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ORIGINAL PAPER

Synthesis of pure (Co) polymers via supported cobalt (II)-catalyzed controlled/“living” radical polymerization

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Abstract Cross-linked polyacrylic resin supported-cobalt (II) catalyst was successfully employed in controlled/“living” radical polymerization of various monomers including *n*-butyl acrylate (BA), ethyl methacrylate (EMA) and styrene (St). Well-defined polymers with predetermined molecular weight and relatively narrow molecular weight distribution were synthesized. After polymerization, the supported cobalt (II) catalyst was easily and effectively removed from the polymerization system by simple centrifugation and very pure polymer products were obtained (Co residue <0.1 ppm). Using the obtained polymers as macroinitiators, polymerization of methyl methacrylate (MMA) and fluorinated methacrylate ether 2-[(perfluorononenyl)oxyl] ethyl methacrylate (FNEMA) were performed, respectively. Well-defined and pure diblock copolymers PBA-b-PMMA, PS-b-PMMA and PS-b-PFNEMA were synthesized.

Keywords Controlled radical polymerization · Atom transfer radical polymerization (ATRP) · Cobalt catalyst · Supported catalyst · Catalyst removal

Introduction

The properties and application of polymers depend on molecular structure, molecular weight and molecular weight distribution. Therefore, controlled polymerization technique enables molecular design to be needed. The transition metal-mediated radical polymerization, termed as atom transfer radical polymerization (ATRP), developed by Matyjaszewski [1] and Sawamoto [2], is a versatile controlled/“living”

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radical polymerization technique in polymer design. Using ATRP, polymers with predetermined molecular weight and narrow molecular weight distribution can be synthesized [3, 4]. More importantly, the polymers synthesized by ATRP contain functionally active terminal end, thus they can be applied as macroinitiators to prepare various diblock copolymers [5, 6]. This is one of the “beauties” of ATRP. With the development of controlled/“living” radical polymerization technology, there will be more and more new (co)polymer products being prepared [7].

However, one main limitation of ATRP is that a relatively large amount of transition metal catalyst in the polymerization system is difficult to be removed after polymerization. The transition metal catalyst is colored, generally toxic and can accelerate the aging of polymer material. Therefore, it is rather hazardous if the yielding polymer product contains a significant quantity of transition metal residue [8]. So, to obtain high-qualified polymer materials, transition metal catalyst residue must be removed. However, the purification step to remove the transition metal catalyst at the end of the polymerization may result in further costs and environmental problems, which makes it less attractive for commercial polymer synthesis [9–11]. To solve the problem of catalyst residue, two routes were developed. One was the application of ARGET (activators regenerated by electron transfer) ATRP catalyst developed by Matyjaszewski [12, 13]. In this case the concentration of catalyst was very low, which made the removal of catalyst unnecessary. But expensive ligands and special reducing agents were needed. The other was the development of supported catalyst, in which way the catalyst could be easily removed during post-polymerization purification and even recycled. However, the reported supported catalysts based on Cu(II), Ni(II) were difficult to be prepared [9] and also the ligands applied in the catalyst systems were much expensive, which was not benefit for the application on large scale. Therefore, the development of new catalysts which can be easily separated and recoverable becomes more and more urgent for the application of ATRP in industry [14].

We have recently reported that cobalt acetate could work as an effective ATRP catalyst [15]. It has been proved that carboxylate could be used as ligand for cobalt-based ATRP catalyst. If using cross-linked polyacrylic resin to provide carboxylate as ligand for Co(II), the immobilization of cobalt catalyst can be rather easily realized. This kind of catalytic system can not only overcome the difficulty of catalyst removal, but also reduce the cost of preparation of supported catalyst, which is benefit for industrial application. Recently, we have successfully developed the “hybrid” catalytic system which was composed of a supported cobalt catalyst in conjunction with a small quantity of soluble Cu (II) complex as deactivator [16] and the supported cobalt (II)/copper (II) bimetallic catalytic system [17] for polymerization of MMA. The catalyst could be effectively removed after polymerization, resulting in very low content of transition metal in the polymer product.

The application scope of the supported catalyst for monomers is an important factor in the practical use. To expand the application scope of the cross-linked polyacrylic resin supported cobalt catalytic system, polymerizations of *n*-butyl acrylate, ethyl methacrylate and styrene catalyzed by the supported cobalt catalyst without any additional soluble deactivator or ligand were carried out. Using the supported cobalt catalyst, block copolymers PBA-b-PMMA, PS-b-PMMA and fluorinated functional copolymer PS-b-PFNEMA were also synthesized. Polymer products with very low residual transition metal contents were achieved.

Experimental

Materials

Macroporous cross-linked polyacrylic resin, DK110 (9.5 mmol/g $-COO^{-}Na^{+}$ groups), was purchased from Shanghai Huazhen Science and Technology Company. 2-[(perfluorononenyl)oxyl] ethyl methacrylate (FNEMA) was synthesized from 2-hydroxyethyl methacrylate and hexafluoropropene trimer (from Sigma). Other materials were purchased from Sinopharm Chemical Reagent Co. Ltd. *n*-Butyl acrylate (BA, 99%) and ethyl methacrylate (EMA, 99%) were vacuum distilled from CaH_2, respectively. Styrene (St, 99%) and methyl methacrylate (MMA, 99%) were washed with 5% NaOH solution, dried over anhydrous $MgSO_4$, vacuum distilled from CaH_2, respectively. *N*, *N*-Dimethylformamide (DMF) was dried by 4A molecular sieve and anhydrous $MgSO_4$ and vacuum distilled. The initiator *p*-toluenesulfonyl chloride (*p*-TsCl) was recrystallized twice in petroleum ether. Other chemicals m-xylene, α,α,α-trifluorotoluene and ethyl 2-bromoisobutyrate (EtBrIB) were used without further treatment.

Preparation of supported cobalt (II) catalyst

97.8 mg of $CoCl_2 \cdot 6H_2O$ (0.376 mmol) were put in 10 ml of deionized water, and then 1.0 g of resin DK110 was added. After reaction for 12 h, the resin became red. Then the resin was washed with 10 ml of deionized water. Later it was carefully ground into 2–5 μm and vacuum dried at 90 °C, blue supported catalyst DK110/Co(II) was achieved.

Polymerization procedure

DK110/Co(II), monomer, solvent, initiator *p*-TsCl or EtBrIB were added into a 50 ml dried round-bottom flask. The flask was sealed with a rubber septum and bubbled with high-purity nitrogen for 15 min to remove the oxygen. Then the flask was immersed in an oil bath maintained at the desired temperature and stirred. At different time intervals, samples were withdrawn from the flask using a degassed syringe and cooled down to stop the polymerization in order to measure the monomer conversion later by gas chromatograph (GC). Polymers were obtained after the samples being centrifuged at the rate of 5000 rpm for 5 min to remove the catalyst and being dried under vacuum at 60 °C.

Synthesis of PBA-b-PMMA

Using the synthesized PBA-Cl as macroinitiator, the polymerization of MMA catalyzed by DK110/Co(II) was performed under the following conditions:

temperature 90 °C, $[MMA]_0/[PBA\text{-}Cl]_0/[Co(II)]_0 = 100/1/1$, $[MMA] = 1.88 \times 10^{-2}$ mol, m-xylene [MMA/m-xylene = 1/6 (v/v)] as solvent.

Synthesis of PS-b-PMMA

Using the synthesized PS-Cl as macroinitiator, the polymerization of MMA catalyzed by DK110/Co(II) was performed under the following conditions: temperature 90 °C, $[MMA]_0/[PS\text{-}Cl]_0/[Co(II)]_0 = 100/1/1$, $[MMA]_0 = 3.76 \times 10^{-2}$ mol, m-xylene [MMA/m-xylene = 1/6 (v/v)] as solvent.

Synthesis of PS-b-PFNEMA

Using the synthesized PS-Cl as macroinitiator, the polymerization of FNEMA catalyzed by DK110/Co(II) was carried out under the following conditions: temperature 90 °C, $[FNEMA]_0/[PS\text{-}Cl]_0/[Co(II)]_0 = 100/1/1$, $[FNEMA]_0 = 1.88 \times 10^{-2}$ mol, α,α,α-trifluorotoluene and DMF (α,α,α-trifluorotoluene/DMF = 10/1, v/v) as solvent.

Characterization

The monomer conversion was measured on a GC (GC-9790II, Fuli Corp., China) equipped with a 3 mm × 3 m, OV-17 packing column and a thermal conductivity detector. The absolute molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined on a gel permeation chromatograph (GPC) system equipped with a Multi-angle Laser Light Scattering Instrument (DAWN EOS, Wyatt Technology Corp., USA), a Waters interferometric refractometer (Optilab DSP) and a Waters 515 HPLC pump. The samples were run in THF at 30 °C with a flow rate of 1.0 ml/min. The data were collected and analyzed with ASTRA software from Wyatt Technology. The ^{1}H NMR spectrum was recorded on a MERCURYplus 400 NMR spectrometer (Varian, Inc., USA) in $CDCl_3$ and TMS as a standard for chemical shifts. IR spectrum of the block copolymer was recorded on a FT-IR spectrometer (Paragon 1000, Perkin Elmer, Inc., USA). The concentration of transition metal residue in the polymer product was determined by inductively coupled plasma emission spectrometer (ICP) (Iris Advangtage 1000, USA). UV–Vis analysis was conducted on a UV–Vis spectrophotometer (TU-1901, China).

Results and discussion

Polymerization of *n*-butyl acrylate

Polyacrylate materials have various applications in the fields of coating, adhesive, finishing agent for fabric and cosmetics and so on. BA also is a common monomer for ATRP. The reported ATRP catalytic systems of BA were generally Cu based catalytic system [18–22] or Ni based catalytic system [23]. In this section, the

Table 1 Results of ATRP of *n*-butyl acrylate using DK110/Co(II) as catalytic system

Entry	$[BA]_0/[TsCl]_0/[Co(II)]_0$	Time (h)	Conv. (%)	$M_{n,exp}$ ($\times 10^3$)	$M_{n,th}$ ($\times 10^3$)	M_w/M_n	Cobalt residue (ppm)
1	156/1/1	24	81.1	47.03	16.22	1.19	<0.1
2[a]	78/1/1	48	72.3	15.90	7.23	1.16	<0.1

Reaction conditions: $[BA]_0 = 3.76 \times 10^{-2}$ mol, the amount of DK110/Co(II) = 0.5 g (DK110/Co(II) = 1.0 g/3.76×10^{-4} mol), BA/DMF = 1/6 (v/v), 90 °C

[a] BA/DMF = 1/12 (v/v)

polymerization of BA using supported cobalt based catalytic system was investigated.

Table 1 shows the results of ATRP of BA catalyzed by the supported cobalt catalyst. It can be seen that, the polymerization of BA was well controlled using DK110/Co(II) without any additional organic ligand or soluble deactivator. After polymerization for 24 h, the monomer conversion could reach to 81.1%. Although the experimental molecular weight ($M_{n,exp} = 47{,}030$) of PBA was higher than the predicted molecular weight ($M_{n,th} = 16{,}220$), the molecular weight distribution was rather narrow ($M_w/M_n = 1.19$). When the initial concentration of monomer was lower, narrower molecular weight distribution was obtained ($M_w/M_n = 1.16$).

Because the catalyst was solid and no soluble transition metal complex or ligand was presented in the polymerization system, the catalytic system could be easily removed from the polymerization mixture by simply centrifugation. To determine the concentration of catalyst residue in the polymer product, ICP analysis was carried out. As shown in Table 1, the transition metal residue in polymer product was lower than the detection limit of ICP (residue of Co < 0.1 ppm), indicating that high-purity polymer product could be easily prepared using the supported cobalt catalyst. To understand whether the catalyst leaked from the support or not, the following experiments were carried out: 1.0 g PBA, 0.5 g catalyst and 24 ml DMF were added into a flask. After oxygen removal with high-purified N_2, the flask was immersed into an oil bath at 90 °C and stirred for 24 h. Then the solid catalyst was removed by centrifugation immediately while it was hot. After the solution was dried, PBA was measured by ICP, and interestingly, no Co residue was detected, meaning its content was low enough or even zero. To confirm this result, another experiment was also carried out: the solid catalyst was added to DMF, and then the upper layer solution was analyzed by UV–Vis spectrometer using DMF as reference. No absorbance was detected. Then the system was heated at 90 °C for 24 h and the upper layer solution was withdrawn at 90 °C. Then the UV–Vis analysis was carried out at 90 °C with the heat unit of the spectrometer. Also, no absorbance of the solution was observed. Because Co(II) was bound with the resin by COO^-, and if no other ion presented in the solution, the Co ion could not leak from the solid support. Therefore, the catalyst residue in the polymer was low enough.

The first-order kinetic plots of polymerization of BA (Fig. 1) catalyzed by the supported cobalt catalyst, indicating that the radical concentration during polymerization maintained constant, which coincided with the character of ATRP. The

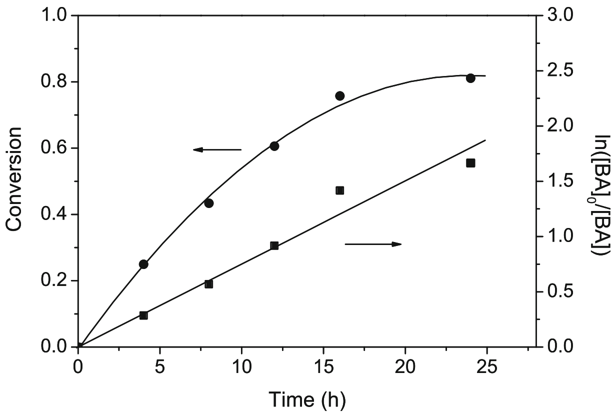

Fig. 1 Kinetic plot of polymerization of BA catalyzed by DK110/Co(II) at 90 °C without any additives (Experiment in Table 2, entry 1)

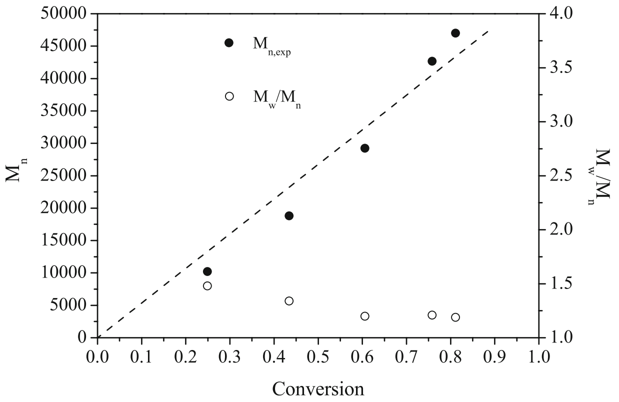

Fig. 2 Molecular weight and molecular weight distribution of PBA vs monomer conversion of the polymerization of n-butyl acrylate catalyzed by DK110/Co(II) (Experiment in Table 2, entry 1)

Table 2 Polymerization of styrene using DK110/Co(II) as catalytic system

Entry	Initiator	Time (h)	Conv. (%)	$M_{n,exp}$ ($\times10^3$)	$M_{n,th}$ ($\times10^3$)	M_w/M_n	f[a]	Co residue[b] (ppm)
1	p-TsCl	140	66.8	15.3	13.4	1.54	0.88	<0.1
2	EtBrIB	135	53.3	14.2	10.7	1.43	0.75	<0.1

Reaction conditions: $[St]_0/[initiator]_0/[Co(II)]_0 = 194/1/1$, $[St]_0 = 3.76 \times 10^{-2}$ mol, the amount of DK110/Co(II) = 0.5 g (DK110/Co(II) = 1.0 g/3.76×10^{-4} mol), St/m-xylene = 1/6 (v/v), 110 °C

[a] f: initiator efficiency calculated from $M_{n,th}/M_{n,exp}$

[b] Transition metal residue in polymer product determined by ICP

dependence of molecular weight and molecular weight distribution of PBA on monomer conversion is shown in Fig. 2. With the increase of monomer conversion, the molecular weight of PBA linearly increased and the molecular weight

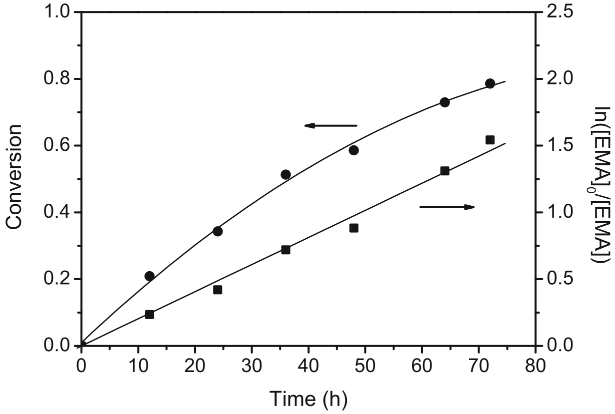

Fig. 3 Kinetic plot of polymerization of EMA catalyzed by DK110/Co(II) at 90 °C in DMF. $[EMA]_0/[TsCl]_0/[Co(II)]_0/[Cu(II)]_0 = 175/1/1/0.02$, $[EMA]_0 = 3.29 \times 10^{-2}$ mol, the amount of DK110/Co(II) = 0.5 g. EMA/DMF = 1/6 (v/v)

distribution decrease from 1.48 down to 1.19. This implied that the polymerization was well controlled and the polymerization was living.

Polymerization of ethyl methacrylate (EMA)

Poly(ethyl methacrylate) is also a very useful polymer material, which is of excellent optical property and weatherability. However, few ATRP of EMA has been reported. This section aimed to investigate the polymerization of EMA catalyzed by the supported cobalt catalyst and to achieve pure PEMA product.

Well-controlled polymerization of EMA also could be achieved using the supported cobalt (II) catalyst without addition any soluble ligand or other additive. After 72 h, the conversion of EMA reached to 78.6%. The experimental molecular weight ($M_{n,exp} = 20600$) of the obtained PEMA was close to the theoretical value ($M_{n,th} = 15700$), and the molecular weight distribution was relative narrow ($M_w/M_n = 1.26$). As no soluble catalytic system presented in the polymerization system, the solid catalyst could be effectively separated from the system by centrifugation method, resulting in very low residual catalyst (<0.1 ppm) in the PEMA product. Thus, pure PEMA material was obtained. Figure 3 shows the kinetic plots of polymerization of EMA catalyzed by the supported cobalt catalyst. The kinetic plots were linear, indicating that the radical concentration during polymerization maintained constant.

Molecular weight and molecular weight distribution of PEMA vs monomer conversion of the polymerization of ethyl methacrylate catalyzed by DK110/Co(II) is shown in Fig. 4. The corresponding GPC curves of PEMA are shown in Fig. 5. With the increase of EMA conversion from 34.3 to 78.6%, the corresponding molecular weight of PEMA increased from 10,900 to 20,600, while the molecular weight distribution decreased from 1.47 to 1.26. The linear increase of molecular weight of PEMA with the increase of monomer conversion and the molecular

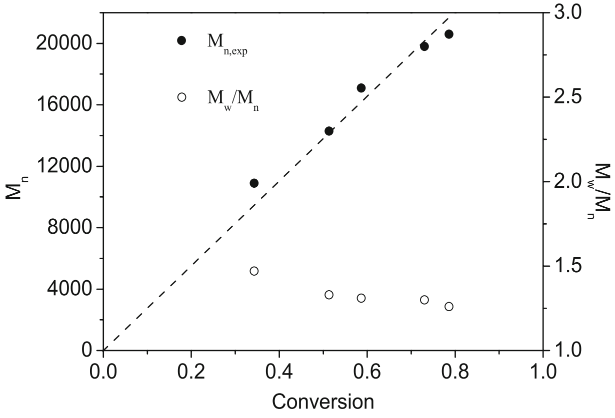

Fig. 4 Molecular weight and molecular weight distribution of PEMA versus monomer conversion of the polymerization of ethyl methacrylate catalyzed by DK110/Co(II)

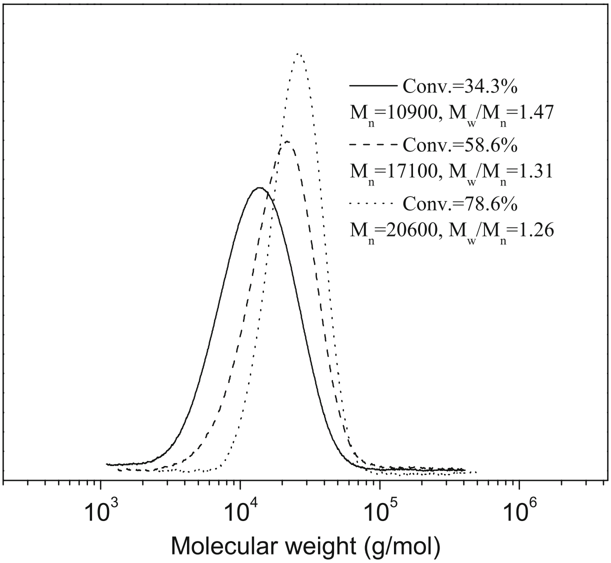

Fig. 5 GPC curves of PEMA obtained by DK110/Co(II) catalyst

weight distribution was in a low scope, elucidating the polymerization of EMA was well controlled.

Polymerization of styrene

The results of controlled radical polymerization of styrene are shown in Table 2. When p-TsCl was used as initiator, the molecular weight of PS was 15,300, close to the calculated value 13,400, indicating that the molecular weight of PS could be

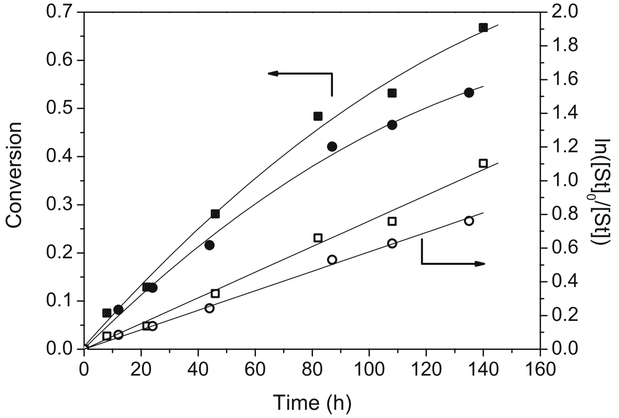

Fig. 6 Kinetic plots of polymerization of styrene catalyzed by DK110/Co(II) at 110 °C: (*filled and open square*) TsCl as initiator; (*filled and open cirlce*) EtBrIB as initiator

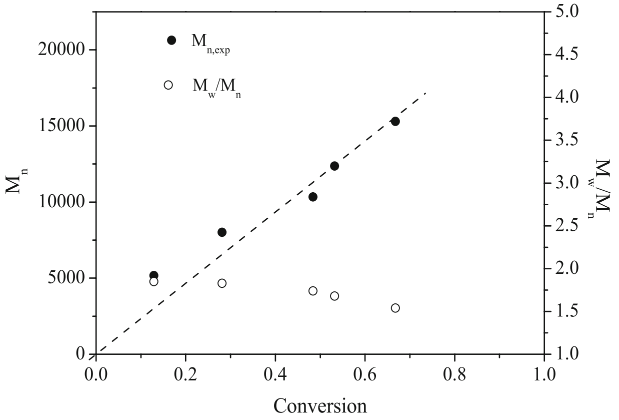

Fig. 7 Molecular weight and molecular weight distribution of PS vs monomer conversion of the polymerization of styrene catalyzed by DK110/Co(II) (entry 1 in Table 1)

well controlled, but the molecular weight distribution was a little broad ($M_w/M_n = 1.54$). Using EtBrIB as initiator, the PS molecular weight ($M_{n,exp} = 14,200$) agreed with the theoretical value ($M_{n,th} = 10,700$) and molecular weight distribution was ($M_w/M_n = 1.43$). The activity of styrene was lower than the (methyl)acrylate monomer, therefore, to get higher polymerization rate, higher temperature was needed (110 °C or higher). Under this condition, the radical concentration would increase and radical termination would occur. So, the molecular weight distribution was a little broad.

Figure 6 shows the kinetic plots of polymerization of styrene catalyzed by the supported cobalt catalyst. The kinetic plots were linear, indicating that the radical concentration was constant during the polymerization. Figure 7 shows the dependence of molecular weight and molecular weight distribution of PS upon

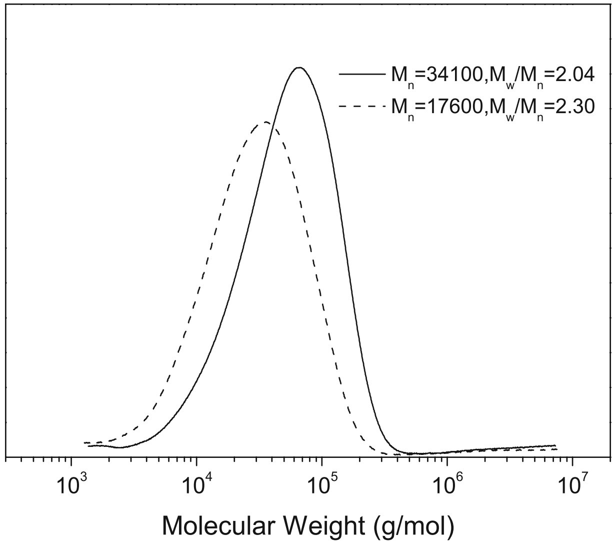

Fig. 8 GPC curves of PS. PS obtained by thermal self-initiation of styrene (*solid line*). PS obtained by addition of TsCl after thermal self-initiation polymerization of styrene for 48 h (*broken line*)

conversion of styrene catalyzed by DK110/Co(II). Although the molecular weight distribution of the final polymer was slightly broad ($M_w/M_n \sim 1.54$), molecular weight increased with the increase of styrene conversion and molecular weight distribution became narrower, indicating living feature of polymerization.

Under the experimental conditions (110 °C, 140 h), thermal self-initiation of styrene could occur. This was the reason why the molecular weight of PS was not high but the molecular weight distribution was broad. To prove this, the following experiments were carefully designed. First: styrene, solvent and catalyst without initiator were mixed and heated at 110 °C after oxygen removal. Polymerization of styrene under this condition occurred, indicating that self-initiation of styrene occurred. After 140 h, the conversion reached 65.2%. The GPC result showed that the molecular weight was 34,100 and the molecular weight distribution was 2.04 (Fig. 8). Second: the reaction system was the same as the above experiment. After reaction 48 h, the conversion reached 22.7%. And then initiator, TsCl was added. The reaction continued. After total 140 h, conversion reached 62.4%. The molecular weight was 17600, much lower than that of the system without initiator (Fig. 8). This indicated that initiator TsCl indeed participated in the polymerization with the catalyst. Because self-initiation of styrene also generated radical, after initiator TsCl was added, the catalyst reacted with TsCl and the corresponding deactivator generated. Thus the radical of thermal self-initiation could also be deactivated by the generated deactivator. Radical concentration increased with additional initiator, but at the same time the self-initiation radical could be deactivated, causing the concentration decrease. These two conversed processed resulted in little change of polymerization rate. When TsCl was added at the beginning, deactivator could form immediately, resulting in lower molecular weight (Table 2 entry 1).

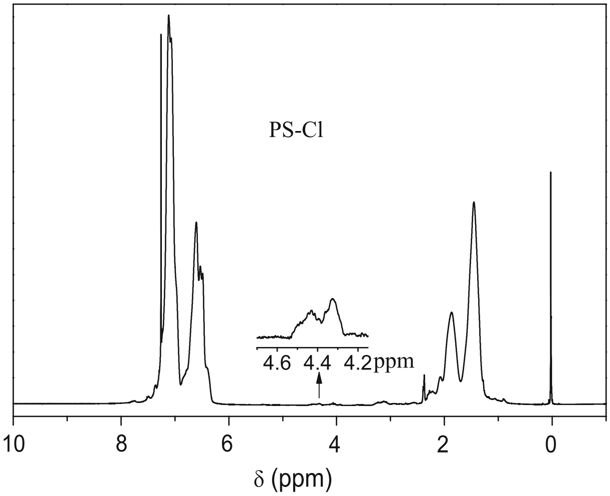

Fig. 9 ^{1}H NMR spectrum of PS obtained by DK110/Co(II)

^{1}H NMR spectroscopy analysis was performed to measure the chain terminal group of the obtained PS (Fig. 9). The characteristic signals of both the main chain of PS and the terminal styrene unit terminated by an ω-end chlorine atom appeared. The signals observed at 1.2–2.2 ppm were originated from the methene and methine protons of the main chain of PS, and the signals located at 6.2–7.4 ppm were assigned to the aromatic protons at phenyl of PS. The peak at 4.4 ppm was assigned to the methine proton of the terminal styrene unit containing an ω-end chlorine [24]. These results implied that the supported cobalt-catalyzed polymerization of styrene proceeded via an ATRP process.

Preparation of PBA-b-PMMA

Using the synthesized PBA ($M_n = 15900$, $M_w/M_n = 1.16$) as macroinitiator copolymerization of BA and MMA was carried out to synthesize diblock copolymer, PBA-b-PMMA. After 48 h, the conversion of MMA reached 81.9%. GPC curves of the macroinitiator PBA-Cl and the yielding diblock copolymer PBA-b-PMMA are shown in Fig. 10. After polymerization, the molecular weight of the yielding polymer increased. PBA-b-PMMA with well-controlled molecular weight ($M_n = 29{,}700$) and narrow molecular weight distribution ($M_w/M_n = 1.35$) was obtained. The experimental molecular weight of the block copolymer agreed well with the theoretical value ($M_{n,th} = 24{,}100$).

Preparation of PS-b-PMMA

The achieved PS-Cl ($M_n = 15300$, $M_w/M_n = 1.54$) was used as macroinitiator and polymerization of MMA catalyzed by DK110/Co(II) was conducted at 90 °C in m-xylene. GPC curves of the macroinitiator PS-Cl and the yielding diblock

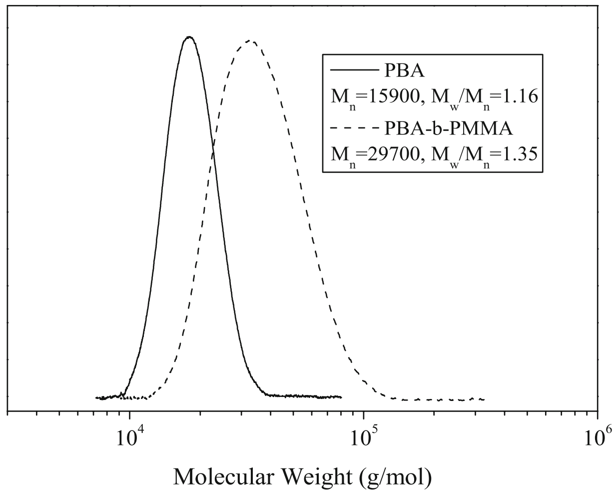

Fig. 10 GPC curves of PBA and the resulting PBA-b-PMMA obtained by DK110/Co(II) catalyst. Reaction conditions: temperature = 90 °C, $[MMA]_0/[PBA\text{-}Cl]_0/[Co(II)]_0 = 100/1/1$, $[MMA] = 1.88 \times 10^{-2}$ mol, MMA/m-xylene = 1/6

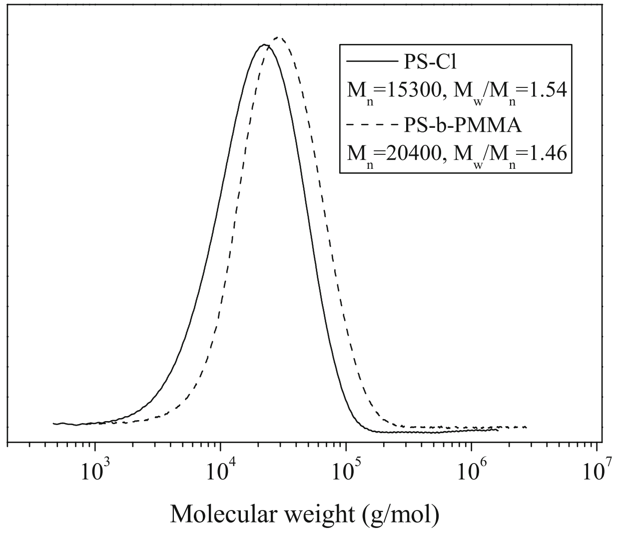

Fig. 11 GPC Curves of macroinitiator PS-Cl (*solid line*) and diblock copolymer PS-b-PMMA (*broken line*) obtained by DK110/Co(II). Temperature = 90 °C; $[MMA]_0/[PS\text{-}Cl]_0/[Co(II)]_0 = 100/1/1$; MMA/m-xylene = 1/6 (v/v)

copolymer PS-b-PMMA are shown in Fig. 11. After polymerization, the molecular weight of the yielding polymer increased. PS-b-PMMA with well-controlled molecular weight ($M_n = 20400$) and narrow molecular weight distribution ($M_w/M_n = 1.46$) was obtained.

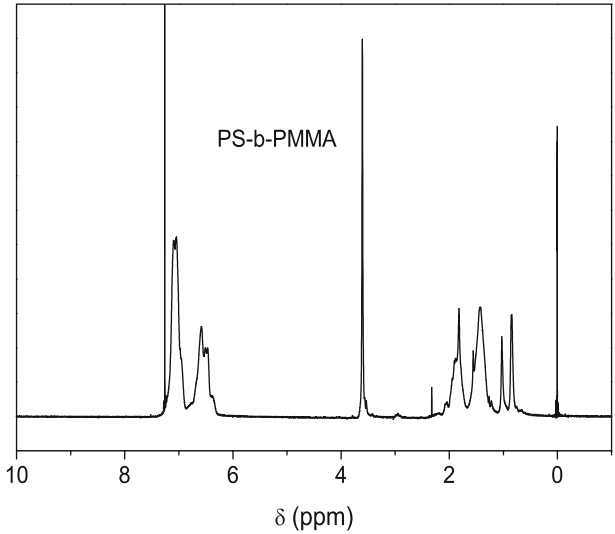

Fig. 12 ^{1}H NMR spectrum of copolymer PS-b-PMMA recorded at ambient temperature (solvent: $CDCl_3$, TMS as standard)

The diblock copolymer PS-b-PMMA was characterized by ^{1}H NMR spectroscopy (Fig. 12). The typical signals of PS and PMMA were observed for PS-b-PMMA. For the diblock copolymer, the chemical shift at around 3.6 ppm was assigned to the alkoxy protons and the signals at 0.8–1.1 ppm were attributed to methyl protons for PMMA. The signals at 1.2–2.2 ppm were assigned to the backbone CH_2 and CH of the copolymer. And the signals at 6.4–7.2 ppm were attributed to the aromatic protons. The ^{1}H NMR spectrum combined with the GPC results suggested that the diblock copolymerization were successfully synthesized and further confirmed that the polymerization catalyzed by the supported cobalt catalyst was "living". From the integration intensity ratio of the aromatic protons (6.2–7.4 ppm) of PS chain to the methoxy protons (3.6 ppm) of the PMMA chain, the molar ratio of styrene unit to MMA unit in diblock copolymer could be calculated. The molar ratio of styrene unit to MMA unit calculated from NMR (St:MMA = 0.771:0.229) was close to the value calculated from the GPC results (St:MMA = 0.743:0.257), implying that MMA was quantitatively initiated by the macroinitiator PS-Cl.

Preparation of PS-b-PFNEMA

In recent years, fluorinated polymer has attracted considerable interest because of their unique low surface energies, biocompatibility and biostability, low water absorptivity, lubricity, thermal and oxidative stability and nonsticking behavior [7]. To investigate the catalytic activity and controllability of the supported cobalt catalyst for polymerization of fluorinated monomer, polymerization of FNEMA using the prior synthesized PS-Cl (Mn = 7,600, Mw/Mn = 1.63) as macroinitiator was carried out. The GPC curves of macroinitiator PS-Cl and the resulting diblock

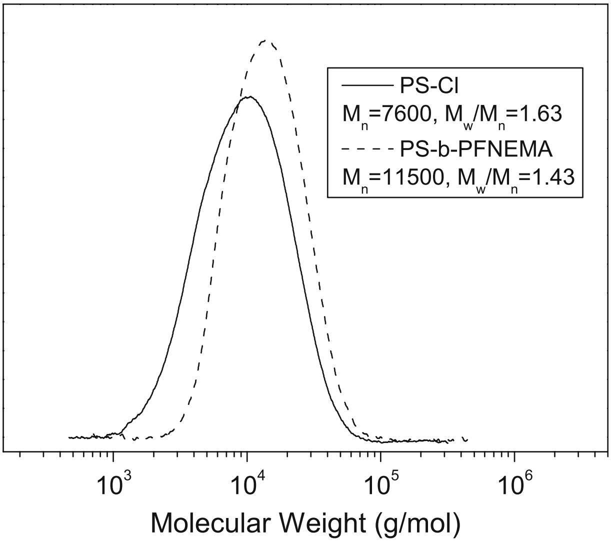

Fig. 13 GPC Curves of macroinitiator PS-Cl (*solid line*) and diblock copolymer PS-b-PMMA (*broken line*) obtained by DK110/Co(II). Temperature = 90 °C; $[FNEMA]_0/[PS\text{-}Cl]_0/[Co(II)]_0 = 100/1/1$; α,α,α-trifluorotoluene/DMF = 9/1, (v/v); FNEMA/solvent = 1/10 (v/v)

copolymer PS-b-PFNEMA are shown in Fig. 13. From Fig. 13 we can see that the molecular weight of the product increased after chain extension reaction. PS-b-PFNEMA with well-controlled molecular weight (Mn = 11,500) and narrow molecular weight distribution ($M_w/M_n = 1.43$) was obtained, which indicated that this catalyst system could also be applied in fluorinated copolymer synthesis. In addition, ICP result showed that the cobalt residue in the block copolymer was lower than 0.1 ppm, indicated that the catalyst was effectively removed by centrifugation.

The FTIR spectra of diblock copolymer PS-b-PFNEMA is shown in Fig. 14. The strong broad absorption peaks at 1,300–1,140 cm^{-1} were characteristic absorptions of R_F groups ($R_F = C_9F_{17}$). A single stretching band was observed near 1,738 cm^{-1} corresponding to the C = O stretching vibration of PFNEMA. The characteristic absorption bands at 3,090, 3,060, 3,030, 2,950, 2,850 cm^{-1} for Ar–H groups and 750, 690 cm^{-1} for monosubstituted benzene indicated the success in synthesis of diblock copolymer PS-b-PFNEMA.

Conclusion

Supported cobalt (II) catalyst through electrovalent bond could be applied as effective ATRP catalyst for the different types of vinyl monomers: styrene, n-butyl acrylate and ethyl methacrylate. Controlled radical polymerizations were successfully carried out using supported cobalt (II) catalyst without any other organic ligand or soluble deactivator. Molecular weights of polymers linearly increased

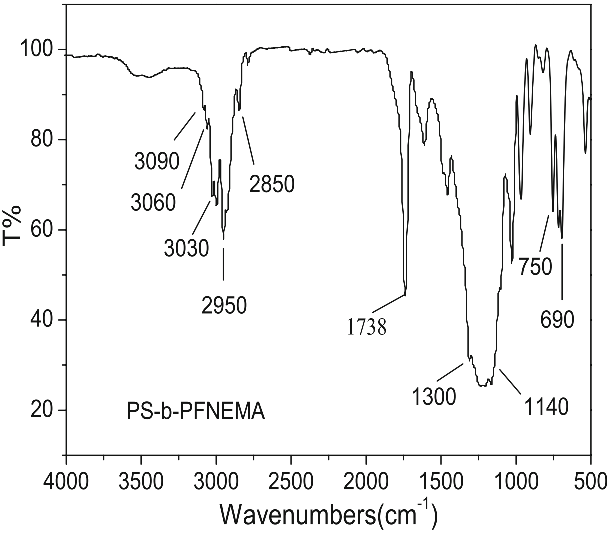

Fig. 14 FT-IR spectrum of copolymer PS-b-PFNEMA

with the increase of monomer conversion, indicating living polymerization fashion. Using the obtained polymers as macroinitiators, well-defined copolymers PS-b-PMMA, PS-b-PFNEMA and PBA-b-PMMA could be synthesized. As the catalyst was supported on solid support, it could be conveniently removed from the polymerization system after polymerization and the catalyst residue in polymer was lower than 0.1 ppm, which was benefit for the application of ATRP to produce pure (co) polymers on large scale.

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