polyurethane, etc. For a successful step growth polymerization, the used reaction should meet the prerequisites: (a) the reaction could happen with high efficiency under mild conditions; (b) the concerned functional monomers should be easily designed and introduced. For example, the widely used reactions in step growth polymerization are the esterification or amidation between anhydride, carboxyl or acyl halide and hydroxyl or amine groups. With the increasing requirements from applications, the polymers with novel architectures or compositions are urgently needed, and the exploring of a novel reaction to a versatile step growth polymerization mechanism is becoming a rather significant and challenging work.

Up to now, a library of efficient reactions, including the thiol−bromide reaction,[1] thiol−ene addition,[2] thiol−yne addition,[3] atom transfer radical coupling (ATRC) reaction,[4] Glaser coupling,[5] Suzuki reaction,[6] copper-catalyzed azide/alkyne click (CuAAC) chemistry, and Diels−Alder (DA) [4 + 2] reaction,[7] and so on, have been innovatively presented and widely used in polymer chemistry. Because of their high efficiencies and particular versatility, some of these reactions have also been introduced into the step growth polymerization mechanism, and certain promising results have been achieved. For example, based on CuAAC Chemistry, the click polymerization realized in a step growth manner was presented by Tang et al.[8] and further developed by several other groups.[9] Similarly, the Suzuki reaction was introduced into the step growth polymerization for the construction of a certain functional polymer, and especially, this reaction was mainly aimed to some conjugated polymers.[10] Also, the thiol−ene addition had been widely used in polymer industry in a step growth manner under UV conditions.[2] Alternatively, the carbon radical based reactions were also considered and tentatively combined into the step growth polymerization. That was, using the atom transfer radical addition (ATRA) reaction, the specially designed monomers with a halogen group and a double bond were polymerized in a step growth manner by Kamigaito et al.[11] Using the ATRC reaction, the difunctional atom transfer radical polymerization (ATRP) initiators could be polymerized into certain polymers by step growth polymerization.[12] Later, the nitrone-assisted radical coupling reactions was also introduced into the step growth polymerization and termed as nitrone-mediated radical coupling (NMRC) reaction by Barner-Kowollik et al.[13] or step growth radical addition−coupling polymerization (RACP) by Wang et al.[14] Obviously, most coupling reactions have been successfully cooperated into the step growth polymerization to meet some versatile applications.

Previously, on the basis of the ATRP[15] and single electron transfer living radical polymerization (SET-LRP)[16] mechanisms, our group developed a novel coupling reaction termed as nitroxide radical coupling (NRC) by the typical capture reaction of stable nitroxide radicals to the active carbon radicals

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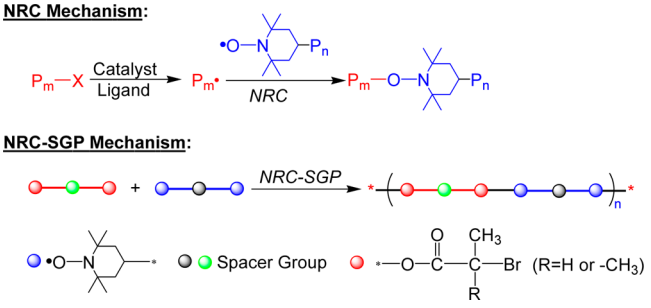
in situ generated from halogen containing precursors (Scheme 1).[17] This NRC reaction has been proved to be a rather robust

Scheme 1. Illustration of NRC and NRC-SGP Mechanisms



and orthogonal technique with quantitative efficiency in wide temperature range of 25−90 °C and thus endowed with the "click" character. Also, the concerned precursors with halogen or nitroxide radical groups could be easily obtained and stored under normal conditions with long-time stability. This NRC reaction has been widely used in postmodification of polymers,[18] construction of polymers with defined architectures,[17,19] and preparation of organic−inorganic composites.[20] Furthermore, the formed alkoxyamine by NRC reaction was a dynamic reversible covalent bond, which could be thermally disassociated and used in some promising applications. For example, the alkoxyamine bond was used to construct "dynamic covalent polymers" by radical crossover reaction,[21] to act as the initiator of the nitroxide-mediated radical polymerization (NMRP) mechanism,[22] and to design some thermal degradable materials.

Undoubtedly, the NRC reaction could also meet the above prerequisites of (a) and (b) and might be introduced into the step growth polymerization. Different from other radical based coupling reaction, the carbon radical can be selectively and efficiently captured by the stable nitroxide radicals in the NRC system, and almost no side reactions (such as bimolecular combination termination, disproportionation termination, or chain transfer reactions) happened.[23] Thus, the NRC based step growth polymerization might have some potential advantages to the synthesis of polymer with high molecular weight and designed compositions. For example, the spacer connected on TEMPO or carbon radicals could be selectively designed, and the functional segment could be deliberately introduced to construct some particular poly(alkoxyamine). Herein, based on the well-developed NRC reaction, a novel mechanism termed as the nitroxide radical coupling step growth polymerization (NRC-SGP) mechanism was presented, and the novel poly(alkoxyamine) with multiple dynamic covalent bonds was prepared from the monomers contained two bromide groups or two nitroxide radical groups (Scheme 1). The factors (including polymerization time, temperature, solvents, catalysts, ligand, monomer concentration, and structures connected to halogen groups) on the NRC-SGP mechanism were investigated in detail, and the thermal degradation behavior of formed poly(alkoxyamine) was studied.

EXPERIMENTAL SECTION

Materials. Hydroquinone (>99.0%, Aldrich) was dried by azeotropic distillation with toluene before use. Tetrahydrofuran (THF, >99.0%, Sinopharm Chemical Reagent Co., Ltd. (SCR)) was refluxed and distilled from sodium naphthalenide solution. Propargyl bromide (>98.0%, SCR) was purified by distillation from CaH_2 under reduced pressure. Triethylamine (TEA, >99.0%, SCR) was purified by distillation from CaH_2. Copper(I) bromide (Cu(I)Br, 95.0%, SCR) was stirred overnight in acetic acid, filtered, washed with ethanol and ethyl ether successively, and dried under vacuum. 4-Hydroxy-2,2,6,6-teramethylpiperidinyl-1-oxyl (HO-TEMPO, >99.0%), sodium hydride (NaH, 60% dispersion in mineral oil), 2-bromoisobutyryl bromide (>99.0%), copper powder (Cu(0), 99.8%), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99.0%), tris(2-dimethylaminoethy)amine (Me_6TREN, 99.0%), and 2,2′-bipyridine (Bpy, 99.0%) were all purchased from Aldrich and used as received. All other reagents were purchased from SCR and used as received except for declaration.

Measurements. Size exclusion chromatography (SEC) of polymers was performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector. One 5 μm LP gel column (500 Å, molecular range 500−2 × 10^4 g/mol) and two 5 μm LP gel mixed bed column (molecular range 200−3 × 10^6 g/mol) were calibrated by PS standard samples. The injection volume was 20 μL, and the concentration was 5−10 mg/mL. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker (400 MHz) spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference at 298 K. Gas chromatograph−mass spectrometer−computer (GC-MS, Thermo Focus DSQ, US) was operated using an HP-5MS capillary column of 30 m × 0.25 mm with a phase thickness of 0.25 μm from HP. Helium (99.999%) was the carrier gas maintained at a flow rate of 1 mL/min. The split rate was 100:1, and the inlet volume was 1.0 μL. High-performance liquid chromatography (HPLC) was performed on an instrument composed of a Waters 515 pump, a C-18 column (Symmetry Shield PRP-18, 5.0 μm, 4.6 × 250 mm), a Waters 486 UV detector, and a Waters 410 RI detector. The matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) measurement was performed using a Perspective Biosystem Voyager-DESTR MALDI-TOF MS (PE Applied Biosystems, Framingham, MA). Matrix of dithranol (10 mg/ml), sample (10 mg/ml) and cationizing salt of sodium trifluoroacetate (10 mg/ml) in THF were mixed in the ratio of matrix: cationizing salt: sample =10:1:5, and 0.8 μL of mixed solution was deposited on the sample holder. Differential scanning calorimetry (DSC) was carried on a DSC Q2000 thermal analysis system (Shimadzu, Japan). Samples were first heated from 25 to 80 °C at a heating rate of 10 °C/min under a nitrogen atmosphere, followed by cooling to 25 °C at −10 °C/min. Similarly, the DSC traces were monitored in the temperature range of 25−100, 25−120, and 25−140 °C, respectively, and the procedure was the same as that in the first cycle of 25−80 °C. The thermogravimetric analysis (TGA) curves of polymers and monomers were obtained using a PerkinElmer Pyris 1 at a heating rate of 10 °C/min.

Synthesis of 1,4-Phenylene Bis(2-bromo-2-methylpropanoate) (Monomer 1) (Scheme 2). Typically, hydroquinone (7.77 g, 40.0 mmol), TEA (6.2 mL, 44.0 mmol), and dry THF (250 mL) were sequentially charged into a 250 mL round-bottom flask. Then, the system was placed into an ice bath, and 2-bromoisobutyryl bromide (5.5 mL, 44.0 mmol) was slowly added with stirring in 30 min, and the reaction was continued for another 6.0 h. The formed salts was removed by filtration, and the solvent was removed under reduced pressure. The final product was recovered by recrystallization three times from methanol, and the obtained white solid was dried under vacuum. Yield = 14.9 g (99.2%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 2.07 (s, $-C(CH_3)_2Br$), 7.18 (s, $-CH-$ on phenyl group). ^{13}C NMR ($CDCl_3$, 400 MHz), δ (ppm): 30.21 ($-C(CH_3)_2Br$), 54.89 ($-C(CH_3)_2Br$), 169.90 ($-C(=O)O-$), 122.31 ($-CH-$ on phenyl group), 148.34, ($-CO-$ on phenyl group). GC-MS (EI): m/z = 408, and the calculated purity was 99.2%.

Synthesis of 1,4-Phenylene Bis(2-bromo-2-methylpropanoate) (Monomer 1′) (Scheme 2). The synthetic process of monomer **1′** was similar to that of monomer **1**, except that the added 2-bromoisobutyryl bromide was changed as 2-bromopropiomyl bromide. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.91 (d,

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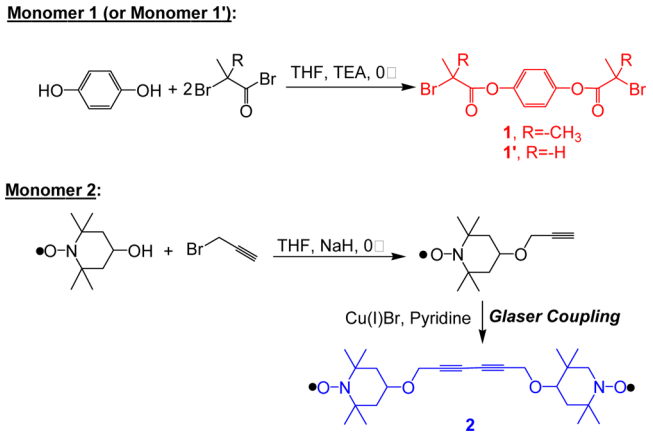
Scheme 2. Synthetic Procedures of Monomers 1 or 1′ with Two Bromide Groups and Monomer 2 with Two Nitroxide Radical Groups



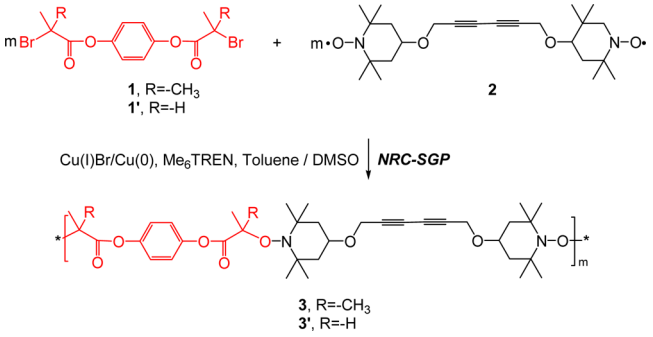
$-CHCH_3Br$), 4.58 (q, $-CHCH_3Br$), 7.20 (s, $-CH-$on phenyl group). ^{13}C NMR ($CDCl_3$, 400 MHz), δ (ppm): 21.21 ($-CH(CH_3)$-Br), 39.43 ($-CH(CH_3)Br$), 168.53 ($-C(=O)O-$), 122.08 ($-CH-$ on phenyl group), 147.90 ($-CO-$ on phenyl group). GC-MS (EI): m/z = 380, and the calculated purity was 98.8%.

Synthesis of 1,6-Di(4-(2,2,6,6-tetramethylpiperidine-1-oxyl))-hexa-2,4-diyne (Monomer 2) (Scheme 2). First, the compound 4-(prop-2-ynyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (Alkyne-TEMPO) was synthesized by reaction between HO-TEMPO and propargyl bromide. To a stirring suspension of NaH (60% in mineral oil, 2.51 g, 100.0 mmol) in dry THF (100 mL) in a 250 mL round-bottom flask, HO-TEMPO (15.0 g, 87.0 mmol) was added at 0 °C and stirred at room temperature for 1.0 h. Then, propargyl bromide (8.9 mL, 110.0 mmol) was added dropwise at 0 °C in 45 min. After the system was stirred at room temperature for another 24.0 h, the reaction mixture was poured into ice water (500 mL) and extracted with ethyl acetate (4 × 250 mL). The combined organics were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by recrystallization from cyclohexane to give the orange powder of compound Alkyne-TEMPO. Yield = 16.4 g (89.3%). ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 2.37 (s, $-C\equiv CH$), 4.02 (s, $-OCH_2-C\equiv C-$) (not all signals were observable due to paramagnetic broadening by the nitroxide radicals). GC-MS (EI): m/z = 210, and the calculated purity was 99.9%.

Then, monomer **2** was obtained by Glaser coupling reaction between Alkyne-TEMPO. Into a 250 mL round-bottom flask, Alkyne-TEMPO (6.00 g, 29 mmol), Cu(I)Br (0.41 g, 2.9 mmol), and pyridine (150 mL) were added. After the system was stirred at room temperature for 24.0 h, the pyridine was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and extracted with aqueous solution by three times; the organics were dried with $MgSO_4$ and concentrated. After the crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, v/v = 10/1), the orange powder of compound monomer **2** was obtained. ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 4.12 (s, $-OCH_2-C\equiv C-$) (not all signals were observable due to paramagnetic broadening by the nitroxide radicals). MALDI-TOF MS: m/z = 441.2 ($M + Na^+$), 457.2 ($M + K^+$). HPLC: the calculated purity was 99.9%.

General Process of Nitroxide Radical Coupling Step Growth Polymerization (NRC-SGP) (Scheme 3). Typically, monomer **1** (0.4880 g, 1.20 mmol), monomer **2** (0.5000 g, 1.20 mmol), Cu(I)Br (0.1716 g, 1.20 mmol), Cu(0) (0.0760 g, 1.20 mmol), Me_6TREN (0.2756 g, 1.20 mmol), toluene (4.0 mL), and DMSO (4.0 mL) were sequentially added into a 100 mL ampule. After the reaction mixture was operated by three freeze−pump−thaw cycles and purged with N_2, the system was immersed into an oil bath at 25 °C for 48.0 h. The system was terminated by dipping into liquid nitrogen to stop the reactions. The crude product was extracted with CH_2Cl_2/water to remove the copper complex. The organic layer was dried with $MgSO_4$,

Scheme 3. Synthetic Procedure of Poly(alkoxyamine) by the NRC-SGP Mechanism



concentrated under reduced pressure, and precipitated into petroleum ether three times to give poly(alkoxyamine). ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 0.80−2.10 (m, $-C(CH_3)_2O-$, $-C(CH_3)_2-$ and $-CH_2-$ on TEMPO residue), 3.80 (m, $-OCH-$ on TEMPO residue), 4.25 (m, $-OCH_2C\equiv C-$), 5.78 and 6.35 (s, $-C=CH_2$ at chain end of polymer), 7.10 (m, $-CH-$ on phenyl group). ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 21.57 ($-C(CH_3)_2-$ on TEMPO residue), 24.75 ($-C(CH_3)_2O-$), 45.33 ($-CH_2-$, and $-C(CH_3)_2-$ on TEMPO residue), 55.76 ($-OCH_2C\equiv C-$), 60.36 ($-OCH-$ on TEMPO residue), 69.85 ($-C\equiv C-$), 81.28 ($-C(CH_3)_2O-$), 122.08 ($-CH-$ on phenyl group), 148.13 ($-CO-$ on phenyl group), 173.72 ($-C(=O)O-$). $M_{w,SEC}$ = 10 060 g/mol, PDI = 2.56.

In order to investigate the factors on NRC-SGP mechanism, the polymerization temperature (25, 50, 70, and 90 °C), time (12, 24, 48, 96, and 144 h), solvents ($v_{DMSO}/v_{toluene}$ = 0/8, 4/4, 2/6, and 8/0, THF, DMF), concentration of monomers (0.075, 0.15, and 0.30 M), catalyst ([Cu(I)Br]/[Cu(0)] = 2/0, 1/1, and 0/2), ligand (PMEDETA, Me_6TREN, and Bpy), and structures connected to bromide groups (monomers **1** and **1′**) were all modulated according to the above procedure.

Homocoupling Reaction of Monomer 1 in the Presence or Absence of HO-TEMPO (Scheme 4). In order to verify the mechanism of NRC-SGP, the homocoupling reaction of monomer **1** was operated in the presence or absence of HO-TEMPO, respectively. In the case without HO-TEMPO, the monomer **1** (0.4880 g, 1.20 mmol), Cu(I)Br (0.1716 g, 1.20 mmol), Cu(0) (0.0760 g, 1.20 mmol), Me_6TREN (0.2756 g, 1.20 mmol), toluene (4.0 mL), and DMSO (4.0 mL) were sequentially added into a 100 mL ampule. After the reaction mixture was operated by three freeze−pump−thaw cycles and purged with N_2, the system was immersed into an oil bath at 25 °C for 48.0 h. The system was terminated by dipping into liquid nitrogen to stop the reactions. The crude product was extracted with CH_2Cl_2/water to remove the copper complex. The organic layer was dried with $MgSO_4$, concentrated under reduced pressure, and precipitated into petroleum ether three times to give the final products **4**. $M_{w,SEC}$ = 6400 g/mol, PDI = 2.40.

Similarly, in another case, additional HO-TEMPO (0.4115 g, 1.20 mmol) was added, and the product **5** was obtained according to the above procedure. ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 0.80−2.10 (m, $-C(CH_3)_2O-$, $-C(CH_3)_2-$ and $-CH_2-$ on TEMPO residue), 3.80 (m, $-OCH-$ on TEMPO residue), 7.10 (m, $-CH-$ on phenyl group). ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 21.57 ($-CH_3-$ on TEMPO residue), 24.75 ($-C(CH_3)_2O-$), 45.33 ($-CH_2-$, and $-C(CH_3)_2-$ on TEMPO residue), 60.36 ($-OCH-$ on TEMPO group), 81.28 ($-C(CH_3)_2O-$), 122.08 ($-CH-$ on phenyl group), 148.13 ($-CO-$ on phenyl group), 173.72 ($-C(=O)O-$).

RESULTS AND DISCUSSION

Synthesis and Characterization of Functional Monomers. The monomers **1** and **1′**, 1,4-phenylene bis(2-bromo-2-methylpropanoate) and 1,4-phenylene bis(2-bromopropanoate) with two bromide groups, were synthesized by classical

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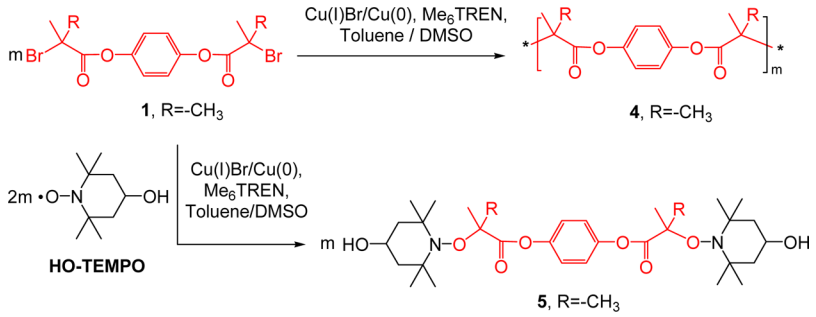
Scheme 4. Homocoupling Reaction of Monomer 1 in the Presence or Absence of HO-TEMPO



esterification reaction between hydroquinone and 2-bromoisobutyryl bromide or 2-bromopropiomyl bromide, respectively (Scheme 2). From the ^{1}H NMR spectrum of monomer **1** (Figure 1A), the characteristic resonance signals of methine

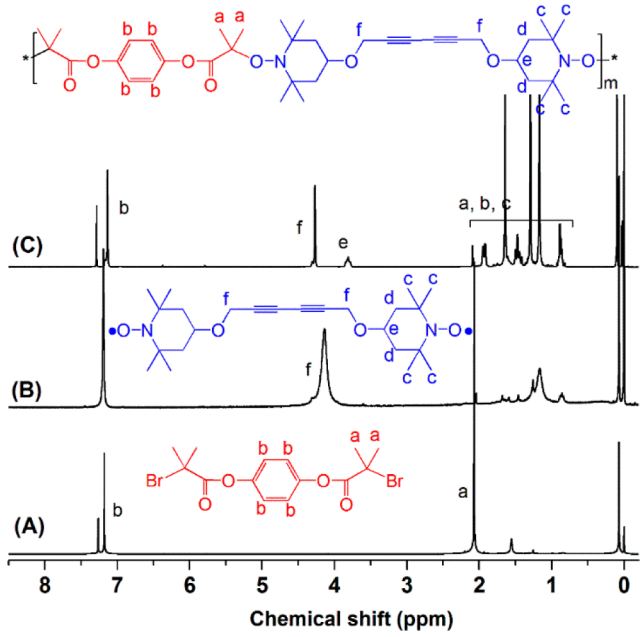


Figure 1. ^{1}H NMR spectra of monomer **1**, monomer **2**, and the target poly(alkoxyamine) (in $CDCl_3$).

protons (−C*H*−) ascribed at 7.18 ppm and methyl protons (−C(CH_3)$_2$) ascribed at 2.07 ppm were all well discriminated. Different from the spectrum of monomer **1**, the occurrence of resonance signal of methine proton (−C*H*(CH_3)) at 4.58 ppm (Figure S4, see Supporting Information) also effectively confirmed the successful synthesis of monomers **1**′. From the ^{13}C NMR spectrum of monomer **1** (Figure S2), the resonance signals of carbon atoms (−C(CH_3)$_2$Br), (−*C*(CH_3)$_2$Br), (−*C*(═O)O−), (−CH− on phenyl group), and (−*C*O− on phenyl group) were well ascribed at 30.21, 54.89, 169.90, 122.31, and 148.34 ppm, respectively. However, from the ^{13}C NMR spectrum of monomer **1**′ (Figure S5), a different signal at 54.89 ppm was attributed to (−*C*(CH_3)$_2$Br). In order to further give the information on synthesized monomers, the GC-MS measurement was also adopted, the obtained m/z = 408 of monomer **1** was rather close to the theoretical value of 408, and the purity of 99.2% was provided (Figure S3). Similarly, the GC-MS measurement of monomer **1**′ gave the m/z value of 380 and the purity of 98.8% (Figure S6).

For monomer **2**, 1,6-di(4-(2,2,6,6-tetramethylpiperidine-1-oxyl))hexa-2,4-diyne with two nitroxide radical groups, the Glaser coupling reaction between Alkyne-TEMPO was carried out using the pyridine/Cu(I)Br catalyst system (Scheme 2), and the precursor Alkyne-TEMPO was first prepared from HO-TEMPO and propargyl bromide in the presence of NaH. However, due to the paramagnetic nature of nitroxide radical groups,[24] the ^{1}H NMR spectrum (Figure S10) of Alkyne-TEMPO was significantly interrupted, and the resonance signals could not be well discriminated, except that the resonance signals of methylene protons (−CH_2C≡CH) and methine proton (−C≡C*H*) connected to alkyne group were ascribed at 4.02 and 2.37 ppm, respectively. From ^{1}H NMR spectrum of monomer **2** (Figure 1B), the complete disappearance of resonance signal at 2.37 ppm might be a strong evidence of the successful Glaser coupling between Alkyne-TEMPO. Alternatively, the detailed information on monomer **2** was further verified by MALDI-TOF MS (Figure S8), and the main peak of m/z was observed at 457.2 (monomer **2** + K^+). By HPLC measurement (Figure S9), the purity was obtained as 99.9%. Thus, all the above results confirmed that the monomers **1**, **1**′, and **2** with high purity were actually synthesized.

Investigation of Factors on the NRC-SGP Mechanism. Using the above designed monomers with two bromide groups and two nitroxide radical groups, the NRC-SGP mechanism was systematically investigated. From Figure 2, the SEC curves of two synthesized polymers of poly(alkoxyamine) were

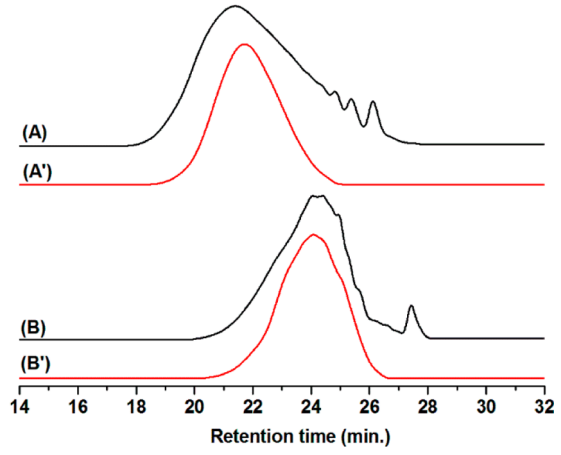


Figure 2. SEC curves of poly(alkoxyamine): (A) before (M_w = 35 520 g/mol, PDI = 3.69) and (A′) after purification purification by fractional precipitation; (B) before (M_w = 10 060 g/mol, PDI = 2.56) and (B′) after purification by fractional precipitation.

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exemplified. Before purification, curves A and B gave the curves with multipeak at longer elution time, which might be ascribed to the formed oligomers with lower degree of polymerization. This phenomenon was rather accordant to the mechanism of a typical step growth polymerization. After the careful fractional precipitation of poly(alkoxyamine) in cosolvents of THF/petroleum ether (60−90 °C), the smooth curves (A′ and B′) with Gaussian distribution were obtained. The formed poly(alkoxyamine) was further characterized and verified by ^{1}H NMR spectrum (Figure 1C). The characteristic resonance signal of methine proton (−C*H*) derived from monomer **1** was observed at 7.10 ppm, and the signals of methylene protons (−OCH_2C≡C−) and methine proton (−OC*H*−) derived from monomer **2** were observed at 4.25 and 3.80 ppm, respectively. Unlike the spectrum in Figure 1B, the signals were all clearly ascribed without any interruption, which further confirmed that the alkoxylamine linkages were actually formed and the nitroxide radical groups were almost consumed. The integration area ratio of methylene protons (−OCH_2C≡C−) to methine proton (−C*H*−) was 1.00:1.08, which was rather close to the theoretical value 1:1 of the polymer obtained by consecutive NRC reactions. Thus, it can be concluded that the monomers **1** and **2** are simultaneously consumed, and the polymers formed in an alternative manner buy our NRC-SGP mechanism. Alternatively, in the ^{13}C NMR spectrum (Figure 3), all the signals of carbon atoms were clearly ascribed and used to verify the formation of poly(alkoxyamine).

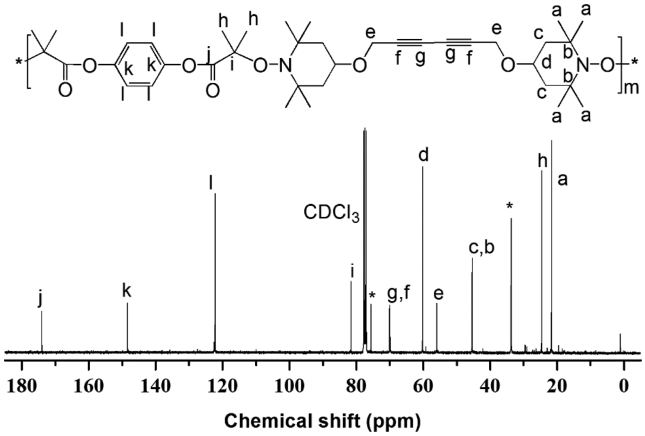

Figure 3. ^{13}C NMR spectrum of poly(alkoxyamine) synthesized from polymerization system of monomer **1**/monomer **2** (in $CDCl_3$).

As reported in previous works,[17−20] the NRC reaction was seriously affected by several factors, such as the polymerization time, temperature, solvents, ligand, catalyst, monomer concentration, and structures connected to halogen groups. Thus, the detailed investigation of NRC-SGP was further carried out and discussed in the following sections.

A. Effect of Time on the NRC-SGP Mechanism. Because of the rapid procedure, the NRC reaction was endowed with the "click" character. For example, Monteiro et al. had reported that the NRC reaction could be finished with almost 100% efficiency in 10 min.[18,25] However, this result was concluded from the one-time coupling reaction. In this contribution, when the NRC reaction was introduced into step growth polymerization, the NRC reaction would be repeated for quite a number of times to reach a high extent of reaction. Thus, the polymerization time would be an important factor to be investigated. From Figure 4A, for the polymerization system of monomer **1**/monomer **2**, when polymerization time was prolonged from 12 to 96 h, the peak molecular weights (M_p) of formed poly(alkoxyamine) were regularly shifted to the higher region, and the content of oligomers with lower molecular weight shown at longer elution time was obviously decreased. For polymerization system of monomer **1**′/monomer **2**, a similar tendency was given (Figure 4B). Differently, by comparing the data in Table 1, one could observe that the M_p of poly(alkoxyamine) from the monomer **1**′/monomer **2** system was somewhat higher than that from the monomer **1**/monomer **2** system. For example, at the polymerization time of 48 h, the former system could give the polymer with M_p of 19 150 g/mol; however, the latter only formed the polymer with M_p of 10 060 g/mol. This phenomenon could be explained that, compared with the isopropyl radical formed from monomer **1**′, the isobutyl radical formed from monomer **1** tended to give a larger hindrance and lower activity[26] and finally led to the slower speed of NRC coupling reaction or NRC-SGP polymerization procedure.

B. Effect of Temperature on the NRC-SGP Mechanism. Because of the variable activity of carbon radical under different temperature,[21,24,22,27] the polymerization temperature was another important factor in the NRC-SGP mechanism. On the one hand, the elevated temperature would contribute to the rapid speed of coupling reaction; on the other hand, the unwanted side reactions on carbon radicals (such as disproportionation termination, bimolecular combination termination, chain transfer reaction, and so on) were always simultaneously induced by the elevated temperature.[28] Thus, the effect of temperature on NRC-SGP mechanism should be well optimized to realize an appropriate polymerization speed and minimize the possible side reactions. In our polymerization system, the concerned isobutyl radicals and isopropyl radicals derived from monomer **1** or monomer **1**′ tended to terminate as an alkyl group and double bond by disproportionation or to terminate as a double bond and piperidinol by hydrogen atom transfer with nitroxide radicals (Scheme 5), which would largely interrupt the NRC-SGP procedure. As shown in Figure 5, for both polymerization system of monomer **1**/monomer **2** and monomer **1**′/monomer **2**, the SEC curves of formed poly(alkoxyamine) shifted to the low molecular weight region of oligomers with the increase of polymerization temperature. Under 90 °C, there was almost no any polymers formed. Alternatively, the side reactions could be largely suppressed at low temperature (such as 25 °C), and poly(alkoxyamine) with high molecular weight was produced. Under elevated temperature, not only the formation rate of isobutyl radical and isopropyl radical from monomer **1** and monomer **1**′ was accelerated, but also that the dissociation of formed alkoxyamine bond was speeded up. Correspondingly, the rapidly increased concentration of carbon radicals would lead to a substantial termination (Scheme 5). From Figure 6 for the polymerization system of monomer **1**/monomer **2**, one could observe that the gradually increased intensity of resonance signals at 5.00−6.00 ppm ascribed to double bond was enriched with the increase of polymerization temperature. Similarly, with the increase of polymerization temperature, the relative contents of double bond were also discriminated and increased from the polymerization system of monomer **1**′/monomer **2** (Figure 7). These results further supported the above conclusion from their SEC measurement. Under the same temperature, one could also observe that the M_p obtained from

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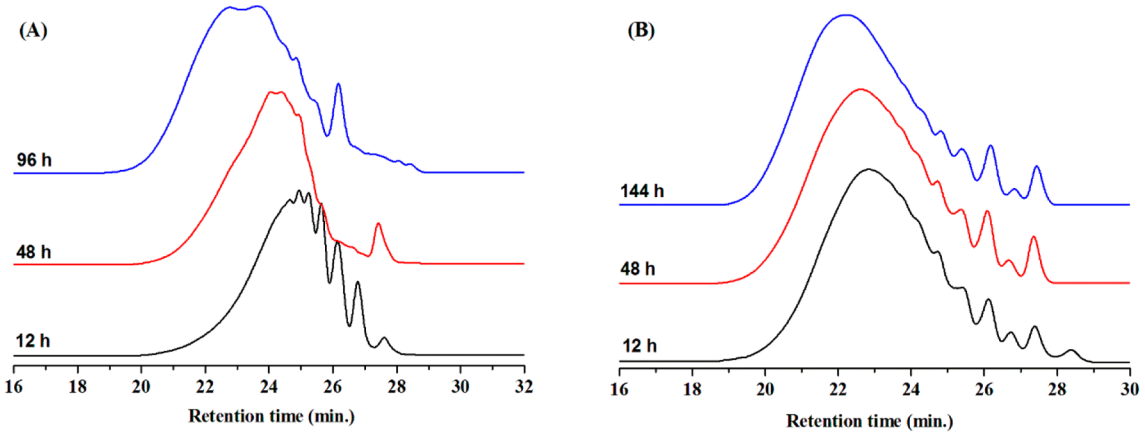


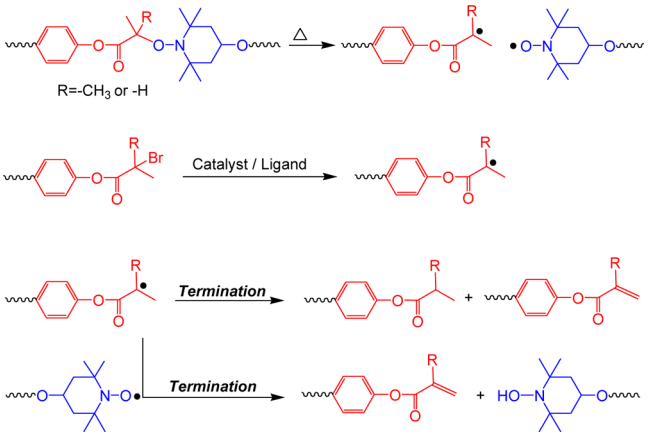
Figure 4. SEC traces of poly(alkoxyamine) synthesized from polymerization system of (A) monomer **1**/monomer **2** and (B) monomer **1**′/monomer **2** with different polymerization time controlled in Table 1.

Table 1. Effect of Polymerization Temperature and Time on NRC-SGP Mechanism[a]

entry	monomer **1** (mol)	monomer **1**′ (mol)	monomer **2** (mol)	time (h)	temp (°C)	M_p[b] (g/mol)	M_w[b] (g/mol)	PDI[b]
1	0.15		0.15	12	25	4420	7030	2.17
2	0.15		0.15	24	25	6260	8330	2.17
3	0.15		0.15	48	25	6010	10060	2.56
4	0.15		0.15	96	25	9330	15390	3.01
5	0.15		0.15	48	50	15150	13490	4.26
6	0.15		0.15	48	70	7330	9890	4.18
7	0.15		0.15	48	90	330	940	2.04
8		0.15	0.15	12	25	14920	17080	3.00
9		0.15	0.15	48	25	16970	19150	2.97
10		0.15	0.15	144	25	21790	21970	3.53
11		0.15	0.15	48	50	10580	13390	2.90
12		0.15	0.15	48	70	8510	9860	2.18
13		0.15	0.15	48	90	270	1550	2.27

[a]The polymerization was carried out in mixed solvent of 4.0 mL of DMSO and 4.0 mL of toluene, and the molar ratio of fed reagents was [monomer **2**]$_0$:[monomer **1** (or **1**′)]$_0$:[Me_6TREN]$_0$:[Cu]$_0$:[Cu(I)Br]$_0$ = 1:1:1:1:1. [b]The M_p, M_w, and PDI of polymers were estimated by SEC measurement in THF elution and PS was used as calibration.

Scheme 5. Termination of in Situ Generated Carbon Radicals and Dissociation of Formed Alkoxyamine Bond



polymerization system of monomer **1**/monomer **2** was somewhat lower than that from system of monomer **1**′/monomer **2** (Table 1). This result could be attribute to the easier disproportionation of the isobutyl radical than that of isopropyl radical, which was again originated from the larger hindrance and lower activity of isobutyl radicals.

C. Effect of Solvent on the NRC-SGP Mechanism. According to the ATRP or SETLRP mechanisms, the used solvent could largely affect the kinetics of polymerization system.[15,16] Accordingly, the kinds of used solvent would also modulate the NRC reaction and the related NRC-SGP procedure. Usually, the used solvent not only played the role to dissolve the monomers and formed polymers but also suppress or accelerate the reaction speed by modulating the polar of solvents. As shown in Table 2, different solvents were adopted in our NRC-SGP mechanism. When only toluene or DMSO solvent was used as solvent, the polymer with lower M_p was obtained (Figure 8). However, when the cosolvent of toluene/DMSO was used and the polarity of solvents was modulated, the polymer with higher M_p could be formed. The solvent of DMSO could disproportionate Cu(I)Br into Cu(II)Br_2 and nascent Cu(0), which again speed up the production of carbon radicals by single-electron-transfer (SET) mechanism;[16] however, the toluene could not realize this function. On the other hand, the DMSO was not a good solvent to the formed poly(alkoxyamine), while the toluene was a good solvent. Thus, in order to realize the synthesis of polymers with higher molecular weight, the ratio of toluene to DMSO must be modulated and optimized. Under such conditions, the appropriate disproportionation of Cu(I)Br and good solubility of the formed polymers should be

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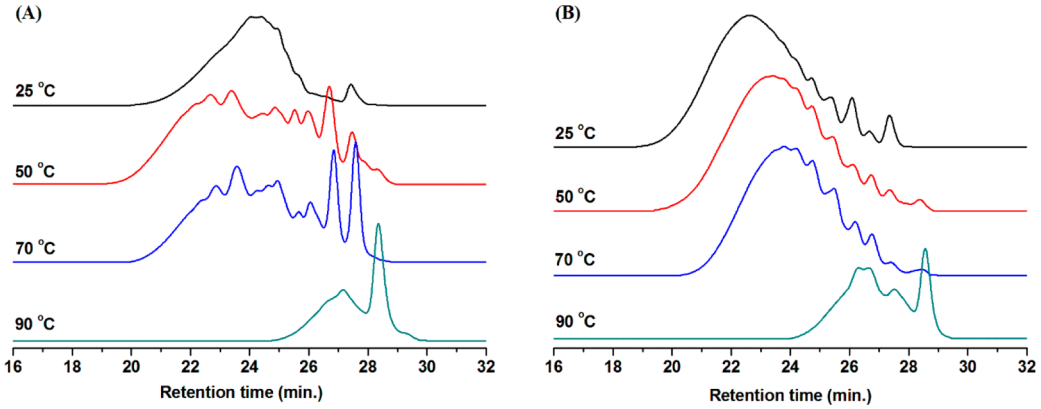

Figure 5. SEC traces of poly(alkoxyamine) synthesized from polymerization system of (A) monomer **1**/monomer **2** and (B) monomer **1**′/monomer **2** with different polymerization temperature controlled in Table 1.

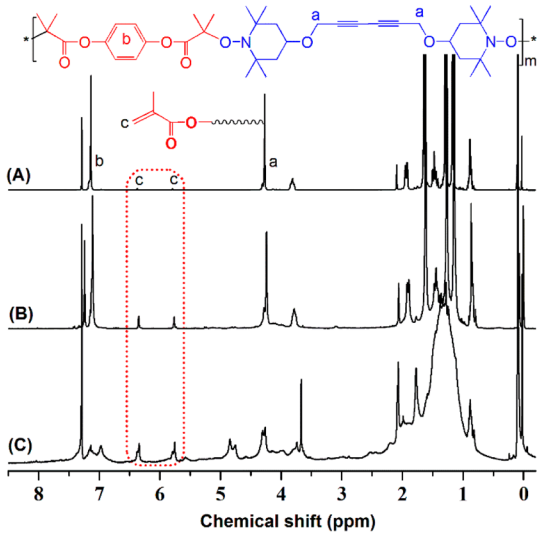

Figure 6. ^{1}H NMR spectra of poly(alkoxyamine) formed at different polymerization temperatures: (A) 25, (B) 70, and (C) 90 °C from polymerization system of the monomer **1**/monomer **2** system (in $CDCl_3$).

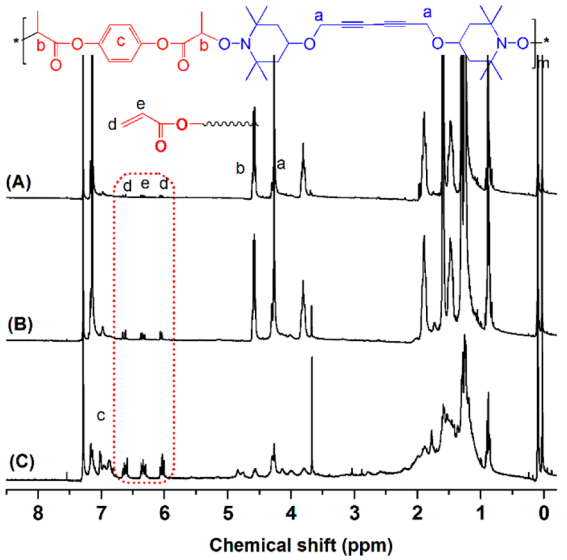

Figure 7. ^{1}H NMR spectra of poly(alkoxyamine) formed at different polymerization temperatures: (A) 25, (B) 70, and (C) 90 °C from polymerization system of the monomer **1**′/monomer **2** system (in $CDCl_3$).

simultaneously balanced. By changing the amounts of used cosolvent (also as monomer concentration), no obvious differences were observed from Figure S11 and Table 2. Alternatively, the other solvents such as DMF and THF were also introduced into our NRC-SGP mechanism. As shown in Figure 8, the successful polymerization could also be realized in these two solvents. These exciting results might help to further explore the application of NRC-SGP mechanism in a wide range.

D. Effect of Catalyst on the NRC-SGP Mechanism. In a typical NRC reaction, some nanosize Cu(0) was usually additionally added to accelerate the NRC procedure.[17] The first function of nanosize Cu(0) was to coordinate the halogen and generate the carbon radicals, and the second function was to react with Cu(II)Br_2 to regenerate Cu(I)Br and further speed up the cyclization.[16] Similarly, in order to accelerate the NRC-SGP mechanism, the nanosize Cu(0) was also supplied in our catalyst system. As shown in Figure 9, under the same conditions, with the increase of Cu(0) content, the M_p of formed polymers shift to the high molecular weight region. Obviously, the only Cu(I)Br gave the slowest polymerization speed and the only Cu(0) gave the highest one. Thus, the proper combination of Cu(I)Br and Cu(0) could be used to realize the NRC-SGP in a controlled style. Furthermore, different ligands of PMDETA, Me_6TREN, and Bpy were concerned in our NRC-SGP system, and the results gave the promising information that all ligands could help to realize the successful polymerization (Figure S12 and Table S1).

Finally, in order to further verify the mechanism of NRC-SGP, the homocoupling reaction of monomer **1** was proceeded in the presence or absence of HO-TEMPO (Scheme 4). In the case without HO-TEMPO, the homocoupling of monomers **1** happened, and the polymer **4** with molecular weight of 6400 g/mol was obtained (Figure S13). According to previous work,[23] the homocoupling reaction was proceeded in an ATRC style. However, when HO-TEMPO was added, the formed carbon radical would be captured by TEMPO group immediately, and no any polymers could be found. The formed compound **5** was collected and analyzed by SEC and NMR measurements in detail. As shown in Figure S13, a single peak with rather low PDI was attributed to compound **5**. Compared with its precursor of monomer **1**, the elution time of compound **5** shifts to the shorter region. From Figure S14, the characteristic

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Table 2. Effect of Solvent, Catalyst, and Monomer Concentration on the NRC-SGP Mechanism[a]

entry	[Cu(0)] (mol/L)	[Cu(I)Br] (mol/L)	DMSO (mL)	toluene (mL)	M_p[b] (g/mol)	M_w[b] (g/mol)	PDI[b]
1	0.15	0.15	8.0		4200	6320	2.50
2	0.15	0.15	4.0	4.0	6010	10060	2.56
3	0.15	0.15	2.0	6.0	23050	24970	2.34
4	0.15	0.15		8.0	4900	11000	2.76
5	0.15	0.15	2.0	2.0	5000	11570	2.23
6	0.15	0.15	8.0	8.0	6040	10800	2.36
7		0.30	4.0	4.0	2810	5340	2.40
8	0.30		4.0	4.0	35730	35520	3.69
9	0.15	0.15	8.0[c]		3990	5490	2.00
10	0.15	0.15	8.0[d]		6630	10570	2.15

[a]The fed [monomer **2**] was 0.15 mol/L, and the molar ratio of fed reagents was [monomer **2**]$_0$:[monomer **1**]$_0$:[Me_6TREN]$_0$ = 1:1:1. [b]The M_p, M_w, and PDI of polymers were estimated by SEC measurement in THF elution and PS was used as calibration. [c]The used solvent was THF. [d]The used solvent was DMF.

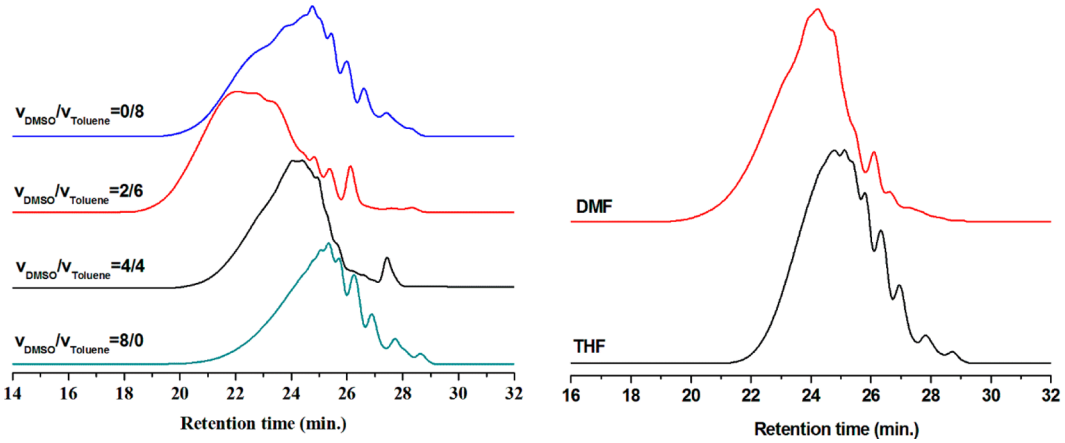

Figure 8. SEC traces of poly(alkoxyamine) synthesized from polymerization system of monomer **1**/monomer **2** in different solvents controlled in Table 2.

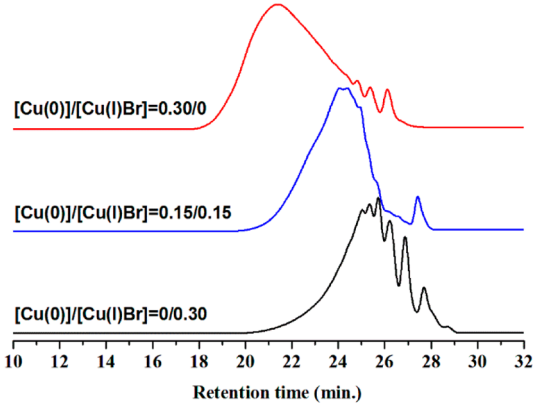

Figure 9. SEC traces of poly(alkoxyamine) synthesized from monomer **1** with different catalyst composition controlled in Table 2.

resonance signal of methine proton (−C_6H_4) derived from monomer **1** and that of methine proton (−OC*H*−) derived from monomer **2** were observed at 7.10 and 3.80 ppm, respectively. By comparing the integration area ratio at 7.10 ppm to that at 3.80 ppm, the obtained value of 4.02:1.00 confirmed that two HO-TEMPO were quantitatively attached onto monomer **1**, and almost no any homocoupling product of monomer **1** could be detected. From ^{13}C NMR (Figure S15), all the resonance signals of compound **5** were also well ascribed. Thus, from the above results, we can again conclude that the monomers **1** and **2** were actually combined into the polymer chain in an alternative style. This result was rather consistent with that reported in the literature and our previous works.[17,23]

Thus, the above results showed that this versatile NRC-SGP mechanism could be realized with extensively selected factors of temperature, structure of monomers, solvents, catalyst system, and so on. Among all factors, the temperature should be placed on the first position to be balanced to suppress the disproportionation termination. By combining all the factors on NRC-SGP mechanism into an optimized system, an ideal polymerization procedure could be realized. Especially, based on the step growth characteristic of this mechanism and the serious cross-coupling reaction between carbon radical and TEMPO groups, plenty of polymers with defined compositions and architectures are hoped to be synthesized.

Thermal Degradation of Poly(alkoxyamine). Using the thermal reversible character of alkoxyamine bond, Takahara et al. developed some "dynamic covalent polymers", whose structures and properties were changeable and tunable after polymerization.[21,29] Herein, the thermal degradation of target poly(alkoxyamine) was investigated and aimed to explore some thermal degradable materials. First, the samples was monitored by TG instrument (Figure 10). Typically, the weight loss of poly(alkoxyamine) was started at 140 °C and completely finished at 550 °C, which was less affected by the molecular weight of poly(alkoxyamine) and the adopted atmosphere (nitrogen or air conditions). Additionally, the weight loss of

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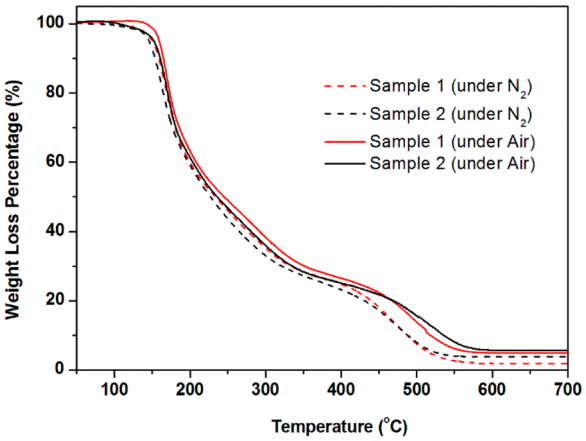

Figure 10. TGA curves (10 °C/min) of sample 1 (entry 8 in Table 2) and sample 2 (entry 2 in Table 2).

monomers **1** and **2** was also monitored. From Figure S16, one can observed that the monomer **1** decomposed completely between 140 and at 220 °C, and monomer **2** decomposed between 180 and 600 °C. By combining these results, we can inferred that the above poly(alkoxyamine) was first degraded into the two kinds of monomer units corresponding to monomers **1** and **2** by thermal degradation (at the temperature above 140 °C), and the decomposition of monomer units was subsequently followed. Also, these data further confirmed that the monomer units derived from monomers **1** and **2** were rather stable under the polymerization conditions (below 90 °C).

Also, the samples were traced with DSC instrument, and the samples after DSC were further characterized by SEC measurement. As shown in Figure 11, in the first cycle to the highest temperature of 80 °C and the second cycle to the highest temperature of 100 °C, the heating and cooling curves were given without any abrupt changes. In the third cycle to the highest temperature of 120 °C, the slightly ascending or descending of curves was discriminated. In the fourth cycle to the highest temperature of 140 °C, the obvious changing of signals of heat flow were detected. Correspondingly, compared to the SEC curves of polymers with that before the DSC measurement, the product from the first cycle seemed to have no any change (Figure 12). In the second cycle, the obviously lowered M_w of product from SEC measurement confirmed that the polymer had begun to degrade. In the third cycle, some oligomers were formed, and the poly(alkoxyamine) was almost degraded into small compounds in the fourth cycle. Thus, we concluded that the poly(alkoxyamine) might suffer a balance of dissociation and recombination procedure at 80 °C. When the temperature was increased to 100 °C, some dissociated alkoxyamine bond began to subject the termination (Scheme 5), and the M_w of polymers moved to the low molecular weight region. Continuously, when temperature was increased to 120 or 140 °C, the dissociation of alkoxyamine was accelerated and the system was mainly dominated by disproportionation termination on the formed carbon radicals, and polymers were degraded into small fragments and ultimately to small compounds. All the information obtained from TG, DSC, and SEC measurements reached a perfect accordance. Also, these results further led the synthesized poly(alkoxyamine) to be a novel thermal degradable material.

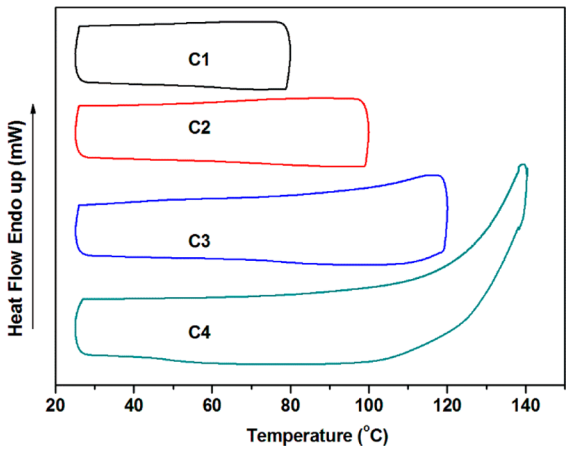

Figure 11. DSC curves (10 °C/min) of sample 1 (entry 8 in Table 2) under a nitrogen atomosphere: (C1) heated from 25 to 80 °C and then cooled to 25 °C; (C2) heated from 25 to 100 °C and then cooled to 25 °C; (C3) heated from 25 to 120 °C and then cooled to 25 °C; (C4) heated from 25 to 140 °C and then cooled to 25 °C.

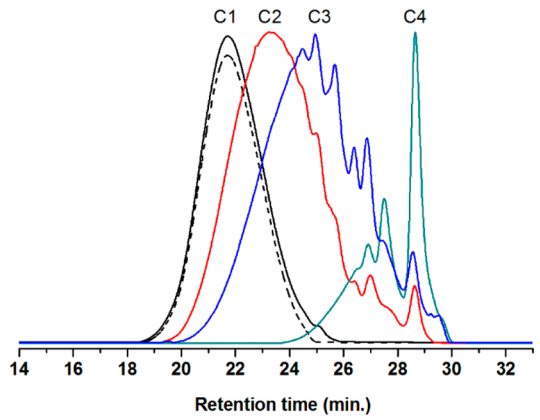

Figure 12. SEC curves of products after DSC measurement of sample 1 (entry 8 in Table 2) (dashed line, M_w = 35 520 g/mol) by different procedures as described in Figure 11: (C1) M_w = 32 000 g/mol, (C2) M_w = 13 700 g/mol, (C3) M_w = 980 g/mol, and (C4) M_w = 340 g/mol.

CONCLUSIONS

To sum up, the novel NRC-SGP mechanism was innovatively presented, optimized, and used to synthesize a series of poly(alkoxyamine)s. The termination by disproportionation was the major side reaction that exerts an important effect on the NRC-SGP mechanism, and the lower temperature (25 °C) would favor a better controlling of the polymerization. The proper combination of time, temperature, monomer concentration, structure of monomers, solvent, and catalyst system could lead to an ideal NRC-SGP procedure. Also, the obtained poly(alkoxyamine) might be used to construct dynamic covalent polymers by radical crossover reaction or to act as the initiator of NMRP mechanism or to design some degradable materials. The promising application of this NRC-SGP mechanism might be presented and confirmed by plenty of further works in the future.

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■ ASSOCIATED CONTENT

Supporting Information

Characterization of functional monomers and some additional information. 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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