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Atom transfer radical polymerization of styrene with $FeCl_2$/acetic acid as the catalyst system

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Summary

Atom transfer radical polymerization with $FeCl_2/CH_3COOH$ as the catalyst has been successfully implemented for styrene. Various initiators have been used, among which carbon tetrachloride is the most effective one. High molecular weight products were obtained when CCl_4 was used as the initiator, and the measured molecular weight was close to the calculated one. Block copolymerization (PS-b-PMMA) was performed to confirm the living/controlled nature of the polymerization. ^1H NMR was used to characterize the structure of the macromolecular initiator and the block copolymer. If other initiators, such as benzyl bromide, ethyl 2-bromopropionate and α -bromoethyl benzene, were used, the polymerization occurred at ambient temperature resulting in oligomer. The molecular weight of the oligomer approaches to 4600 ($M_{n,th}$ = 10000). Thus acetic acid, which is cheaper and less toxicity, can be used as coordinative ligand in ATRP initiated by CCl_4 mediated by iron.

Introduction

Since Matyjaszewski (1) reported the atom transfer radical polymerization using alkyl halides as initiators and copper (I) coordinated by a ligand as the catalyst, a variety of monomers have been polymerized in a controlled fashion(2)-(4). The catalytic transition metal compound acts as a carrier of the halogen atom in a redox process. The choice of the ligand turns to be one of the most important factors affecting the reactivity of the catalyst. Multidentate nitrogen ligands such as aromatic nitrogens(1)-(7), imine type nitrogens(8)-(9) and aliphatic nitrogens(10)-(11)work very well for copper mediated ATRP by providing the desired reactivity. Monodentate nitrogen ligands produce polymers with uncontrolled molecular weights and high polydispersities. Sulfur, oxygen, or phosphorous ligands are reported less effective in ATRP catalyzed by copper. As far as $iron^{II}$ catalytic system is concerned, various ligands of nitrogen, phosphorus donors and mixed coordinating ligands have been successfully used in the ATRP of styrene(12)-(14). However organic amines and phosphorus are harmful to human being and are rather expensive. In this work, $FeCl_2$/Acetic acid was developed and successfully used for the controlled/"living" radical polymerization of styrene. The acids are generally believed to deactivate the metal organic catalyst resulting in poor control of the polymerization(15)-(17). But acetic acid can complex with $iron^{II}$ and $iron^{III}$ with the equilibrium constants of the

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same order of magnitude. Acetic acid is able to stabilize iron cations in both low oxidation states and high oxidation states. Therefore it is possible to use acetic acid as the catalyst in conjunction with iron dichloride. Efficiency of the new catalytic system was investigated using a variety of initiators. Furthermore block copolymer was prepared to verify the living nature of the polymerization.

Experimental

Materials: Styrene was vacuum distilled over CaH_2 just before polymerization. $FeCl_2$ was washed with acetone and dried under vacuum at 60°C before use. Carbon tetrachloride, benzyl bromide, ethyl 2-bromopropionate, α -bromoethyl benzene and acetic acid were used as received.

Polymerization: Catalyst, ligand, initiator, monomer were added to a flask with stirrer. Three cycles of vacuum-nitrogen were applied in order to remove oxygen. Then the flask was immersed in an oil bath at the required temperature. After a specific time, the flask was opened and THF was added to the sample to dissolve the polymer. PS was isolated by precipitating with methanol.

Characterization: The monomer conversion was determined by gravimetry. Molecular weight and molecular weight distribution were obtained by gel permeation chromatography (GPC) that was carried out with a Waters 208 instrument, using tetrahydrofuran as eluent, and calibration with polystyrene standards. ^1H NMR spectra was taken on 500 MHz spectrometers at room temperature in $CDCl_3$.

Results and discussion

Polymerization of St initiated by CCl_4

Polymerization of St with $[CCl_4]_0$ = 0.044 M, $[FeCl_2]_0$ = 0.044 M, $[\text{acetic acid}]_0$ = 0.13 M and $[St]_0$ = 8.7 M was carried out in bulk at 120°C; the polymerization reached 75% within 23hrs. at 120°C to yield PS of $M_{n,\ exp}$ = 14600 and M_w/M_n = 1.46. Figure 1 shows that the measured molecular weight linearly increases with the monomer conversion, and matches the theoretical value calculated.

As demonstrated in Figure 2, the first-order rate plots are linear before the monomer conversion reaching 65%, implying the polymerization is internally of first order with respect to monomer. A decrease of reaction rate is observed at about 70% conversion, in conjunction with deviation of molecular weight in Figure 1. indicating termination occurred at the last stage. Polydispersity is relatively low (1.46) comparing with that of conventional radical polymerization.

In order to investigate whether the binary system of $FeCl_2/CH_3COOH$ can induce cationic polymerization or not, we carried out the polymerization in various conditions of $[CCL_4]_0:[CH_3COOH]_0:[St]_0$ = 1:3:200 (Figure 3), $[CCL_4]_0:[FeCl_2]_0:[St]_0$=1:1:200 (Figure 4), and $[FeCl_2]_0:[CH_3COOH]_0:[St]_0$=1:1:3:200 (Figure 5). The dependence of molecular weight, Mn, and molecular weight distribution, Mw/Mn, on monomer conversion are shown in Figs. 3-5, respectively. Comparing Figs. 3-5 with Fig. 1, it can be seen that the polymerization lacking one of the components of the initiating system results in a polymer with very high molecular weight (>10^5) and relatively wide molecular weight distribution (M_w/M_n > 2.0) since the beginning of the reaction. These are the characters of a conventional radical polymerization. On the contrary, controlled molecular weight and relatively low polydispersity (1.46) were obtained in the presence of $CCl_4$with $FeCl_2/CH_3COOH$ as the catalyst. Furthermore, the inhibitor of cationic polymerization, triethylamine, was introduced into the polymerization system with $St/FeCl_2/CH_3COOH$ and without CCl_4 at 120°C ($[St]_0$: $[FeCl_2]_0$: $[CH_3COOH]_0$: $[Triethylamine]_0$ = 200:1:3:6), after 5 h the monomer conversion reached 81% and the number-average molecular weight was 2.6 X 10^5 with M_w/M_n = 1.79. It further verified that Figs. 3-5 involved in a conventional polymerization in stead of a cationic one.

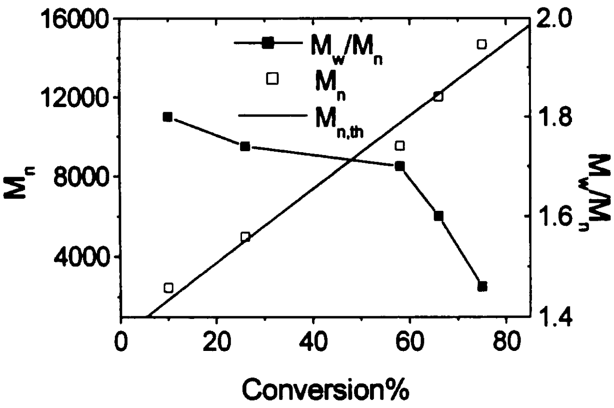

Fig. 1. Molecular weight, Mn, and molecular weight distribution, Mw/Mn, dependence on monomer conversion for the heterogeneous ATRP of styrene initiated by CCl_4 at 120°C, $[CCl_4]_0$: $[FeCl_2]_0$: $[CH_3COOH]_0$: $[St]_0$ = 1:1:3:200, [St] = 8.7 M

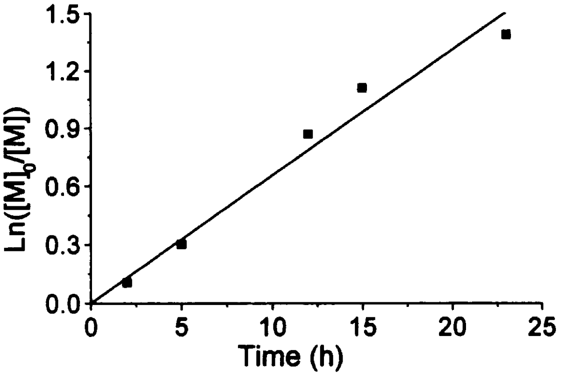

Fig. 2. Semilogarithmic kinetic plot for the bulk ATRP of Styrene initiated CCl_4 at 120 °C $[CCl_4]_0$: $[FeCl_2]_0$: $[CH_3COOH]_0$: $[St]_0$ = 1:1:3:200, $[St]_0$ = 8.7 M

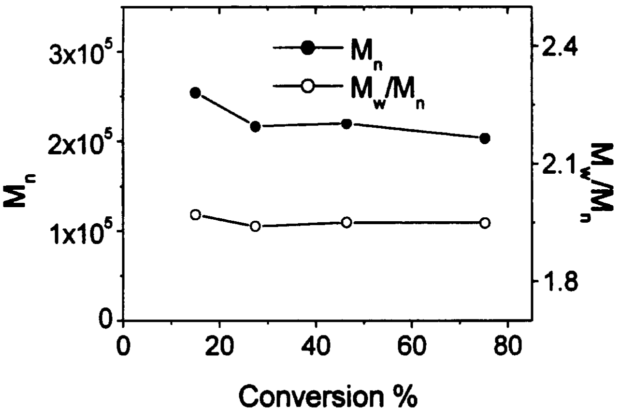

Fig. 3. Molecular weight, Mn, and molecular weight distribution, Mw/Mn, dependence on monomer conversion for the heterogeneous ATRP of styrene initiated by CCl_4 at 120°C, $[CCl_4]$: $[CH_3COOH]$: [St] = 1:3:200, [St] = 8.7 M

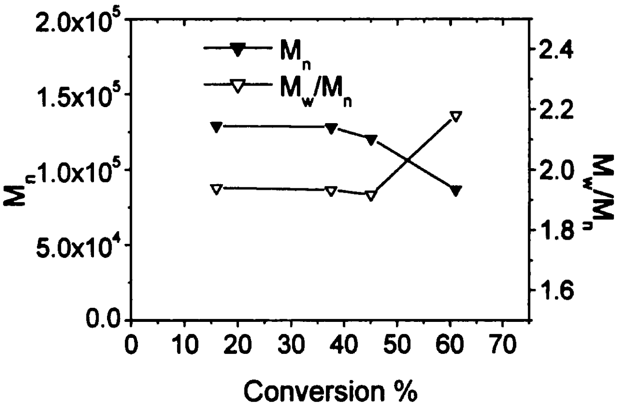

Fig. 4. Molecular weight, Mn, and molecular weight distribution, Mw/Mn, dependence on monomer conversion for the heterogeneous ATRP of styrene initiated by CCl_4 at 120°C, $[CCl_4]$: $[FeCl_2]$: [St] = 1:1:200, [St] = 8.7 M

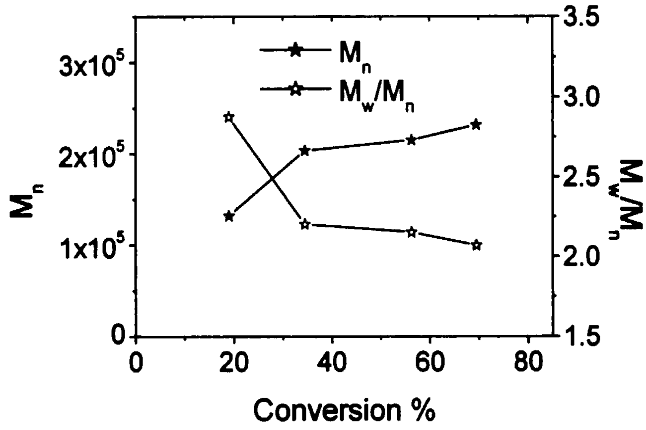

Fig. 5. Molecular weight, Mn, and molecular weight distribution, Mw/Mn, dependence on monomer conversion for the heterogeneous ATRP of styrene initiated by CCl_4 at 120°C, [$FeCl_2$]: [CH_3COOH]: [St] = 1:3:200, [St] = 8.7 M

Preparation of PS-b-PMMA block copolymer

In order to verify living/controlled nature of the polymerization catalyzed by $FeCl_2$/aetic acid system, block polymer of St with MMA was synthesized. First, macroinitiator was prepared using CCl_4 (0.095 g, 0.060 M), $FeCl_2$ (0.10 g, 0.080 M), acetic acid (0.15 g, 0.24 M) and St (10 ml, 8.7 M) in bulk at 110°C. After a given time, the flask was opened and added a certain amount of tetrahydrofuran (THF), then the product was precipitated in menthol, and desiccation in vacuum at 65°C. Second, the prepolymer was dissolved into the solvent (DMF); subsequently the second monomer MMA together with a suitable amount of $FeCl_2$/isophthalic acid were added, and the polymerization was carried out under 100 °C. Because CCl_4/$FeCl_2$/acetic acid system can not initiate the polymerization of MMA, the $FeCl_2$/isophthalic acid catalyst system (18) was used in the second step of the copolymerization. This may be due to the complex constant between isophthalic acid and $FeCl_2$ is strong enough to abstract halogen from the organic halide initiating polymerization of MMA). GPC curves of the resulting polymers are shown in Figure 6. The molecular weight increases to 17600 from 14600 and the polydispersity index reduces to 1.50 from 1.64. It indicates that the dead polystyrene in macroinitiator is insignificant. The GPC traces show that the polymerization of the second monomer was initiated quantitatively by the macroinitiator. In the FT-IR spectrum of PS-PMMA block copolymer, the characteristic peaks at 1731cm^{-1}, 1193cm^{-1} correspond to the ester carbonyl of PMMA and 3060 cm^{-1}, 3026 cm^{-1}, 756cm^{-1} and 700cm^{-1} represent the existence of the benzene ring present in the block copolymer (Figure 7).

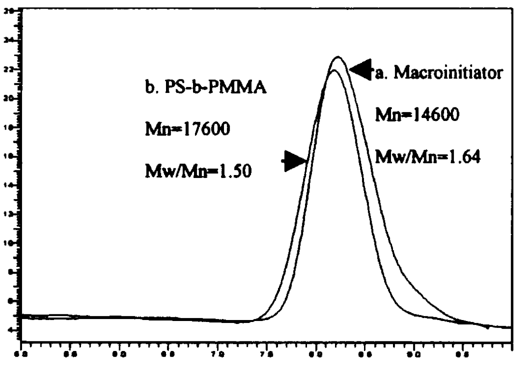

Fig. 6. GPC curves of macroinitiator PS-X and block copolymer PS-b-PMMA

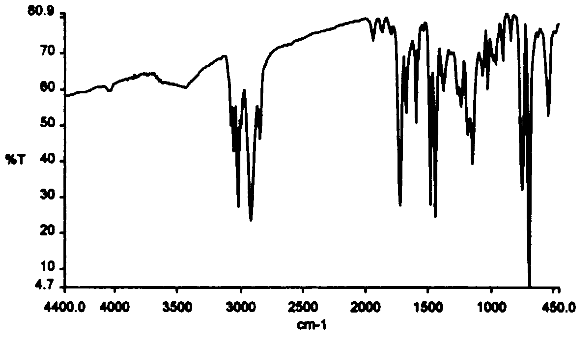

Fig. 7. The FT-IR spectrum of PS-b-PMMA block copolymer

The structures of the macroinitiator and the block polymer were analyzed by ^{1}H NMR. The ^{1}H NMR spectra of the resulting PS and PS-b-PMMA are illustrated in Figs. 8 and 9, respectively. As showed in Fig 8, signals are observed at 1.2-2.1ppm, originating from the methene and methine prontons of the main chain, A signal was discerned at 6.4-7.2ppm, assigned to the aromatic protons at phenyl. The broad triplets at 4.4ppm are attributed to the methine proton geminal to chloride end group, while the peak at 1.0ppm is assigned to the methyl group from the initiator. Figure 9 shows ^{1}H NMR spectrum of the block copolymer, which exhibits signals at 0.8-1.1ppm(CH_3), 1.3-2.3ppm (backbone CH_2 and CH), 3.6ppm(OCH_3), and 6.33-7.1ppm (phenyl protons), and signals around 4.4ppm disappear. The peak at 3.8ppm derived from the methyl ester group adjacent to the terminal halide at the end. By comparing the integral value of PS backbone protons and OCH_3 protons, it is determined that the content of PMMA is 18 % in the PS-PMMA block copolymer. Comparison of the integration of the end group with those of methene and methine and phenyl in the main chan gives a molecular weight, $M_{n,NMR}$ = 17000, which approaches to the value from GPC based on PS standards, $M_{n,GPC}$=17600. The ^{1}H NMR spectrum of the block copolymer, and the molecular weight data verify that the synthesis of the macroinitiator and the block copolymerization were successful.

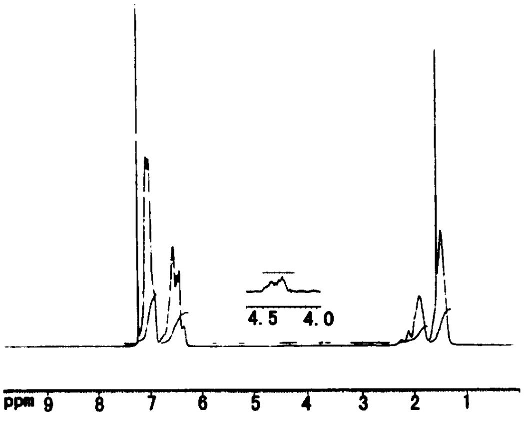

Fig. 8. ^{1}H NMR spectrum of PS catalyzed by $FeCl_2/CH_3COOH$

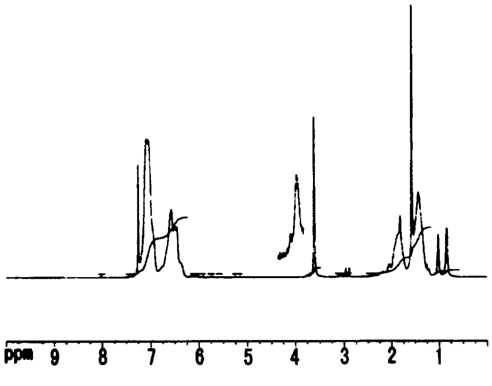

Fig. 9. ^{1}H NMR spectrum of the block copolymer PS-b-PMMA

Polymerization of St initiated by α-bromoethyl benzene

When St was polymerized using α -bromoethyl benzene as the initiator and $FeCl_2/CH_3COOH$ as the catalyst (1.0eq to initiator) in a sealed tube at room temperature, the monomer conversion reached 80% within 3h at 25°C, and the characterization data of GPC are M_n = 4600 and M_w/M_n = 1.24. The measured molecular weight increases with monomer conversion. A linear plot of $Ln([M]_0/[M])$ verse time was observed throughout the polymerization, indicating a constant number of growing chains. The molecular weight distribution of the resultant polymer was rather narrow even though the measured molecular weight was considerable smaller than the calculated one. At 25°C thermal initiation can be neglected. The exact reason why the measured molecular weight was lower is not known.

To further confirm the living nature of the polymerization, chain extension was implemented. The prepolymer was prepared using α-bromoethyl benzene (0.080 g, 0.044 M), acetic acid (0.070 g, 0.12 M), $FeCl_2$ (0.050 g, 0.040 M), styrene (8.7 M). After a period the reaction was stopped and the molecular weight reached 3500 with conversion 50%. Chain extension reaction of the second part of styrene was carried out in o-xylene. After 16 h, the conversion reached 84% with the number-average molecular weight 12100. The measured molecular weight is in agreement with the calculated value ($M_{n,th}$ = 12000). It is evident that the molecular weight of the polymer further increased after chain extension. These facts indicated that the polymerization proceeds in a living fashion.

Table 1 summarizes the results of St polymerization using $FeCl_2/CH_3COOH$ as the catalyst initiated by PEBr under various experimental conditions. The data in Table 1 indicate that controlled polymerization were achieved with different monomer-to-initiator ratios. All of resulting polymers show low polydispersities and the molecular weights are smaller than the theoretical ones, especially with increasing the ratio of [St]/[initiator].

Table 1. Polymerization of St with α -bromoethyl benzene/$FeCl_2/CH_3COOH$ as the initiated system under various conditions

Solvent	[St]/[In]	temperature /°C	time/h	$M_{n,GPC}$	PDI	Conv.%
cyclohexan	500	90	10	0		
bulk	500	60	1	5170	1.30	45
bulk	1000	60	9	7400	1.48	38
bulk	100	40	2	4660	1.05	70
o-xylene	500	90	1.5	2600	1.17	23

Reaction condition:[α -bromoethyl benzene]$_0$: [$FeCl_2$]$_0$: [CH_3COOH]$_0$ = 1:1:4, [St]$_0$ = 8.7 M

In order to explain this phenomenon, experiments are run to determine the effect of various initiators on ATRP using this new catalytic system. The experimental results are shown in table 2. Four kinds of initiators were used including 1-phenylethyl bromide, ethyl 2-bromopropionate, benzyl bromide and CCl_4. Low polydispersity was obtained for each kind of initiators. When CCl_4 was used, molecular weight is more close to the calculated ones. The molecular weights of the resulting polymer initiated by 1-phenylethyl bromide and benzyl bromide were lower than the predetermined ones. A possible explanation would be that chain transfer reaction and other side reaction would occur in the systems initiated by 1-phenylethyl bromide and benzyl bromide. In contrast, chain transfer reaction was less significant in the system initiated by CCl_4. Moreover, high reaction temperature (120°C) for the system initiated by CCl_4 provide fast dynamic exchange between Fe^{II} and Fe^{III}, side reaction would decrease. As a result, molecular weight of the resulting polymer initiated by CCl_4 is more close to the calculated ones.

Tab. 2. Polymerization of St with various initiators catalyzed by $FeCl_2/CH_3COOH$

Initiator	$[St]_0/[In]_0$	Time (h)	Conv.%	M_n	M_w/M_n
PEBr[a]	228	8.5	50	4760	1.23
Benzyl bromide[a]	224	8.5	50	4500	1.15
CCl_4[b]	200	8.5	63	9530	1.6
ethyl 2-bromopropionate[a]	200	8.5	5	–	–

Reaction condition: a $[RX]_0$: $[FeCl_2]_0$: $[CH_3COOH]_0 = 1:1:3$, $[St]_0 = 8.7$ *M at 70°C*

b $[RX]_0$: $[FeCl_2]_0$: $[CH_3COOH]_0 = 1:1:3$, $[St]_0 = 8.7$ *M at 120°C*

UV/Vis spectra curves

An UV-Vis spectroscopic analysis of the catalytic system was implemented in order to characterize the elementary process leading to the formation of active species. As it can be seen in Figure 10, The corresponding $FeCl_2/CH_3COOH$ complex does not show any absorption bands from 290 nm to 400 nm. As the reaction proceeded, a new absorption appeared at 311 nm and 358nm. The absorption bands of $FeCl_3/CH_3COOH$ locate at 311nm and 358nm (d in Figure 10). Therefore, the change in absorption spectra of the reaction system can be attributed to the formation of $FeCl_3/CH_3COOH$ complex through halogen transformation.

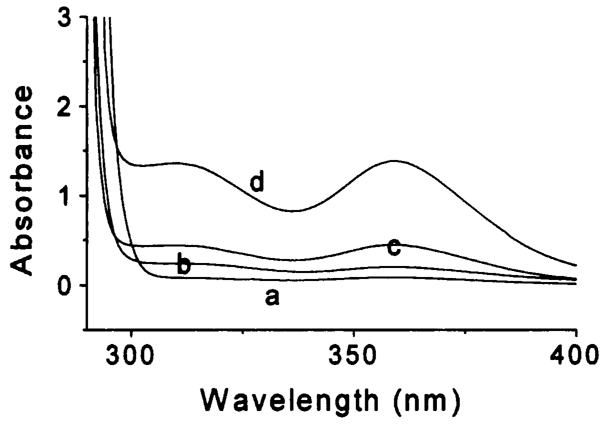

Figure 10. UV/Vis spectra curves of $FeCl_2/CH_3COOH$ during the polymerization of St in the condition of [CCL4]:[FeCl2]0:[CH3COOH]0:[St]0=1:1:3:200

Reactions time: a. o b. 2 h c. 20 h d. Complex of $FeCl_3/CH_3COOH/St$ in acrylonitrile

Conclusion

Controlled radical polymerization of styrene was performed using $FeCl_2/CH_3COOH$ as the catalyst system. Different initiators have important effect on the polymerization. When CCl_4 was used as the initiator, high molecular weight products were obtained, and the measured molecular weight was close to the calculated one. Therefore the polymerization was controlled even though the molecular weight distribution of resulting polymers was not so narrow as expected. If PEBr was used as the initiator, the polymerization could be implemented at ambient temperature, however, the molecular weights did not exceed 4600 ($M_{n,\ th}$=10000). The choice of initiator is the key aspect for maintaining the living nature.

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