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Synthesis of Thermally Cleavable Multisegmented Polystyrene by Atom Transfer Nitroxide Radical Polymerization (ATNRP) Mechanism

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Based on the common features of well-defined nitroxide radical coupling (NRC) reaction, atom transfer radical polymerization (ATRP) and nitroxide mediated radical polymerization (NMRP) mechanisms, an Atom Transfer Nitroxide Radical Polymerization (ATNRP) mechanism was presented by integrating these three mechanisms into one polymerization system simultaneously, and further used to construct the multisegmented polystyrene (PS_m) embedded with multiple alkoxyamine linkages. The initiator of 1-oxyl-2,2,6,6-teramethylpiperidinyl-4-yl 2-bromo-2-methylpropanoate (Br-TEMPO) contained one bromoisobutyryl group and one stable nitroxide radical was firstly designed and synthesized. Then, the ATNRP mechanism was systematically investigated by optimizing the factors such as polymerization temperature, solvent, catalyst, time and technology. The result showed that the NRC reaction, ATRP and NMRP mechanisms can be synergistically proceeded in ATNRP due to the thermally reversible dissociation-combination behavior of the formed alkoxyamine linkages, and the polymerization temperature and solvent were the key factors. Finally, the thermal behaviour of the formed PS_m was monitored by TGA and DSC analysis. The result showed that the alkoxyamine linkages can suffer a thermal cleavage at the elevated temperature of 110 ℃ and the PS_m can be cleaved in the presence of excess stable nitroxide radicals. The PS_m embedded with multiple alkoxyamine linkages and the cleaved PS possessed one nitroxide radical have the same thermal stability, however, the T_g of PS_m gradually approached to that of the cleaved PS when several heating-cooling (-40~150 ℃) cycles were performed. Due to the versatile functions of as-prepared PS_m and cleaved PS, this ATNRP mechanism is hoped to find more potential applications in polymer chemistry.

Introduction

Up to now, the polymer chemistry has been well developed due to the presentation of several "living" / controlled polymerization mechanisms and the development of plenty of efficient coupling reactions. The architectures and compositions of polymers can thus be conveniently constructed, and the functions of polymers can also be deliberately realized for unique physical properties and versatile applications. Especially, the coupling reactions are always playing some important roles, for example, in the construction or post-modification of polymers. The efficient coupling reactions can be exemplified as 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] *etc*, and the versatility of these reactions are always verified by introducing them into a step-growth polymerization by means of certain functional (macro)monomer.[8-] Interestingly, when a macromonomer is considered, the step-growth polymerization based on a certain coupling reaction would lead to some functional multisegmented polymers. For example, by ATRC reaction, the multisegmented [polystyrene(PS)-*b*-poly(isotactic polypropylene)(P*i*PP)]$_m$,[14] [PS-*b*-poly(propylene oxide)(PPO)]$_m$ and [PS-*b*-poly(bisphenol A carbonate)(PC)][15] had been realized. By CuAAC chemistry, the [PS-*b*-poly(isoprene)(PI)]$_m$,[16] [PS-*b*-poly(acrylic acid)(PAA)]$_m$,[17] [PS-*b*-poly(ethylene oxide)(PEO)]$_m$[18] and PS_m[9,19] had been achieved. By a continuous addition of different monomers or an iterative methodology in the anionic mechanism, the (PS-*b*-PI)$_m$,[20] [PS-*b*-poly(methyl methacrylate)(PMMA)]$_m$, [PS-*b*-poly(*tert*-butyl methacrylate)(P*t*BMA)]$_m$ and [PS-*b*-poly(2-Vinylpyridine)(P2VP)]$_m$[21] had been synthesized. Also, the [PS-*b*-poly(butadiene)(PB)]$_m$,[22] [PS-*b*-poly(tetrahydrofuran)(PTHF)]$_m$,[23] [PS-*b*-poly(tetramethylene oxide)(PTMO)]$_m$[24] and (PEO-*b*-PS)$_m$[25] were

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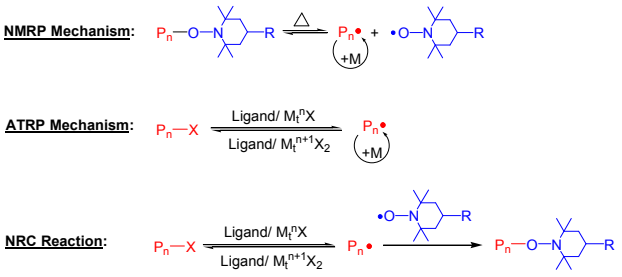
produced by the reaction between isocyanate and hydroxyl groups, and the (PI-*b*-PS)$_m$[26] and [PS-*b*-poly(arylate)(PAr)]$_m$[27] were formed by the reaction between acyl chloride and hydroxyl groups or amine groups. However, with the increasing requirements from various walks of life, the polymers with defined architectures, compositions and functions are endlessly needed, and the exploring of more versatile and efficient mechanisms or coupling reactions is still a significant and challenging work.

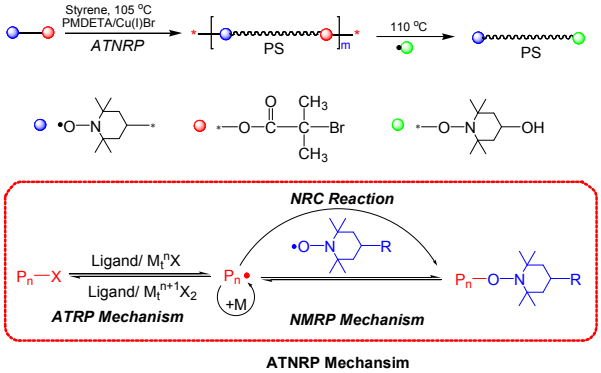


Scheme 1. The Illustration of NRC Reaction, ATRP and NMRP Mechanisms.

Previously, based on the atom transfer radical polymerization (ATRP)[28] and Single Electron Transfer Living Radical Polymerization (SET-LRP)[29] mechanisms, our group developed a novel coupling reaction termed as nitroxide radical coupling (NRC) reaction by the rapid capture reaction between the stable nitroxide radicals and the active carbon radicals *in situ* generated from halogenated precursors (**Scheme 1**).[30] Different from the other radical based coupling reactions, the carbon radicals can be instantly, selectively and efficiently captured by the stable nitroxide radicals in NRC system, and almost no any side reactions (such as bimolecular combination termination, disproportionation termination or chain transfer reactions on the active carbon radicals) can be discriminated.[31] The NRC reaction has been proved to be a rather robust and orthogonal technique with quantitative efficiency in wide temperature range of 25~90 ℃, and thus endowed with the "Click" character. Also, the concerned halogenated or stable nitroxide radical contained precursors can be easily obtained and stored under normal conditions with long-time stability. Until now, the NRC reaction has been widely used in post-modification of polymers,[32] construction of complicated architectures[31c,33] and preparation of organic-inorganic composites.[34] For example, Matyjaszewski *et al.*[35] and Monteiro *et al.*[36] had prepared some multisegmented PS$_m$ or P*t*BA$_m$ with cleavable units in the main chain by the NRC reaction between difunctional halogenated precursors and dinitroxides. Wang *et al*[37] synthesized the multisegmented PS$_m$ by an improved strategy using the compound of 2-methyl-2-nitrosopropane (MNP), which can *in situ* generate a stable radical by combination with a carbon radical and subsequently captured by another carbon radical. Recently, based on the versatility of NRC reaction, we further introduced the NRC reaction into the step-growth polymerization system and presented a novel mechanism termed as Nitroxide Radical Coupling Step Growth Polymerization (NRC-SGP), which had been used to synthesize series of poly(alkoxyamine) from the monomers contained two bromide groups or two stable nitroxide radical groups.[38] Actually, the above NRC reaction has shown some potential applications in polymer chemistry and material science fields, however, the NRC reaction is always separately operated (in the absence of any monomers) after the ATRP or SETLRP mechanism, and several tedious purification procedures are always accompanied.

Typically, in ATRP mechanism, the chain propagation was modulated by the dormant and active carbon radicals in the presence of certain ligand/metal salt system (**Scheme 1**).[28] Alternatively, in NMRP mechanism, the chain propagation was tuned by the thermally reversible dissociation-combination of alkoxyamine linkages formed from the active carbon radicals and stable nitroxide radicals (such as 2,2,6,6-teramethylpiperidinyl-1-oxyl TEMPO) (**Scheme 1**).[39] Both these two polymerization mechanisms were proceeded according to the principle of transforming the major "living" radicals into the dormant ones and decreased the concentration of active radicals for minimizing irreversible termination reactions. Coincidentally, the NRC reaction could bridge the ATRP and NMRP mechanism based some common features of these three mechanisms.[32-34]

Herein, considered the orthogonality of NRC reaction, ATRP and NMRP mechanisms, we attempted to present a Atom Transfer Nitroxide Radical Polymerization (ATNRP) mechanism, in which the NRC reaction, ATRP and NMRP mechanisms are simultaneously integrated into one polymerization system (**Scheme 2**). For this purpose, a special heterofunctional initiator of 1-oxyl-2,2,6,6-teramethylpiperidinyl-4-yl 2-bromo-2-methylpropanoate (Br-TEMPO) with one bromoisobutyryl group and one nitroxide radical was firstly designed and synthesized. Then the ATNRP of styrene monomer was systematically investigated by optimizing the factors such as polymerization temperature, solvent, catalyst, time and operation technology. Furthermore, considered the thermally reversible dissociation-recombination behavior and the potential application of the formed alkoxyamine linkages by NRC reaction,[40,41] the thermal behaviour of the formed PS$_m$ was further monitored and compared with the corresponding cleaved PS segment by TGA and DSC analysis.



ATNRP Mechansim

Scheme 2. The Illustration of ATNRP Mechanism and Its Application in the Synthesis of Multisegmented PS$_m$.

Experimental

Materials

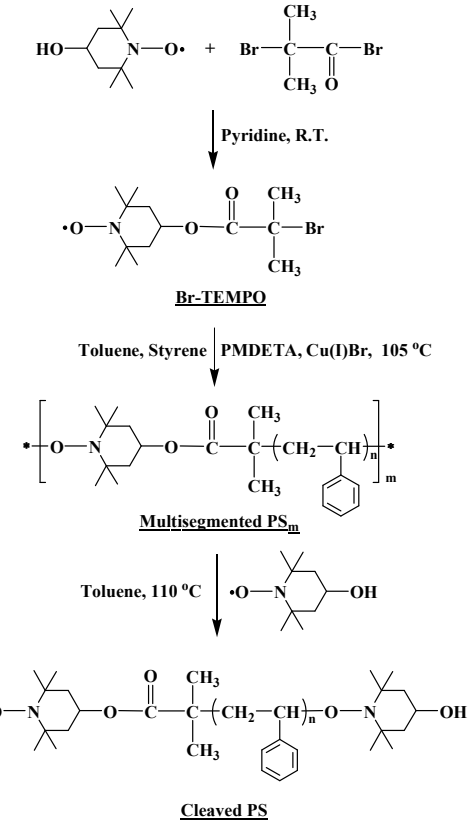
Styrene [St, 99 %, Sinopharm Chemical Reagent Co., Ltd. (SCRC)] was washed by 10 % NaOH aqueous solution and followed by water three times successively, dried over anhydrous $MgSO_4$ for 24 h and further dried over CaH_2 and distilled under reduced pressure before use. Pyridine (99 %, SCRC) was refluxed and distilled from potassium solution. Copper(I) bromide [Cu(I)Br, 95.0 %, SCRC] was stirred overnight in acetic acid, filtered, washed with ethanol and ethyl ether successively, and dried in vacuum. 4-Hydroxy-2,2,6,6-teramethylpiperidinyl-1-oxyl (HO-TEMPO, J&K, 98 %), 2-bromoisobutyryl bromide (Aldrich, 99 %), and N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99 %) were all used as received. All other reagents were purchased from SCRC and used as received except for additional declaration.

Measurements

Size exclusion chromatography (SEC) analysis of polymers was performed in tetrahydrofuran (THF) at 35 ℃ 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 (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 standards. The injection volume was 20 μL, and the concentration was 5~10 mg/mL. ^{1}H NMR spectra of polymers were recorded on a Bruker (400 MHz) spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference at 298 K. Elemental analysis (EA) was performed on a vario EL Ⅲequipment. 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 1.0 mL / min. The split rate was 100:1, and the inlet volume was 1.0 μL. The thermo gravimetric analysis (TGA) of polymers was operated using a Perkin Elmer Pyris 1 at a heating rate of 10 ℃/min. The differential scanning calorimetry (DSC) was carried out on a DSC Q2000 thermal analysis system (Shimadzu, Japan). The samples were first heated from 40 ℃ to 150 ℃ at a heating rate of 10 ℃/min under nitrogen atmosphere, followed by cooling to 40 ℃ at -10℃/min after stopping at 150 ℃ for 3 minutes. For the subsequent cycles, the same procedures were repeated.

Synthesis of the Heterofunctional Initiator of 1-Oxyl-2,2,6,6-teramethylpiperidinyl-4-yl 2-bromo-2-methylpropanoate (Br-TEMPO) (Scheme 3).

Typically, the starting agent of HO-TEMPO (35.0 g, 0.2035 mol) dried by an azeotropic distillation with toluene and dry pyridine (300 mL) were sequentially charged into a 500 mL round-bottomed flask. The flask was then placed into an ice bath and 2-bromoisobutyryl bromide (31.40 mL, 0.2540 mol) was dropwisely added within 30 minutes under stirring, and the reaction was continued for another 24 h under room temperature. The formed salt was removed by filtration, and the pyridine solvent in filtrate was evaporated under reduced pressure. Subsequently, the remained crude product was dissolved in dichloromethane (CH_2Cl_2) and washed by water three times. After the CH_2Cl_2 layer was concentrated, the product was recovered by recrystallization from petroleum ether (30~60 ℃) three times, and the obtained red powder of Br-TEMPO was further dried under vacuum at 45 ℃ till to a constant weight (Yield=54.5 g, 83.6 %). ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 1.08 (m, -C(C***H***$_3$)$_2$N-), 1.24-1.75 (m, -C***H***$_2$-), 1.77-2.18 (m, -C(=O)C(C***H***$_3$)$_2$Br), 3.59 (-C***H***(O-)-),. GC-MS (EI) gave *m/z*=321, and the calculated purity was 99.5 %. Elemental Analysis (%): C (exp. 48.29, theo. 48.67), H (exp. 7.26, theo. 7.22), N (exp. 4.13, theo. 4.36).



Scheme 3. The Synthetic Procedure for Multisegmented PS_m and Cleaved PS.

General Protocol for the ATNRP of Styrene Monomer (Scheme 3).

Typically, the monomer of styrene (12.0 mL, 105 mmol), initiator of Br-TEMPO (0.3211 g, 1.00 mmol), catalyst of Cu(I)Br (0.1436 g, 1.00 mmol), ligand of PMDETA (0.41 mL, 2.00 mmol), and solvent of toluene (3.0 mL) were sequentially added into a 100 mL ampule. After the reaction system was operated by three freeze–pump–thaw cycles and backfilled with N_2, the ampoule was immersed into an oil bath at 105 ℃ and maintained for 24 h. The reaction system was terminated by dipping into liquid nitrogen and diluted with CH_2Cl_2, which was then purified by passing through a neutral alumina column. After the CH_2Cl_2 solvent was evaporated under reduced pressure, the multisegmented PS_m was obtained by precipitation into methanol three times and dried under vacuum at 45 ℃ till to a constant weight. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 0.75-0.93 (m, -C(=O)C(C***H***$_3$)$_2$-), 0.95-2.22 (m, -C***H***$_2$- and -C***H***- on styrene unit, -C(C***H***$_3$)$_2$N- and -C***H***$_2$- on alkoxyamine linkage), 6.25-7.20 (m, C_6***H***$_5$- on styrene unit). $M_{n,SEC}$ = 11,300 g/mol, $M_{p,SEC}$ = 19,600 g/mol, PDI = 1.89.

Using the similar operation procedure, the factors of

polymerization temperature (90 ℃, 100 ℃, 105℃, 110 ℃, 120 ℃), volume ratio of toluene solvent to styrene monomer ($V_{Toluene}/V_{Styrene}$=0, 0.25, 1.0, 2.0), molar ratio of styrene monomer to initiator ($[Styrene]_0/[Br\text{-}TEMPO]_0$=105, 210, 315), molar ratio of Cu(I)Br catalyst to initiator ($[Cu(I)Br]_0/[Br\text{-}TEMPO]_0$=1/1, 2/1, 4/1), as well as polymerization time and the operation technology were all investigated and optimized.

Thermal Cleavage of the Multisegmented PS_m (Scheme 3).

In an example, the synthesized multisegmented PS_m (0.50 g, $M_{n,SEC}$ = 11,300 g/mol) was dissolved in toluene (20 mL) and mixed with excess HO-TEMPO (0.25 g) in a 100 mL ampoule. The mixture was operated by three freeze–pump–thaw cycles and backfilled with N_2, and then the ampoule was immersed into an oil bath at 110 ℃ and maintained for 24 h. The crude product was precipitated into methanol three times, and the cleaved PS was obtained and further dried under vaccum at 45 ℃ till to a constant weight. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 0.75-0.93 (m, -C(=O)C$(CH_3)_2$-), 0.95-2.22 (m, -CH_2- and -CH- on styrene unit, -C$(CH_3)_2$N- and -CH_2- on alkoxyamine linkage and TEMPO groups), 6.25-7.20 (m, C_6H_5- on styrene unit). $M_{n,SEC}$ = 4,600 g/mol, $M_{p,SEC}$ = 5,100 g/mol, PDI=1.17.

Results and discussion

Synthesis and Characterization of the Heterofunctional Initiator of Br-TEMPO.

The initiator of Br-TEMPO with one bromoisobutyryl group and one nitroxide radical was synthesized by the classical esterification reaction between HO-TEMPO and excess 2-bromoisobutyryl bromide (**Scheme 3**). The target Br-TEMPO was carefully purified by recrystallization from petroleum ether (30~60 ℃) and its structure was further confirmed. Using CH_2Cl_2 as developing agent, the crude Br-TEMPO and its starting agent of HO-TEMPO gave two different R_f values of 0.74 and 0.24 by thin-layer chromatography (TLC). Thus, the TLC result confirmed that the HO-TEMPO had been completely consumed and the Br-TEMPO was actually produced. From the ^{1}H NMR spectrum for Br-TEMPO (**Fig. 1(A)**), the characteristic resonance signal for methyl protons (-C(=O)C(C***H***$_3)_2$Br) was well ascribed at 1.77-2.18 ppm. The signals for methyl (-C(C***H***$_3)_2$N-) methylene (-C***H***$_2$-) and methine (-C***H***(O-)-) protons were ascribed at 1.08 ppm, 1.24-1.75 ppm and 3.59 ppm, respectively. However, due to the paramagnetic nature of nitroxide radicals,[42] their integrations could not be well discriminated to further confirm the structure of Br-TEMPO. In order to further give the accurate information of Br-TEMPO, the GC-MS measurement was also adopted. The obtained *m/z*=321 was rather close to the theoretical value, and the high purity of 99.5 % was achieved. Also, the elemental analysis provided the consistent contents of elements (C, H, N) in experiment and theory, which provided another solid evidence for the successful synthesis of the pure Br-TEMPO.

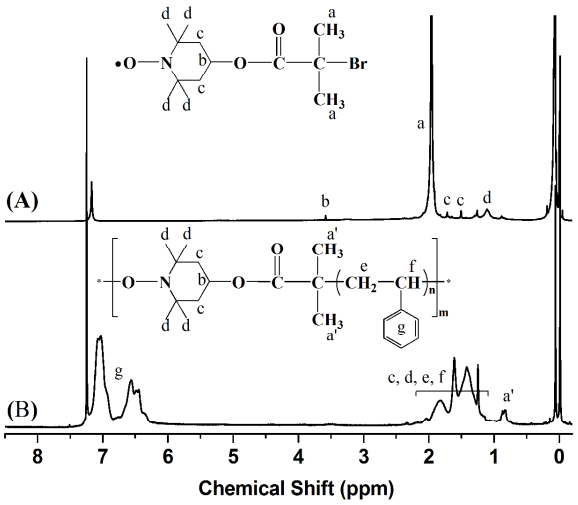


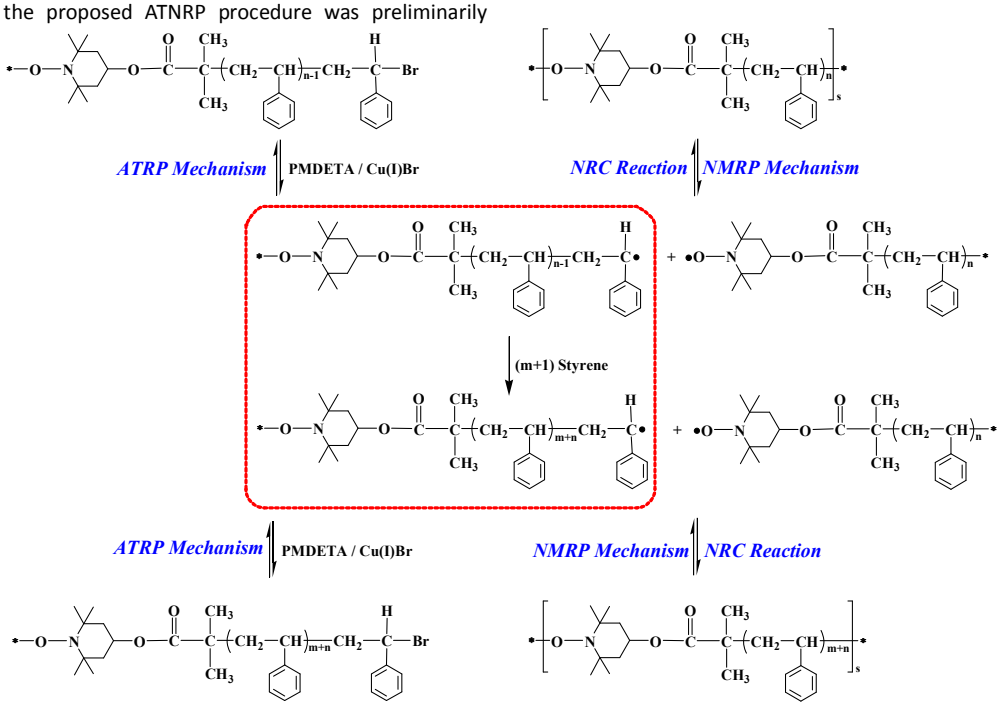
Fig. 1. ^{1}H NMR spectra of Br-TEMPO and multisegmented PS_m (in $CDCl_3$ solvent).

Investigation on the ATNRP Mechanism.

Using the above synthesized heterofunctional Br-TEMPO as initiator, PMDETA as ligand and Cu(I)Br as catalyst, the ATNRP of styrene was proceeded (**Scheme 2**). In the proposed ATNRP mechanism, the NRC reaction, ATRP and NMRP mechanisms should be synergistically happened and the multisegmented PS_m embedded with multiple alkoxyamine linkages can be realized (**Scheme 4)**. As described in the literatures,[40] the formed alkoxyamine linkages could subject to a thermally reversible dissociation at high temperature (above 60 ℃) to form a stable nitroxide radical and a highly active carbon radical, and the carbon radical could be reversibly and rapidly captured by another nitroxide radical to recombine as a new alkoxyamine linkage. Thus, in order to explore more information of the formed PS_m and the ATNRP mechanism, the PS_m was further cleaved at elevated temperature (110 ℃) in the presence of excess HO-TEMPO agent.

By SEC measurement, the broad peaks with high PDIs for PS_m were always provided (**Fig. 2**), which can be attributed to the step-growth manner of NRC reaction in ATNRP. However, the SEC curves of the cleaved PS were always endowed with controlled molecular weight and low PDIs, which were rather consistent with the "living" /controlled chain-growth manner of the ATRP and NMRP mechanism in ATNRP. Furthermore, according the obtained molecular weights of PS_m and cleaved PS, the degree of NRC reaction (D_{NRC}) can be derived (**Table 1** and **Table 2**). On the main chain of PS_m, only limited amount of nitroxide radicals might be remained at the polymer end because the stable nitroxide radical brought by initiator of Br-TEMPO had been dominantly captured by active carbon radicals during the ATNRP mechanism. Thus, the ^{1}H NMR spectrum for PS_m was less interrupted by the paramagnetic nitroxide radicals (**Fig. 1(B)**). The resonance signal for methyl protons (-C(=O)C$(CH_3)_2$-) was ascribed at 0.75-0.93 ppm, and the signals for methyl, methylene and methine (-CH_2- and -CH- on styrene unit, -C$(CH_3)_2$N- and -CH_2- on alkoxyamine linkage) protons were ascribed at 0.95-2.22. Also, the characteristic resonance signal for aromatic protons (C_6H_5-) was discriminated at 6.25-7.20 ppm.

Because of almost the same composition of the PS_m and cleaved PS, both polymers also gave the similar ^1H NMR spectra. Obviously, according to the SEC and ^1H NMR results, the PS_m had been actually prepared and the proposed ATNRP procedure was preliminarily dissected. In the following section, the mechanism of ATNRP was further investigated and the factors were comprehensively optimized.



Scheme 4. The Synergetic ATNRP Based on NRC Reaction, ATRP and NMRP Mechanisms.

Table 1. The polymerization data for PS_m and cleaved PS under different factors.

Entry	Temperature (℃)	Time (h)	Br-TEM PO(mmol)	PMDETA (mmol)	CuBr (mmol)	Styrene (mmol)	$V_{Toluene}$ /$V_{Styrene}$	PS_m [a]			PS [a]			D_{NRC} [b]
								M_p (g/mol)	M_n (g/mol)	PDI	M_p (g/mol)	M_n (g/mol)	PDI	
1	90	48	1	2	1	105	0	2,000	1,500	1.60				
2	100	24	1	2	1	105	0	8,900	6,600	1.68				
3	105	18	1	2	1	105	0	53,400	26,600	2.39	7,800	6,500	1.18	6.8
4	110	18	1	2	1	105	0	56,100	28,700	2.38	11,300	9,400	1.15	5.0
5	120	8	1	2	1	105	0	62,300	41,300	1.93	15,100	13,200	1.11	4.1
3	105	18	1	2	1	105	0	53,400	26,600	2.39	7,800	6,500	1.18	6.8
6	105	24	1	2	1	105	0.25	19,600	11,300	1.89	5,100	4,600	1.17	3.8
7	105	24	1	2	1	105	0.50	3,300	3,100	1.14				
8	105	24	1	2	1	105	1.0	3,800	3,400	1.38				
9	105	24	1	2	1	105	2.0	3,400	3,200	1.12				
3	105	18	1	2	1	105	0	53,400	26,600	2.39	7,800	6,500	1.18	6.8
10	105	18	1	2	1	210	0	125,100	55,500	2.21	17,900	14,900	1.18	7.0
11	105	18	1	2	1	315	0	140,800	72,700	2.07	26,600	21,300	1.24	5.3
6	105	24	1	2	1	105	0.25	19,600	11,300	1.89	5,100	4,600	1.17	3.8
12	105	24	1	4	2	105	0.25	113,400	41,100	2.51	10,800	9,100	1.18	10.5
13	105	18	1	8	4	105	0.25	105,800	52,000	2.15	9,700	7,600	1.26	10.9
14[c]	105/80	12/24	1	8	4	105	0.25	53,900	36,100	1.80	6,200	4,600	1.38	8.7

[a] The $M_{p,SEC}$, $M_{n,SEC}$ and PDI of polymers were estimated by SEC measurement in THF elution using PS as standards. [b] D_{NRC} was calculated according to the Formula: $D_{NRC}=M_{p,SEC,PSm}/M_{p,SEC,PS}$. [c] The polymerization was carry out firstly at 105 ℃ for 12 h, and then the system was maintained at 80 ℃ for another 24 h.

A. Effect of the Temperature on ATNRP Mechanism.

As was well known, the alkoxyamine linkages were rather sensitive to the temperature.[40] Thus, in this contribution, the factor of temperature on ATNRP was firstly considered. From **Table 1** and **Fig. 2**, we could observe that, with the increase of polymerization temperature and, however, the simultaneous shortening of polymerization time, the molecular weights of PS_m and the cleaved PS shift to the higher region. For example, even the polymerization time was prolonged to 48 h, only a $M_{p,SEC}$ of 2,000 g/mol can be obtained when the polymerization temperature of 90 ℃ was employed. However, at 105 ℃, the $M_{p,SEC}$ can reach 53,400 g/mol at 18 h; and at 120 ℃, the $M_{p,SEC}$ can reach 62,000 g/mol at 8 h. These results preliminarily gave the information that, as the general principle for all the polymerization mechanisms, the rate of polymerization was largely dependent on the temperature.

Specially, the ATNRP was synergistically modulated by the NRC reaction, ATRP and NMRP mechanisms. Under the lower temperature, once the carbon radicals was generated by the atom transfer procedure, they will be captured by the nitroxide radicals immediately and the NRC was the dominant reaction. Furthermore, the formed alkoxyamine linkages were difficult to be dissociated and used to modulate the ATRP or NMRP mechanism. Alternatively, under the elevated temperature, the dissociation-combination of alkoxyamine linkages would reach an equilibrium, and the existed active carbon radicals could further induce the proceeding of ATRP or NMRP mechanisms. Typically, the higher temperature, the more active carbon radicals were regenerated from the formed alkoxyamine linkages. From this viewpoint, we could draw a conclusion that modulating a moderate dissociation-combination equilibrium of alkoxylamine linkages was the key in an ATNRP mechanism, which was very coincident to a NMRP mechanism and can be conveniently realized by controlling the polymerization temperature. According to the above results and analysis, the polymerization temperature of 105 ℃ was employed to realize a moderate rate of polymerization in the following experiments.

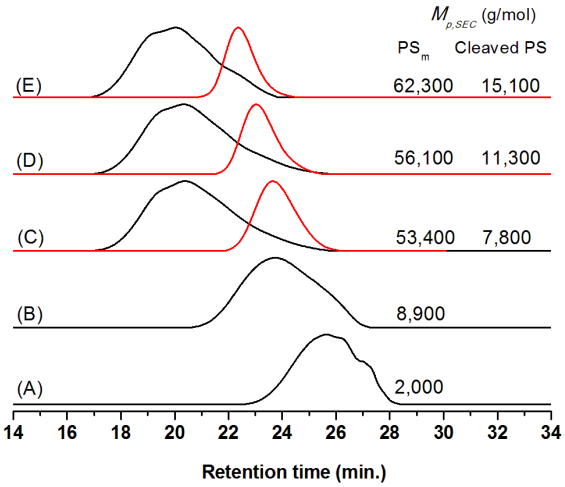


Fig. 2. The SEC traces of PS_m synthesized at different temperatures and times (black lines) and the corresponding cleaved PS (red lines) ((A) 90 ℃, 48 h, Entry 1; (B) 100 ℃, 24 h, Entry 2; (C) 105 ℃, 18 h, Entry 3; (D) 110 ℃, 18 h, Entry 4; (E) 120 ℃, 8 h, Entry 5).

B.Effect of the Volume Ratio of Toluene Solvent to Styrene Monomer ($V_{Toluene}/V_{Styrene}$) on ATNRP Mechanism.

Usually, for a certain polymerization system, the addition of certain solvent was used to improve the solubility of the formed polymers and lower the viscosity of system, convenience the heat exchange, and ultimately modulate the rate of polymerization. For the same reasons, the toluene was also used as solvent in our ATNRP mechanism. As shown in **Table 1** and **Fig. 3**, with the increase of the volume ratio of $V_{Toluene}/V_{Styrene}$, the molecular weights of PS_m and cleaved PS regularly shift to the lower region, which confirmed that the rate of polymerization can also be modulated by the addition of toluene solvent. For example, in the bulk system ($V_{Toluene}/V_{Styrene}$=0), the polymerization can give PS_m with a $M_{p,SEC}$ of 53,400 g/mol even the polymerization time was controlled at 18 h. When the $V_{Toluene}/V_{Styrene}$ of 0.25 was employed, a $M_{p,SEC}$ of 19,600 g/mol was obtained at 24 h and the polymerization showed a lower rate. However, a dramatically slowed rate of polymerization can be achieved when the $V_{Toluene}/V_{Styrene}$ above 0.50 was adopted, and only $M_{p,SEC}$ below 4,000 g/mol can be achieved.

In fact, when the solvent of toluene was used in ATNRP, the solubility of the formed PS_m could be improved and the viscosity of the system would be lowered, which can further prompt the biomolecular NRC reaction between stable nitroxide radicals and the active carbon radicals. Correspondingly, the dissociation-combination equilibrium of alkoxylamine linkages shift and preferred to the formation of the alkoxyamine linkages, and the concentration of active carbon radicals would be largely decreased and led to a slowed rate of polymerization. These results gave the indication that the content of solvent might be another versatile factor used to modulate the ATNRP mechanism. For a moderate rate of polymerization, the $V_{Toluene}/V_{Styrene}$ of 0 or 0.25 can be considered in the following experiments.

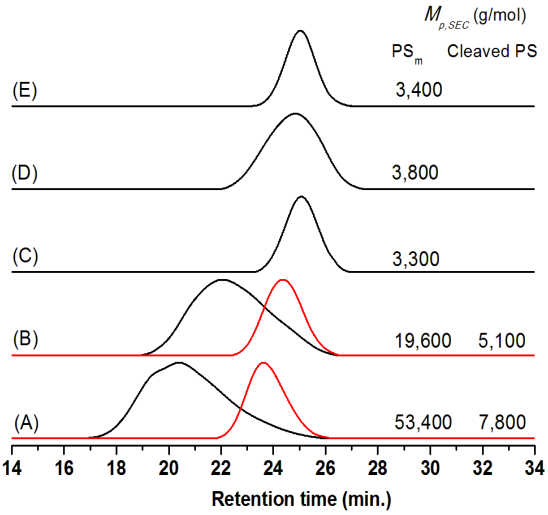


Fig. 3. The SEC traces of PS_m synthesized with different content of

toluene (black lines) and the corresponding cleaved PS (red lines) ($V_{Toluene}/V_{Styrene}$: (A) 0, Entry 3; (B) 0.25, Entry 6; (C) 0.50, Entry 7; (D) 1.0, Entry 8; (E) 2.0, Entry 9).

C.Effect of the Molar Ratio of Styrene Monomer to Initiator ($[Styrene]_0/[Br\text{-}TEMPO]_0$) on ATNRP Mechanism.

Similarly, the effect of molar ratio of $[Styrene]_0/[Br\text{-}TEMPO]_0$ on ATNRP mechanism was also evaluated. Just as shown in **Table 1** and **Fig. 4**, with the increase of molar ratio of $[Styrene]_0/[Br\text{-}TEMPO]_0$, the molecular weights of the formed PS_m and cleaved PS simultaneously and regularly moved to the higher region. The results confirmed that the ATNRP of styrene monomer was actually proceeded in a "living" / controlled manner, which was accorded to a typical ATRP or NMRP mechanisms. Thus, the molecular weight of the each PS segment on PS_m can be well tuned by feeding different molar ratio of $[Styrene]_0/[Br\text{-}TEMPO]_0$, and finally modulate the thermal behaviour of the target polymers.

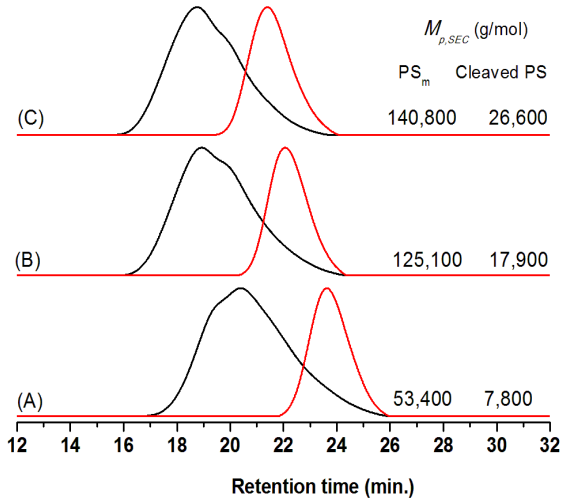


Fig. 4. The SEC traces of PS_m synthesized with different molar ratio $[Styrene]_0/[Br\text{-}TEMPO]_0$ (black lines) and the corresponding cleaved PS (red lines) ($[Styrene]_0/[Br\text{-}TEMPO]_0$: (A) 105, Entry 3; (B) 210, Entry 10; (C) 315, Entry 11).

D.Effect of the Molar Ratio of Cu(I)Br Catalyst to Initiator ($[Cu(I)Br]_0/[Br\text{-}TEMPO]_0$) on ATNRP Mechanism.

As described in previous section, the NRC reaction, ATRP and NMRP mechanisms were synergistically happened in an ATNRP. For ATRP mechanisms, the Cu(I)Br was needed as a catalyst, while the Cu(I)Br was acted as a reagent in the NRC reaction. Obviously, in our ATNRP mechanism, part of Cu(I)Br would participate into the NRC reaction and was oxidized as Cu(II)Br, and the remained Cu(I)Br would help the ATRP mechanism. Thus, the amount of the added Cu(I)Br would also affect the ATNRP mechanism. From the Entry 6, 12 and 13 (**Table 1**), we can achieve the information that, with the increase of the molar ratio of $[Cu(I)Br]_0/[Br\text{-}TEMPO]_0$, the system showed an increased rate of polymerization. Specifically, when the molar ratio $[Cu(I)Br]_0/[Br\text{-}TEMPO]_0$ was controlled as 1/1, the $M_{p,SEC}$ of the formed PS_m only reached 19,600 g/mol at 24 h. However, when the molar ratio of $[Cu(I)Br]_0/[Br\text{-}TEMPO]_0$ was increased to 2/1, the $M_{p,SEC}$ (113,400 g/mol) of the formed PS_m almost have an increase of 10 times at 24 h. From this viewpoint, we can decidedly conclude that the ATRP mechanism was actually happened in ATNRP. Otherwise, the only NMRP mechanism will be independent on the amount of Cu(I)Br. Importantly, with the increase of the molar ratio of $[Cu(I)Br]_0/[Br\text{-}TEMPO]_0$, the D_{NRC} values can exceed 10, which also confirmed that the NRC reaction was actually accompanied and can be enhanced by the adequate catalyst of Cu(I)Br. On the other hand, considered the difficulty to remove the remained copper salt from polymerization system after ATNRP, the $[Cu(I)Br]_0/[Br\text{-}TEMPO]_0$ of 2/1 was suggested.

E.Effect of the Technology on ATNRP Mechanism.

From the above analysis on the ATNRP mechanism, we can conclude that the NRC reaction, ATRP and NMRP mechanisms were actually and synergistically happened in ATNRP. The high temperature was helpful to the ATRP and NMRP mechanisms, however, the high temperature would lead to a rapid dissociation of the formed alkoxyamine linkages and a finally lowered D_{NRC} value for NRC reaction. On the contrary, the low temperature might be helpful to the combination of stable nitroxide radical and active carbon radical by the NRC reaction. Thus, we attempted to carry out the polymerization firstly at 105 ℃ for 12 h, and then the system was maintained at 80 ℃ for another 24 h (**Entry 14** in **Table 1**). Regretfully, the low $M_{p,SEC}$ of the formed PS_m, cleaved PS and D_{NRC} value were obtained by this modified operation technology. In fact, at the lower temperature, although the dissociation of the formed alkoxyamine linkages can be suppressed, the accompanied ATRP and NMRP mechanisms were also largely suppressed. Furthermore, the increased viscosity of the polymerization system at the low temperature would limit the diffusion-controlled bimolecular NRC reaction. Ultimately, the overall effect still led to a reduced D_{NRC} value, almost unchanged PS_m and cleaved PS. Thus, the ATNRP was suggested to be performed at a relatively higher temperature (for example 105 ℃), which can guarantee a higher D_{NRC} by NRC reaction and also a moderate rate of polymerization modulated by the ATRP and NMRP mechanisms. Again, a confirmation that the temperature was actually a dominant factor on ATNRP procedure can be reached.

F. Effect of the Polymerization Time on ATNRP Mechanism.

From the above sections, several parameters on ATNRP mechanism had been systematically optimized. Under an optimized conditions ($[Br\text{-}TEMPO]_0/[PMDETA]_0/[Cu(I)Br]_0/[Styrene]_0$=1/4/2/105, and the $V_{Toluene}/V_{Styrene}$ was controlled as 0.25 in order to realize the polymerization in a controlled time-scale), the ATNRP mechanism was again evaluated against the polymerization time. From **Table 2**, **Fig. 5** and **Fig. 6**, we can discriminate that, the PS_m and cleaved PS were regularly increased with the increase of the polymerization time. There was a linear increasing tendency for the molecular weights of cleaved PS, however, an exponential growth model was drawn for the molecular weights of PS_m. Additionally, there was a long induction period for ATNRP procedure at 10 h.

Thus, we can analyze that, at the beginning of the ATNRP, the carbon radicals generated from the brominated polymer end were dominantly captured by the nitroxide radicals and the NRC reaction was majorly favored. Correspondingly, the ATRP and NMRP mechanisms might be suppressed, and an induction period was

accompanied. Subsequently, the dissociation-combination of the alkoxyamine linkages would reach an equilibrium and the concentration of carbon radicals became a constant. At this stage, the ATRP and NMRP mechanism would also realize a stable state and the polymerization of styrene monomer was proceeded in a "living" / controlled manner, and the molecular weight of cleaved PS increased in a linear mode. Exceptionally, the NRC reaction was always proceeded in a step-growth manner, and the molecular weight of the total PS_m was increased in an exponential model.

Table 2. The polymerization data for PS_m and cleaved PS at different polymerization time.

Entry	Temperature (℃)	Time (h)	Br-TEM PO(mmol)	PMDETA (mmol)	CuBr (mmol)	Styrene (mmol)	$V_{Toluene}$ /$V_{Styrene}$	PS_m[a]			PS[a]			D_{NRC}[b]
								M_p (g/mol)	M_n (g/mol)	PDI	M_p (g/mol)	M_n (g/mol)	PDI	
1	105	12	1	4	2	105	0.25	3,900	3,500	1.36	700	700	1.14	5.8
2	105	15	1	4	2	105	0.25	4,800	4,100	1.47	900	900	1.16	5.5
3	105	18	1	4	2	105	0.25	11,900	6,800	1.92	3,600	3,400	1.18	3.3
4	105	24	1	4	2	105	0.25	31,000	16,800	1.99	5,100	4,800	1.21	6.1
5	105	36	1	4	2	105	0.25	125,200	50,700	2.63	11,700	9,700	1.23	10.7

[a] The $M_{p,SEC}$, $M_{n,SEC}$ and PDI of polymers were estimated by SEC measurement in THF elution using PS as standard. [b] D_{NRC} was calculated according to the Formula: $D_{NRC}=M_{p,SEC,PSm}/M_{p,SEC,PS}$.

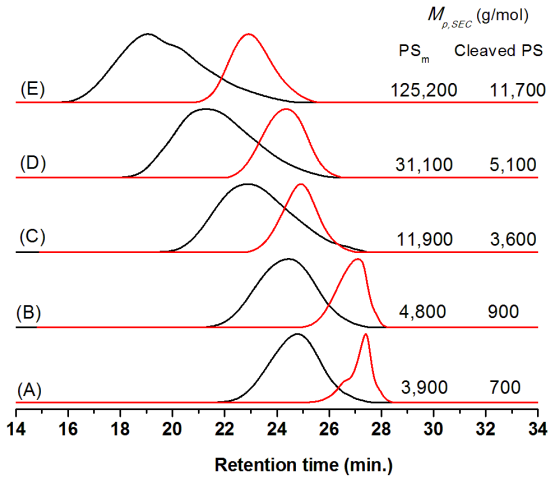


Fig. 5. The SEC traces of PS_m synthesized at different polymerization time (black lines) and the corresponding cleaved PS (red lines) ((A) 12 h, Entry 1; (B) 15 h, Entry 2; (C)18 h, Entry 3; (D) 24 h, Entry 4; (E) 36 h, Entry 5).

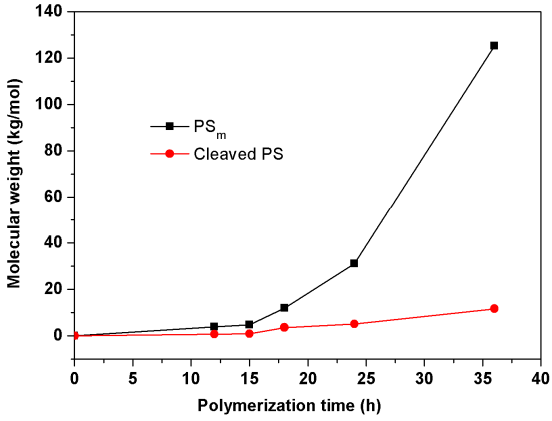


Fig. 6. The evolution tendency of $M_{p,SEC}$ for PS_m and cleaved PS with the increase of polymerization time.

Thermal Behaviour of the PS_m and Cleaved PS.

Using the above ATNRP mechanism, the PS_m with multiple alkoxyamine linkages embedded in the main chain can be realized. Thus, based on the thermally reversible dissociation-combination behavior of alkoxylamine linkages, the PS_m might have some special thermal properties. Firstly, the TGA curve of PS_m and cleaved PS were compared under the same measurement conditions. From **Fig. S1**, we can observe that the PS_m and cleaved PS almost have the same weight loss curves between 50 ℃ and 700 ℃, and both polymers also have the fastest weight loss rate at 420 ℃, which was rather accordance to a typical TGA curve of a PS homopolymer.[43]

Also, the reversible dissociation-combination behaviour of alkoxyamine linkages was clearly discriminated by the DSC measurement (**Fig. 7, Table S1**). The sample of PS_m was firstly subjected to a scanning procedure from 40 ℃ to 150 ℃ at a rate of 10 ℃/min, and the first $T_{g,1st}$ was monitored. After the temperature was again decreased to 40 ℃, the second $T_{g,2nd}$ was evaluated by a similar scanning procedure from 40 ℃ to 150 ℃ at a rate of 10 ℃ /min in the second cycle. Obviously, the T_gs were regularly decreased and approached to the T_g of the cleaved PS. The DSC results clearly provided the information that, the sample of PS_m can be cleaved in the DSC procedure. Ultimately, when the alkoxyamine linkages was completely cleaved, all the segments might have the same T_g with that of cleaved PS. Based on this property, the synthesized PS_m might be endowed with some potential application in the biodegradable and intelligent material science field, or as a poly-macro-initiator of NMRP mechanism for multisegmented polymers.

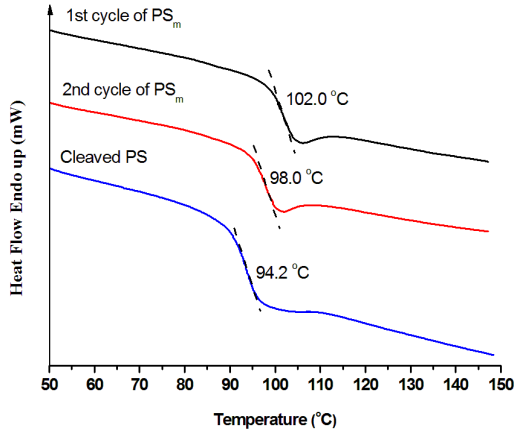


Fig. 7. DSC curves of the PS_m subjected to two heating-cooling cycles between 40~150 ℃ and cleaved PS (Entry 1 in **Table S1**).

Conclusions

In summary, based on the common features of NRC reaction, ATRP and NMRP mechanisms, an ATNRP mechanism was presented and investigated. The heterofunctional initiator of Br-TEMPO with one bromoisobutyryl group and one stable nitroxide radical was firstly designed and synthesized by a typical esterification reaction. During the investigation on ATNRP mechanism, polymerization temperature, volume ratio of toluene solvent to styrene monomer ($V_{Toluene}$ /$V_{Styrene}$), molar ratio of styrene monomer to initiator ($[Styrene]_0/[Br\text{-}TEMPO]_0$), molar ratio of Cu(I)Br catalyst to initiator ($[Cu(I)Br]_0/[Br\text{-}TEMPO]_0$), as well as polymerization time and the operation technology were all optimized. The result showed that the NRC reaction, ATRP and NMRP mechanisms were synergistically proceeded in ATNRP due to the thermally reversible dissociation-combination behavior of the formed alkoxyamine linkages, and the polymerization temperature and solvent were the key factors. Also, the thermal behaviour of the formed PS_m was monitored by TGA and DSC analysis. The result showed that the alkoxyamine linkages can suffer a thermal cleavage at the elevated temperature of 110 ℃ and the PS_m can be cleaved in the presence of excess stable nitroxide radicals. The PS_m and cleaved PS have the same thermal stability, however, the T_g of PS_m gradually approached to that of the cleaved PS when several heating-cooling (-40~150 ℃) cycles was performed. In this contribution, the presented ATNRP mechanism and the as-prepared multisegmented polymers might find some potential applications in intelligent, degradable material science field, as well as in polymer chemistry. Additionally, the ATNRP can also be used as a convenient route to the polymer possessed a stable nitroxide radical at the polymer end (the cleaved style), which can further acted as a versatile precursor in polymer synthesis or for special application, for example, in a NRC reaction. The further progress on ATNRP mechanism is expected and enriched in the future works.

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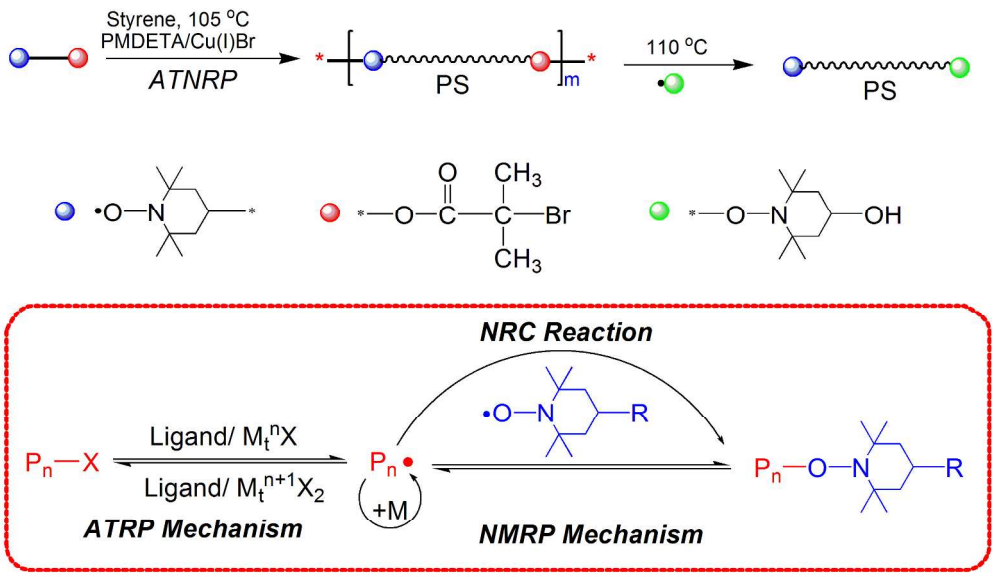

ATNRP Mechansim

Based on the common features of well-defined nitroxide radical coupling (NRC) reaction, atom transfer radical polymerization (ATRP) and nitroxide mediated radical polymerization (NMRP) mechanisms, a novel Atom Transfer Nitroxide Radical Polymerization (ATNRP) mechanism was presented by integrating these three mechanisms into one polymerization system simultaneously, and further used to construct the multisegmented polystyrene (PSm) embedded with multiple alkoxyamine linkages.
244x151mm (300 x 300 DPI)