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Fe(0) Powder-Catalyzed One-Pot Reaction: Concurrent Living Radical Polymerization and Click Chemistry for Topological Polymers

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Fe(0) Powder-catalyzed one-pot reaction, was successfully employed to design linear and star polymers in a well-controlled manner by combination ambient temperature living radical polymerization and click chemistry. The polymerization behavior possessed the characteristics of ''living''/controlled radical polymerization: the first-order kinetic plots, narrow molecular weight distribution (PDI < 1.4), the linear relationships between molecular weights and the monomer conversions and the successful chain-extension with NIPAAM monomer. Furthermore, the NMR and MALDI-TOF-MS data indicated that Fe(0)-catalyzed one-pot strategy is different from our reported Cu(0)-catalyzed one-pot strategies to make targeted polymers.

Introduction

"Click chemistry" introduced by Sharpless and coworkers[1-3] has been considered as an extraordinarily powerful tool for the preparation of advanced materials due to some of most beneficial features, simple reaction conditions, high chemical yield (often above 95%), ease of purification and functional group tolerance. To date, there have been a number of excellent works involved in employing click chemistry to design functional materials with complex architectures and compositions since Hawker et al.[4-6] first applied click chemistry in polymer synthesis and modification in 2004, such as Turro et al.,[7-8] Matyjaszewski et al.,[9-13] Lutz et al.,[14-16] Van Hest et al.,[17-19] Hawker et al.,[20-22] and Haddleton et al.[23-26] etc. In recent years, our group have developed copper(0)-catalyzed one-pot reaction combining living radical polymerization (LRP) and "click chemistry" to produce well-controlled polymers with special side-chain functionality,[27-30] where Cu(I) is generated from Cu(0) by single-electron transfer (SET) mechanism and catalyze the "click chemistry" successfully. Moreover, we have found that the click rate was much faster than that of LRP, and three-steps continuous reaction were also confirmed in the Cu(0)-catalyzed one-pot reaction.[27-30] However, this Cu(0)-catalyzed one-pot reaction have an obvious disadvantage of poor controllability of methyl acrylic monomer. Careful attention must be paid to the choice of mediating agent and reaction conditions. To well-controlled polymerize propargyl methacrylate (PgMA), reversible addition-fragmentation chain transfer (RAFT) agent should be employed to mediate the polymerization.[27-30] However, MALDI-TOF spectrum have suggested that the targeted polymer was end-capped by atom transfer radical polymerization (ATRP) initiator moieties or RAFT moieties at both the α and ω chain ends.[28] More importantly, the SET-RAFT approach may be very difficult to controlled design the predetermined polymeric topology because

of a complex multi-component system.

In recent years, there have been many studies focusing on developing different Cu-catalyzed azide-alkyne click reaction. Such as Cu(II)-catalyzed system (CuSO$_4$·5H$_2$O/sodium ascorbate)[1], Cu(I)-catalyzed system (CuBr/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA)[10], Cu(0)-catalyzed system[27-30] (Cu(0)/PMDETA) and photo-induced system.[31-33] In fact, in metal-catalyzed LRP, copper species (Cu(0), Cu(I) and Cu(II)), were the most used catalysts. In contrast to copper, iron is a preferential metal catalyst for LRP because of its particularly attractive merits, such as biocompatibility, easy separation, and low cost.[34-36] Recently, Matyjaszewski and co-workers reported room temperature polymerization of methyl acrylate (MA) in dimethyl sulfoxide (DMSO) using three zero-valent metal, Zn^0, Mg^0, and Fe^0, as reducing agents to continuously regenerate the activator CuBr/ligand from CuBr$_2$/ligand complex.[37] Most recently, by taking advantage of zero-valent metal, our group reported that Fe(0) powder/CuBr$_2$ -mediated LRP of methyl methacrylate (MMA) or styrene (St) at 25 °C,[38] and supposed that Fe(0) played a dual role, the supplemental activator for the generation of active radical and the reducing agent for CuBr$_2$.[38] As our knowledge of LRP, the dynamic equilibrium between Fe(0), Cu(II) and Cu(I) existing in the above Fe(0) powder/CuBr$_2$ system might provide the possibility of catalyzing LRP and "click chemistry" in one-pot. The new monomer might be formed in situ through the click reaction of the alkyne and azide groups. We reason that this novel catalytic system of Fe(0) powder/CuBr$_2$ is ideal for LRP and catalyzing the click reaction. Moreover, in comparison of our previous works (Cu(0)-catalyzed one-pot strategy), this Fe(0)-catalyzed one-pot approach might give access to the synthesis of polymers with complex structures and end-group control, and the RAFT agent may be avoided.

In this work, we firstly reported that the Fe(0)-catalyzed one-pot reaction combination LRP and "click chemistry" using Fe(0)

Powder/CuBr$_2$ as catalyst. The NMR and MALDI-TOF-MS data were used to confirm the reaction process (Scheme 1). Moreover, the topological star polymers were also successfully obtained by this novel catalyst.
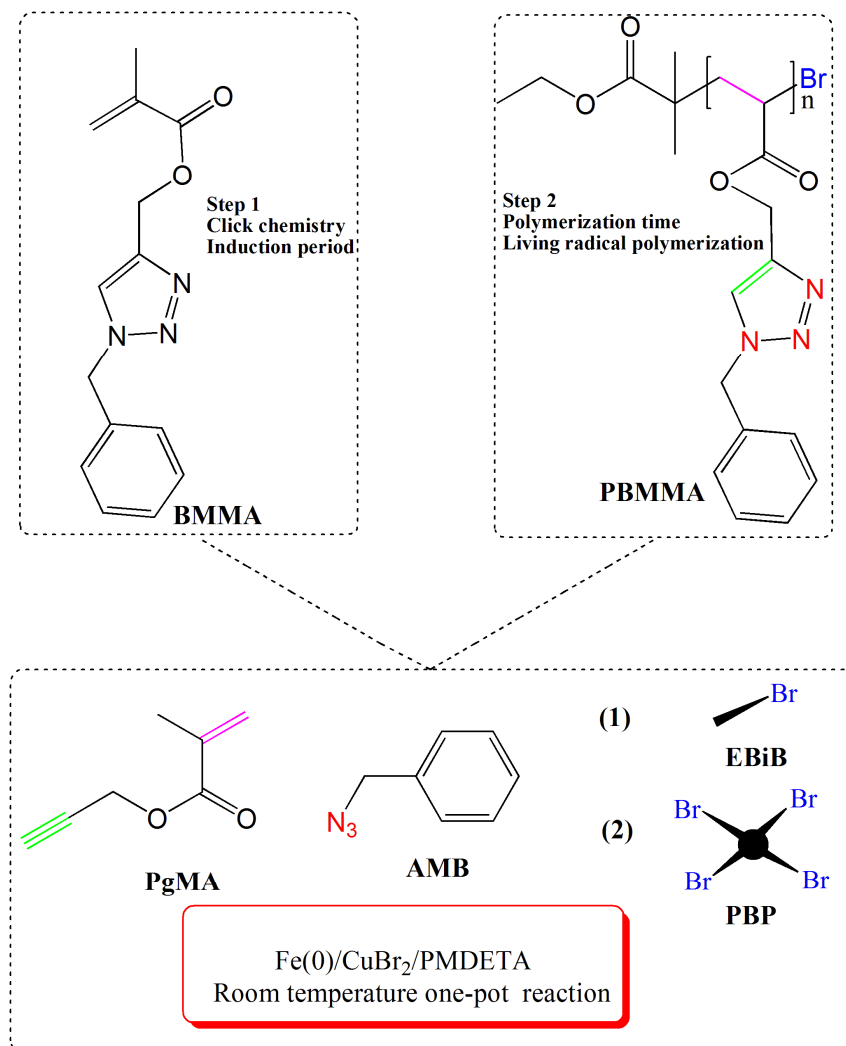
Scheme 1 Synthesis of well-defined linear and star polymers using Fe(0)/CuBr$_2$ as catalyst.

Experimental section

Materials

Propargyl methacrylate (PgMA) (Alfa Aesar, 98%), ethyl-2-bromoisobutyrate (EBiB) (Acros, 98%) (Aladdin, 97%), copper powder (Cu(0), < 75μm, Aldrich, 98%), Zero-valent iron powder (Fe(0), < 200 mesh, 99%, metals basis, Alfa Aesar). Copper(II) bromide (CuBr$_2$, 98.5%, Shanghai Chemical Reagents Co.) was used as received. Azidomethyl benzene (AMB) (Aladdin, 98%). The star initiator pentaerythrityl-2-bromopropionate (PBP) was synthesized according to the references.[39] Dimethyl sulphoxide (DMSO) (analytical reagent, Shanghai Chemical Reagent Co. Ltd) was dried by 4Å molecular sieve before use. Pentamethyldiethylenetriamine (PMDETA) (Jiangsu Liyang Jiangdian Chemical Factory, Liyang, China, 98%) was dried with 4Å molecular sieve and distilled in vacuum. All other solvents were analytical grade and used as received without further purification.

Synthesis

Living radical polymerization of PgMA

A typical procedure for the living radical polymerization is as follows: propargyl methacrylate (PgMA) (1.04 g, 8.37 mmol), ethyl-2-bromoisobutyrate (EBiB) (16.2 mg, 0.0837 mmol), Cu(0) (5.4 mg, 0.0837 mmol) or Fe(0) (4.7 mg, 0.0837 mmol), and solvent DMSO (1.0 mL) were added to a dry glass ampoule with a magnetic bar. The reaction mixture was bubbled with argon for approximately 10 min, and then PMDETA (17.4 µL, 0.0837 mmol) was added to the mixture. The solution was bubbled with argon for approximately 10 min to eliminate the oxygen, and then the ampoule was flame-sealed under argon atmosphere and placed in the water bath at 25 °C. At the designed time, the ampoule was opened, and the contents were diluted with about 2.0 mL THF, and precipitated into a 250 mL methanol. The samples were obtained by filtration and dried to constant weight under vacuum. After that, the sample was again precipitated into 250 mL petroleum ether, filtrated and dried under vacuum. The conversion of the monomer was determined by gravimetry.

Preparation of linear or star PBMMA via one-pot reaction

A typical procedure for the preparation of linear or star PBMMA via one-pot reaction is as follows: PgMA (1.04 g, 8.37 mmol), AMB (1.11 g, 8.37 mmol), EBiB (16.2 mg, 0.0837 mmol) or PBP (56.2 mg, 0.0837 mmol), Fe(0) (4.7 mg, 0.0837 mmol), and DMSO (2 mL) were added to a dry glass ampoule with a magnetic bar. The reaction mixture was bubbled with argon for 10 min, and then PMDETA (17.4 µL, 0.0837 mmol) was added to the mixture. The solution was bubbled with argon for another 10 min to eliminate the oxygen, and then the ampoule was flame-sealed under argon atmosphere and placed in the water bath at 25 ^{o}C. The other procedures were similar to LRP of PgMA described above.

Chain extension using PBMMA as a macroinitiator

PBMMA ($M_{n(GPC)}$ = 11400 g/mol, M_w/M_n = 1.22) was used as a macroinitiator to synthesize PBMMA-*b*-PNIPAM block copolymer with *N*-isopropylacrylamide (NIPAM) as the second monomer in DMSO solution. The reaction was also carried out at 25 ^{o}C ([NIPAM]$_0$: [PBMMA]$_0$: [Fe(0)]$_0$: [CuBr$_2$]$_0$: [PMDETA]$_0$ = 200 : 1 : 1 : 2.5 : 1). The reaction was stopped after 8 h and the

other procedures were similar to those mentioned above.

Characterization

The molecular weights and molecular weight distributions of the polymers were determined with a Waters 1515 gel permeation chromatography (GPC) equipped with refractive index detector, using HR1, HR3, and HR4 column with molecular weight range 100-500,000 calibrated with poly(methyl methacrylate) standard samples, respectively. FT-IR spectra were recorded on a Nicolette-6700 FT-IR spectrometer. ^{1}H NMR spectra of the polymers were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument, using DMSO-d$_6$ as solvent and tetramethylsilane (TMS) as the internal standard. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurement was performed using a Bruker Autoflex III mass spectrometer equipped with a 337 nm nitrogen laser. The polymers were dissolved in THF (5 mg/mL) and added to a layer of super 2,5-dihydroxybenzoic acid matrix (sDHB) casted from a THF solution.
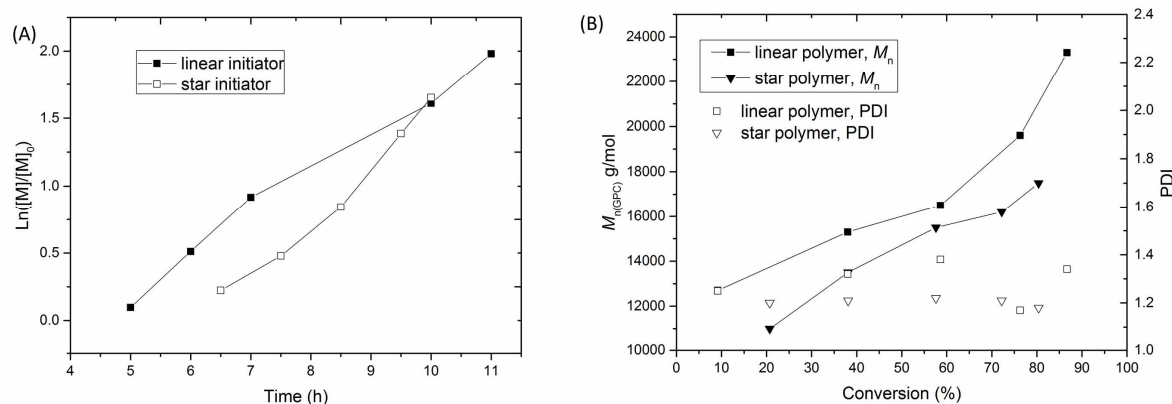

Fig. 1 (A) Kinetic plots of polymerization of PgMA with AMB at 25 ^{o}C; (B) Dependence of the molecular weights and PDI on monomer conversions for polymerization of PgMA with AMB. Polymerization conditions: [PgMA]$_0$:[AMB]$_0$:[initiator]$_0$:[Fe(0)]$_0$: [CuBr$_2$]$_0$:[PMDETA]$_0$ = 100:100:1:1:2.5:1, PgMA/DMSO = 1/1 (v/v).
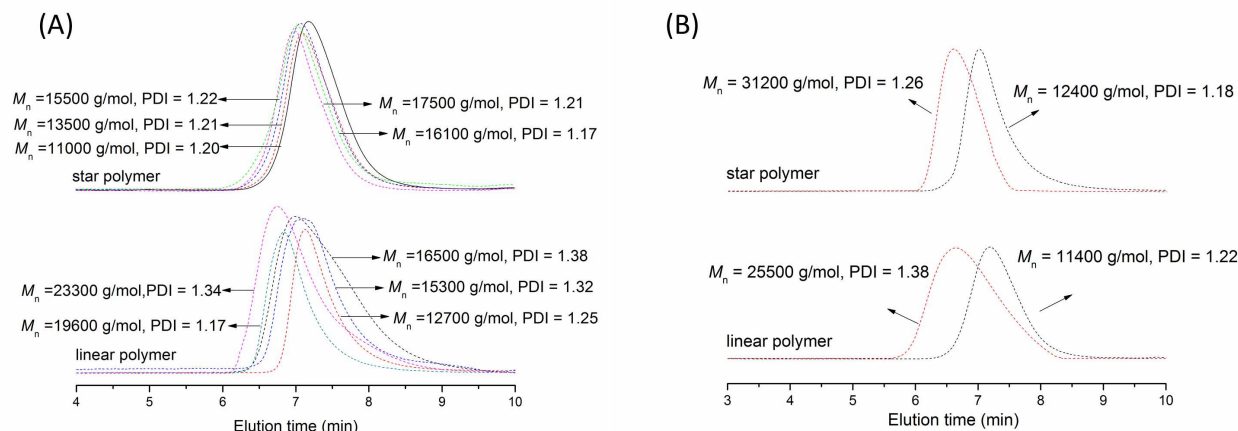
Fig. 2 (A) Gel permeation chromatograph curves of the obtained polymers prepared by one-pot reaction; (B) Gel permeation chromatograph curves of macroinitiator and final polymer after chain extension.

Results and discussion

Traditional controlled/"living" radical polymerizations (LRP) of alkyne monomers were reported to result in the uncontrolled behaviors.[40-41] In this work, the different catalytic system were employed to investigate the controllability over the polymerization of propargyl methacrylate (PgMA) at room temperature, and the representative results were presented in Table 1. From Entries 1-9 in Table 1, we can see that the PgMA were not well controlled at various catalytic systems, in good agreement with the literatures.[28] Control experiments with the use of Cu(0) and $CuBr_2$ for the one-pot reaction were also carried out. From Entries 10-14 in Table 1, it can be found that the molecular weights were uncontrolled, although azidomethyl benzene (AMB) was added to the above system. However, when using Fe(0) instead of Cu(0), the polymerizations were well controlled (entries 15). The catalytic system of Fe(0)/$CuBr_2$ opens up a new avenue to effectively co-catalyze the LRP and click chemistry.

Table 1. The polymerization results mediated by different controlled radical polymerization methods in DMSO solution using EBiB as initiator ($V_{monomer}/V_{solvent} = 1/1$).

Entry	Time (h)	Conversion (%)	$M_{n(GPC)}$ (g/mol)	PDI
1	2	20	141700	2.00
2	2	18	153300	2.71
3	1	85	5180	2.10
4	13	12	22300	1.98
5	5	80	24600	2.68
6	5	35	28200	2.85
7	8	30	27000	3.10
8	16	50	26600	2.67
9	16	85	18700	2.28
10	1	70	26300	2.58
11	2	70	58300	2.19
12	1	90	26800	2.63
13	48	-	-	-
14	48	-	-	-
15	23	93	25300	1.40
16	3	68	32200	1.45
17	6	78	41600	1.21
18	29	72	40000	1.12
19	120	50	13000	1.28

[1] $[PgMA]_0 : [I]_0 : [Cu(0)]_0 : [PMDETA]_0 : [VC]_0 = 100 : 1 : 0.2 : 0.4 : 0.1$
[2] $[PgMA]_0 : [I]_0 : [Cu(0)]_0 : [PMDETA]_0 : [VC]_0 = 100 : 1 : 0.1 : 1 : 0.1$
[3] $[PgMA]_0 : [I]_0 : [Cu(0)]_0 : [PMDETA]_0 = 100 : 1 : 1 : 1$
[4] $[PgMA]_0 : [I]_0 : [Fe(0)]_0 : [PMDETA]_0 : [VC]_0 = 100 : 1 : 1 : 1 : 1$
[5] $[PgMA]_0 : [I]_0 : [Cu(0)]_0 : [PMDETA]_0 : [CuBr_2]_0 = 100 : 1 : 1 : 1 : 0.5$
[6] $[PgMA]_0 : [I]_0 : [Fe(0)]_0 : [PMDETA]_0 : [CuBr_2]_0 = 100 : 1 : 1 : 1 : 0.75$
[7] $[PgMA]_0 : [I]_0 : [Fe(0)]_0 : [PMDETA]_0 : [CuBr_2]_0 = 100 : 1 : 1 : 1 : 1.25$
[8] $[PgMA]_0 : [I]_0 : [Fe(0)]_0 : [PMDETA]_0 : [CuBr_2]_0 = 100 : 1 : 1 : 1 : 1.5$
[9] $[PgMA]_0 : [I]_0 : [Fe(0)]_0 : [PMDETA]_0 : [CuBr_2]_0 = 100 : 1 : 1 : 1 : 2.5$
[10] $[PgMA]_0 : [AMB]_0 : [I]_0 : [Cu(0)]_0 : [PMDETA]_0 = 100 : 100 : 1 : 1 : 1$
[11] $[PgMA]_0 : [AMB]_0 : [I]_0 : [Cu(0)]_0 : [PMDETA]_0 :[CuBr_2] = 100 : 100 :$
[12] $[PgMA]_0 : [AMB]_0 : [I]_0 : [Cu(0)]_0 : [PMDETA]_0 :[CuBr_2] = 100 : 100 : 1 : 1 : 1 : 0.8$
[13] $[PgMA]_0 : [AMB]_0 : [I]_0 : [Cu(0)]_0 : [PMDETA]_0 :[CuBr_2] = 100 : 100 : 1 : 1 : 1 : 2.5$
[14] $[PgMA]_0 : [AMB]_0 : [I]_0 : [Cu(0)]_0 : [PMDETA]_0 :[CuBr_2] = 100 : 100 : 1 : 1 : 1 : 1.5$
[15] $[PgMA]_0 : [AMB]_0 : [I]_0 : [Fe(0)]_0 : [PMDETA]_0 :[CuBr_2] = 100 : 100 : 1 : 1 : 1 : 2.5$
[16] $[PgMA]_0 : [AMB]_0 : [I]_0 : [Fe(0)]_0 : [PMDETA]_0 :[CuBr_2] = 100 : 100 : 1 : 1 : 1 : 0.2$
[17] $[PgMA]_0 : [AMB]_0 : [I]_0 : [Fe(0)]_0 : [PMDETA]_0 :[CuBr_2] = 100 : 100 : 1 : 1 : 1 : 1$
[18] $[PgMA]_0 : [AMB]_0 : [I]_0 : [Fe(0)]_0 : [PMDETA]_0 :[CuBr_2] = 100 : 100 : 1 : 1 : 1 : 3$
[19] $[PgMA]_0 : [AMB]_0 : [I]_0 : [Fe(0)]_0 : [PMDETA]_0 :[CuBr_2] = 100 : 100 : 1 : 0.1 : 0.1 : 0.25$

In the present study, we used two different initiators (linear and star) to trigger the model reaction. The detailed results of one-pot reaction in DMSO solution at room temperature were presented in Fig. 1. Fig. 1(A) illustrated the respective kinetic plots for the one-pot reaction of PgMA and AMB using Fe(0)/$CuBr_2$ as catalyst with two different intiator (EBiB and PBP). In both cases, the linear relationship between $\ln([M]_0/[M])$ and the reaction time can be observed, which indicates that the polymerizations were first-order with respect to the monomer, and the radical concentration of each system remained constant throughout the polymerization processes. As also can be seen

from Figure 1(B), The molecular weight of PBMMA measured by GPC ($M_{n(GPC)}$) both increased linearly with the monomer conversion, while keeping the relatively narrow molecular weight distribution during the polymerization process. These results strongly suggest that the room temperature one-pot reaction progressed in a living manner using Fe(0)/CuBr$_2$ as catalyst. Moreover, as presented in Fig. 2(A), the GPC curves of PBMMA exhibited a monomodal elution peak and shifted higher molecular mass with the polymerization time in all cases. All the results above demonstrated that Fe(0)/CuBr$_2$ catalyzed one-pot technique could prepare well-controlled linear and star polymers.

The results of chain extension with PBMMA as macroinitiator further confirmed that the polymer can be reactivated for the chain propagation. The linear PBMMA sample ($M_{n(GPC)}$ = 11400 g mol^{-1} , PDI = 1.22) obtained from Fe(0)/CuBr$_2$ -mediated one-pot reaction was used as the macroinitiator for the chain extension reaction. The chain extension was successful carried out at ambient temperature by using Fe(0)/CuBr$_2$ as a catalyst. As presented in Fig. 2(B), there was an apparent peak shift from the macroinitiator to the chain-extended PBMMA-*b*-PNIPAM with $M_{n(GPC)}$ = 25500 g mol^{-1} , PDI = 1.38. Moreover, the star polymer showed the similar "living" nature. All the above results proved the functionality and feature of the one-pot reaction.

To further investigate the Fe(0)/CuBr$_2$ -catalyzed one-pot reaction, the obtained PBMMA ($M_{n(GPC)}$ = 12700 g mol^{-1}, PDI = 1.25) prepared in DMSO was analyzed by ^{1}H NMR spectrum as shown in Fig. 3. The peak at δ = 4.12 ppm (h in Fig. 3) should be corresponded to the methylene protons of the ethyl ester unit in the initiator EBiB, which revealed that the initiator EBiB moieties were successfully attached to the polymer chain ends. The signals at δ = 5.0 ppm (d in Fig. 3) were assigned to the methylene group next to the oxygen of the ester group, and the signals at δ = 5.6-5.78 ppm (c in Fig. 3) should be assigned to the methylene group next to benzene ring. The new signals at δ = 7.6-7.96 (ppm) (a in Fig. 3) should be corresponded to the new generation of triazole rings. Moreover, the 2 : 1 ratio of the corresponding integration values for the d and a peaks and the 1 : 1 ratio of the corresponding integration values for the d and c peaks in Fig. 3 suggested that alkyne groups were disappeared. In addition, the FT-IR data were employed to further characterize the structures of the obtained PBMMA with the different polymerization time (PT). As shown in Fig 4, compared with the corresponding characteristic signals of the clickable agent AMB and PgMA, the IR spectra of PBMMA showed that the signal at 2098 cm^{-1} assigned to the azide group and the alkyne group signal at ~3294 cm^{-1} were completely disappeared after one-pot reaction, indicating that the efficient click reaction between PgMA and AMB was successfully achieved. Both NMR and FT-IR demonstrated that the side-chain functionalized polymers could be easily prepared via the one-pot technique.
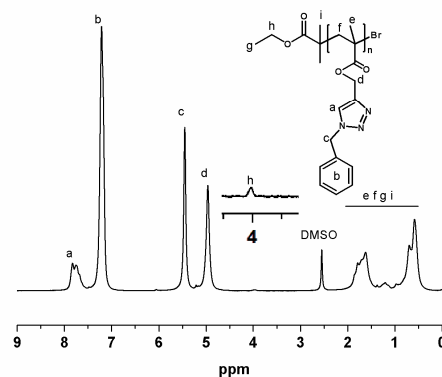

Fig. 3 ^{1}H NMR spectrum of the linear polymer via one-pot technique in DMSO-d$_6$ ($M_{n(GPC)}$ = 12700 g/mol, M_w/M_n = 1.25).
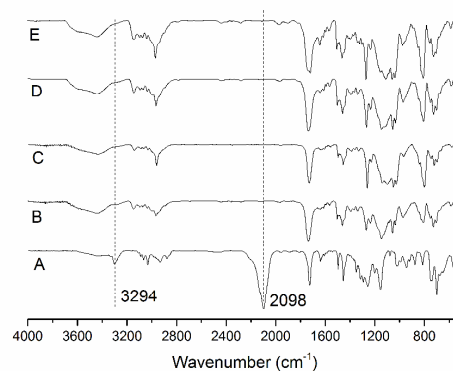

Fig. 4 FT-IR spectra of the monomer and polymers (A) AMB and PgMA; (B) PBMMA, PT = 5 h; (C) PBMMA, PT = 6 h; (D) PBMMA, PT = 7 h; (E) PBMMA, PT = 10 h

To quantitatively describe the click conversion, the reaction mixture at different time was analyzed by ^{1}H-NMR in situ. As displayed in Fig. 5, the signals at δ = 3.41 (ppm) (h in Fig. 5) and δ = 4.81 (ppm) (f in Fig. 5) represented the acetylene group and methylene group of the alkyne monomer unit, respectively. The signal at δ = 4.41 ppm (g in Fig. 5) was assigned to the methylene group next to the azide group of the clickable agent AMB. In addition, the obvious chemical shift was observed with the increase of reaction time. After 3 h, the corresponding characteristic signals of the PgMA and AMB (h, g, f in Fig. 5), almost completely disappeared, and the new signal of the BMMA monomer (a, e, d in Fig. 5) appeared. Moreover, the 1 : 3 : 2 ratio of the corresponding integration values for the c, d and e peaks indicated that the polymerization of new produced monomer BMMA did not carried out. Bases on those results, we can clearly conclude that the rates of click reaction are much faster than the polymerization rates, which is similar to other findings.[28,30] Moreover, the click reaction should be completed in the induction period.
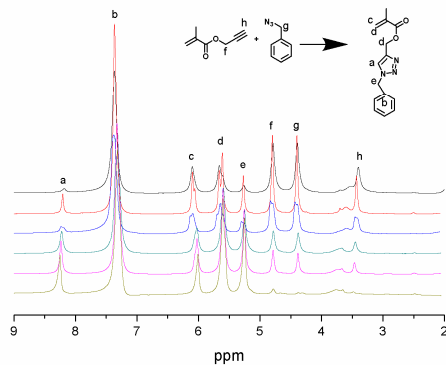
Fig. 5 ^{1}H-NMR spectra of the reaction mixture in DMSO-d[6].

In order to investigate the reaction process, the matrix assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) data of the obtained PBMMA were used to characterize the structures. It can be found from Fig. 6 that there was one main series of peaks, whose interval was regular, ca. 257.1, the molar mass of (1-benzyl-1,2,3-triazol-4-yl)methyl methacrylate (BMMA), which agreed well with the results of ^{1}H NMR, and further confirmed the 100% click efficiency were carried out in one-pot reaction, and the new monomer BMMA were produced in one-pot reaction. Furthermore, we can see that the experimental isotopic mass distribution values in the main peak series of the MALDI-TOF spectrum are in good agreement with the theoretical values. Theoretical value calculated from $M_{\text{theo}} = M_{\alpha} + \text{n} \times 257.1 + M_{\omega}$. Here, 257.1 and n are the average mass of BMMA repeat unit and the number of the BMMA unit in the polymer chain. M_{α} and M_{ω} refer to the molecular weight of the ethyl isobutyryl and bromine species of EBiB, respectively. For instance, the mass of peak A in Fig. 6, indicated this polymer chain contained 9 repeat units (BMMA), and was end-capped by the EBiB moieties at both the α and ω chain ends. In addition, the relatively high-intensity of peak series (B, in Fig. 6) with about 39 mass should be assigned to the potassium cation (K^{+}) cationized chain. These data confirmed that the Fe(0) Powder/CuBr[2] catalyzed one-pot reaction combination LRP and "click chemistry" is a efficient and robust synthetic tool for well-defined and high-performance complex macromolecules.
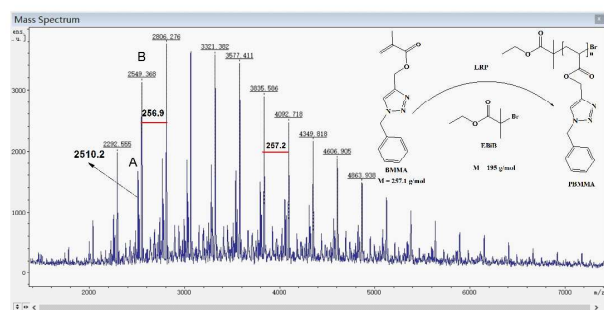

Fig. 6 Matrix assisted laser desorption ionisation time-of-flight mass spectrometry of PBMMA ($M_{\text{n(GPC)}}$ = 6200 g/mol, $M_{\text{w}}/M_{\text{n}}$ = 1.40) prepared via one-pot reaction.
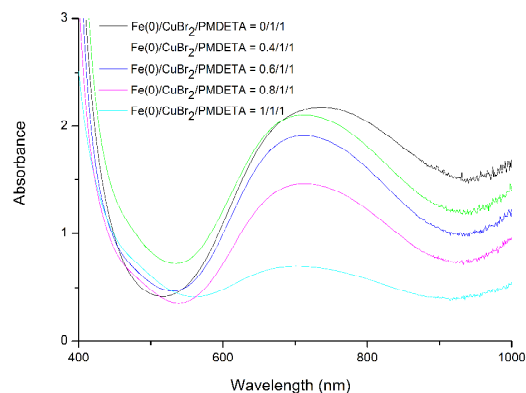
Fig. 7 UV-vis spectra of Fe(0)/[CuBr[2]][0]/[PMDETA][0] and [CuBr[2]][0]/[PMDETA][0] in DMSO.

To well understanding of this process, the reaction media was examined by UV-vis detection. As shown in Fig. 7, the absorption at about 720 nm was ascribed to the Cu(II) species.[42] The absorption intensity of CuBr[2]/PMDETA with DMSO as solvent was weakened after the addition of Fe(0). Moreover, the a significantly decrease in absorbance was detected when increasing the concentration of Fe(0). Indeed, we also study the effect of molar ratio of Fe(0)/CuBr[2] on the polymerization, and the results were given in Table 1. From Entries 16-19 in Table 1, it can be found that the all the polymerizations were well-defined achieved with different Fe(0)/CuBr[2] ratios. Significantly, as the molar ratio of Fe(0)/CuBr[2] increased from 0.2 to 3, the rate of polymerization and PDI distinctly decreased. In addition, a Fe(0)/initiator ratio of 0.1 was enough to prepare one-pot reaction with a PDI as low as 1.28. All the data indicated that Cu(II) was reduced to Cu(I) by Fe(0) under this condition, which was used to effectively trigger the LRP and click chemistry.

Conclusions

Room temperature one-pot technique combining LRP and click chemistry has been successfully employed to prepare the linear and star polymers using Fe(0)/[CuBr[2]][0] as catalyst. The detailed investigation of the reaction process shows that the click rate was much faster than that of LRP in the Fe(0) catalytic system. Compared with Cu(0)-catalyzed one-pot strategy, Fe(0)-catalyzed one-pot reaction possesses the advantage of convenient synthesis of high-performance complex macromolecules with controllable properties. We believe that Fe(0)-catalyzed one-pot strategy provides an easy, efficient and versatile synthetic tool for well-defined topological polymers.

Acknowledgments

Notes and references

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