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Polyallene-based graft copolymer via 6-methyl-1,2-heptadien-4-ol and methyl methacrylate

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Abstract

A series of well-defined graft copolymers with a polyallene-based backbone and poly(methyl methacrylate) side chains were synthesized by the combination of living coordination polymerization of 6-methyl-1,2-heptadien-4-ol and atom transfer radical polymerization of methyl methacrylate. We first prepared poly(alcohol) with polyallene repeating units via 6-methyl-1,2-heptadien-4-ol by living coordination polymerization initiated by $[(\eta^3\text{-allyl})NiOCOCF_3]_2$, followed by transforming the pendant hydroxyl groups into halogen-containing ATRP initiation groups. Next, grafting-from route was used for the synthesis of the well-defined graft copolymer with excellent solubility: poly(methyl methacrylate) was grafted to the backbone via ATRP of methyl methacrylate. This kind of graft copolymer is the first example of graft copolymer via allene derivative and methacrylic monomer.

Keywords: Graft copolymer; ATRP; Polyallene

1. Introduction

It is well known that allene derivatives have cumulated double bonds so that they can be regarded as the isomers of propargyl derivatives. If either part (1,2- or 2,3-) of the cumulated double bonds can be selectively polymerized, a kind of polymer possessing reactive exomethylene substituents directly linked to the main chain can be obtained. Many researches focused on this kind of reactive polymer since they can be used as attractive synthetic precursors for the functional materials due to the versatility of the addition reactions of the double bonds [1].

Allene derivatives can be polymerized by many different methods including the radical, cationic, coordination and zwitterionic polymerizations, etc. [2]. It was found that the controllability of the radical or the cationic polymerization of allene derivatives was poor. Endo and his co-workers developed the living coordination polymerization of allene derivatives, which can proceed under mild conditions to give the well-defined polymers in high yields using $[(\eta^3\text{-allyl})NiOCOCF_3]_2$ as the initiator [3–6]. By this way, molecular weight of the polymer can be controlled by the feed ratio of the monomer to the initiator and molecular weight distribution of the polymer can be kept narrow. Also, the block copolymerization of allene derivatives were carried out due to the stability of the living π-allylnickel end group and the molecular weights can be tuned by the feed ratio [7]. Since $[(\eta^3\text{-allyl})NiOCOCF_3]_2$ can not initiate the polymerization of vinyl monomers such as styrene, acrylate and methacrylate, etc. well-defined copolymers of allene derivatives and vinyl monomers can not be synthesized through this kind of nickel-catalyzed living polymerization. On the other hand, it is easy to introduce the reactive double bonds into the conventional polymers by the radical copolymerization of allene derivatives and vinyl monomers [8]. However, it was very difficult to control the molecular weights of the copolymers and the molecular weight distributions were generally broad.

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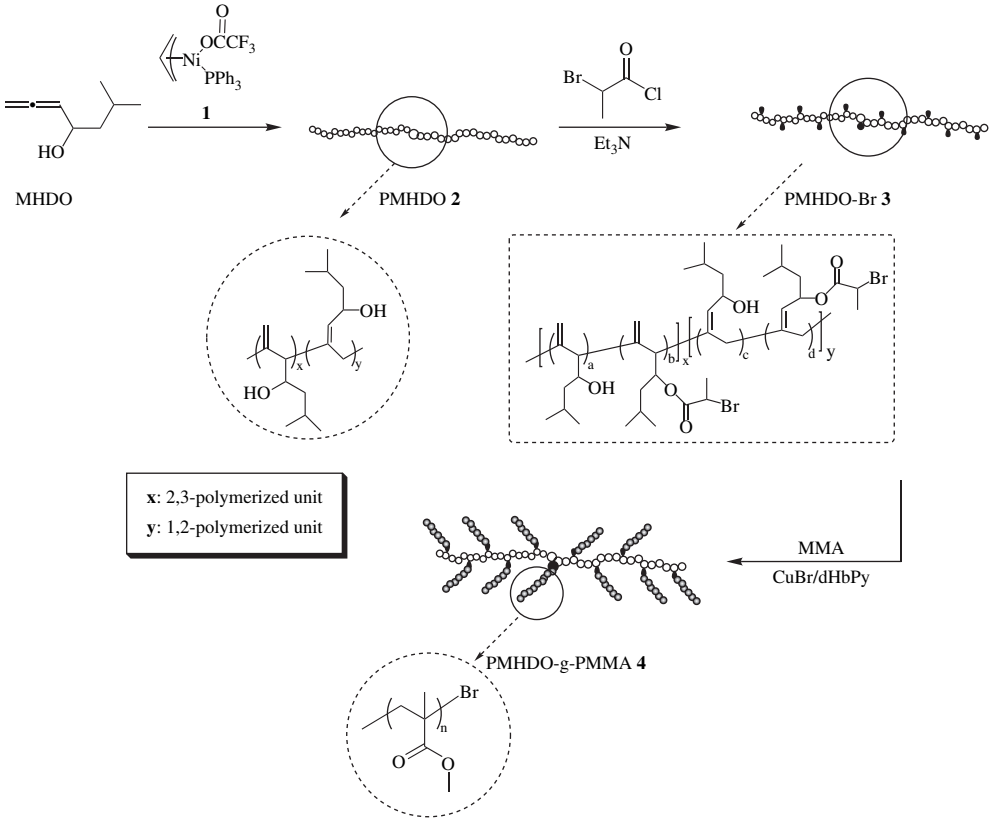
Until now, only few literatures reported the synthesis of the well-defined graft copolymers containing polyallene backbone [9–11] and none has reported the synthesis of well-defined graft copolymers via allene derivatives and common methacrylic monomers. Generally, polymer chemists employed three strategies, including grafting-through, grafting-onto and grafting-from, to synthesize the graft copolymers [12]. The graft copolymers can be obtained via the polymerization of the macromonomers using the grafting-through strategy, the resulting graft copolymers via conventional radical polymerization of the macromonomers possessed a broad chain-length distribution [13]; living polymerization of the macromonomers yielded the well-defined graft copolymers with low molecular weights [14]. The grafting-onto technique is grafting of side chains onto the backbone by a coupling reaction, normally with insufficient grafting efficiency [15]. The grafting-from method utilized the pendant initiation groups on the backbone to initiate the polymerization of another monomer to form side chains [16]. The development of atom transfer radical polymerization (ATRP) [17–19] and modified ATRP [20,21] has made it feasible to prepare the versatile comb copolymers with the well-defined molecular architectures from the grafting-through [22,23] and grafting-from strategies [24,25]. In particular, side chains can be formed in a well-defined way via ATRP initiated by the pendant halogen-containing initiating groups on the backbone through the grafting-from strategy, the living characteristic of ATRP enabled it to control both the molecular weights and the molecular weight distributions of side chains.

In this paper, we first synthesized poly(6-methyl-1,2-heptadien-4-ol) bearing hydroxyl groups by nickel-catalyzed living coordination polymerization. The pendant hydroxyl groups can be easily converted to the pendant halogen-containing ATRP initiation groups by reacting with 2-bromopropionyl chloride. Grafting-from technology was employed to form poly(methyl methacrylate) branches by ATRP of methyl methacrylate (Scheme 1). These grafted PMMA branches might can be used to improve the processability of linear PMMA (such as commercial PMMA like Plexiglas®) due to their structure properties.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, Aldrich, 99%) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over $CaCl_2$ and distilled twice over CaH_2 under reduced pressure prior to use. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over CH_3CO_2H at room temperature, followed by washing the solid with ethanol, diethyl ether and acetone prior to drying at 40 °C *in vacuo* for 1 day. Triethylamine (Aldrich, 99.5%) was dried over KOH for several days followed by distilling from CaH_2 under N_2 atmosphere prior to use. Tetrahydrofuran (THF) and toluene were dried over CaH_2 for several days and distilled from sodium and benzophenone under N_2 prior to use. Bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$, Aldrich),



Scheme 1. Synthesis of PMHDO-*g*-PMMA graft copolymer.

2-bromopropionyl chloride (2-BPC, Aldrich) and 4-(dimethylamino) pyridine (DMAP, Aldrich, 99%) were used as received. Triphenyl phosphorate (PPh_3, Acros, 99%) was recrystallized with CH_2Cl_2/hexane. Allyl trifluoroacetate (Aldrich, 98%) was re-distilled prior to use. 6-Methyl-1,2-heptadien-4-ol (MHDO) [26] and diheptyl-2,2′-bipyridine (dHbpy) [27] were synthesized according to previous literatures.

2.2. Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with 4 cm^{-1} resolution. All ^1H NMR and ^{13}C NMR analyses were performed on a Varian Mercury 300 spectrometer (300 MHz) in $CDCl_3$, TMS (^1H NMR) and $CDCl_3$ (^{13}C NMR) were used as the internal standards. Bromine content was determined by the titration with $Hg(NO_3)_2$. Conversion of methyl methacrylate was determined by ^1H NMR according to the previous literature [28]. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI) and a set of Waters Styragel columns (HR3, HR4 and HR5, 7.8 × 300 mm). GPC measurements were carried out at 35 °C using THF as eluent with a 1.0 mL/min flow rate. The system was calibrated with polystyrene standards. Thermal properties were characterized on a Perkin–Elmer Pyris 1 differential scanning calorimeter (DSC) under N_2 purge with a 10 °C/min heating rate.

2.3. Living coordination polymerization of MHDO

Poly(6-methyl-1,2-heptadien-4-ol) (PMHDO) was prepared by living coordination of MHDO initiated by [(η^3-allyl)NiOCOCF$_3$]$_2$ **1** under N_2. To a 50 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum, $Ni(COD)_2$ (0.2337 g, 0.85 mmol), allyl trifluoroacetate (0.11 mL, 0.85 mmol) and toluene (20 mL) were added. The mixture reacted under N_2 at room temperature for 20 min. Next, PPh_3 (1.0 M in toluene, 0.85 mL, 0.85 mmol) and MHDO (6.48 mL, 42.5 mmol, [MHDO]/[**1**] = 50) were introduced via a gas-tight syringe at 0 °C. The flask was immersed into an oil bath thermostated at 50 °C to start the polymerization. The polymerization lasted for 3 h. The solution was precipitated into hexane. After repeated purification by dissolving in THF and precipitating in hexane for three times, 4.7090 g PMHDO **2** was obtained with a yield of 87.9%. GPC: $M_n = 6600$, $M_w/M_n = 1.15$. DSC: $T_g = 92.3$ °C. FT-IR: ν (cm^{-1}): 3403, 2956, 2919, 2869, 1637, 1468, 1367, 1048. ^1H NMR: δ (ppm): 0.90 (6H, $-CH(CH_3)_2$), 1.25–2.00 (3H, $-CH_2CH(CH_3)_2$), 2.34 (2H × y, $=C-CH_2-C=$), 2.88 (1H × x, $=C-CH-C=$), 3.70 (1H × x, $>CH-OH$), 4.40 (1H × y, $>CH-OH$), 5.39 (2H × x, $=CH_2$ and 1H × y, $-CH=$). ^{13}C NMR: δ (ppm): 23.3, 24.5, 47.2, 66.7, 113.8, 132.6, 141.0, 147.3.

2.4. Synthesis of PMHDO–Br macroinitiator

In a 50 mL sealed three-neck flask, PMHDO **2** (0.2000 g, 1.59 mmol −OH groups, $M_n = 6600$, $M_w/M_n = 1.15$) was dissolved in a mixture of 20 mL dry THF, anhydrous triethylamine (0.26 mL, 1.91 mmol) and DMAP (0.0194 g, 0.159 mmol). Next, 2-bromopropionyl chloride (0.19 mL, 1.91 mmol) was added dropwise at 0 °C. The mixture was stirred at 0 °C for 1 h followed by stirring at room temperature for another 12 h. The mixture was diluted with 20 mL THF. The solution was concentrated, and precipitated into hexane. The product was dried *in vacuo* to give 0.1900 g PMHDO–Br **3** macroinitiator. GPC: $M_n = 8500$, $M_w/M_n = 1.10$. DSC: $T_g = 84.8$ °C. FT-IR: ν (cm^{-1}): 2958, 2932, 2871, 1736, 1638, 1468, 1369, 1342, 1162. EA: Br%: 30.60%. ^1H NMR: δ (ppm): 0.92 (6H, $-CH(CH_3)_2$), 1.30–1.78 (3H, $-CH_2CH(CH_3)_2$ and 3H, $CHBr(CH_3)CO$), 2.00–4.00 (2H × y, $=C-CH_2-C=$ and 1H × x, $=C-CH-C=$), 4.37 (1H × x, $>CH-OCO-$ and 1H, $CHBr(CH_3)CO$), 4.99 (1H × y, $>CH-OCO-$), 5.40 (2H × x, $=CH_2$ and 1H × y, $-CH=$). ^{13}C NMR: δ (ppm): 21.6, 23.3, 24.5, 40.2, 43.9, 52.6, 71.6, 115.4, 127.1, 129.4, 137.8, 143.4, 169.3.

2.5. Graft copolymerization of methyl methacrylate

In a typical procedure, a 25 mL dried Schlenk flask (flame-dried under vacuum prior to use and sealed with a rubber septum) was charged with CuBr (0.0134 g, 0.0933 mmol). The flask was degassed and CuBr was kept under N_2. Next, dHbpy (0.0658 g, 0.1887 mmol) and methyl methacrylate (5 mL, 46.65 mmol) which were stored under N_2, were introduced via a gas-tight syringe. Finally, PMHDO–Br **3** (0.0244 g, 0.0933 mmol ATRP initiation groups, $M_n = 8500$, $M_w/M_n = 1.10$, Br% = 30.60%) was added. The flask was degassed by three cycles of freeze-pump-thaw followed by immersing the flask into an oil bath thermostated at 50 °C. After 2 h, the polymerization was terminated by putting the flask into liquid nitrogen. The reaction mixture was diluted by THF and filtered through an alumina column to remove the catalyst. The solution was concentrated and precipitated into methanol. The final product, poly(6-methyl-1,2-heptadien-4-ol)-*g*-poly(methyl methacrylate) (PMHDO-*g*-PMMA **4d**), was obtained after drying *in vacuo*. GPC: $M_n = 125{,}800$, $M_w/M_n = 1.40$. FT-IR: ν (cm^{-1}): 2996, 2983, 2873, 1732, 1605, 1486, 1450, 1436, 1387, 1369, 1273, 1193, 917. ^1H NMR: δ (ppm): 0.80, 0.96, 1.18 (3H, $-CH_2C(CH_3)-$, 6H, $-CH(CH_3)_2$ and 3H, $-CH(CH_3)CO$), 1.33–2.23 (3H, $-CH_2CH(CH_3)_2$, and 2H, $-CH_2C(CH_3)-$), 2.23–3.30 (2H × y, $=C-CH_2-C=$, 1H × x, $=C-CH-C=$ and 1H, $-CH(CH_3)CO$), 3.53 (3H, $-COOCH_3$), 4.26 (1H × x, $>CH-OCO-$), 4.70–6.00 (1H × y, $>CH-OCO-$, 2H × x, $=CH_2$ and 1H × y, $-CH=$).

3. Results and discussion

3.1. Synthesis of PMHDO backbone

PMHDO homopolymer was prepared by living coordination polymerization of MHDO initiated by [(η^3-allyl)NiOCOCF$_3$]$_2$ **1** ([MHDO]/[**1**] = 50) in the presence of PPh_3 ([PPh_3]/[**1**] = 1.0) at 50 °C using toluene as the solvent. The polymerization was complete in 3 h with a yield of 87.9%.

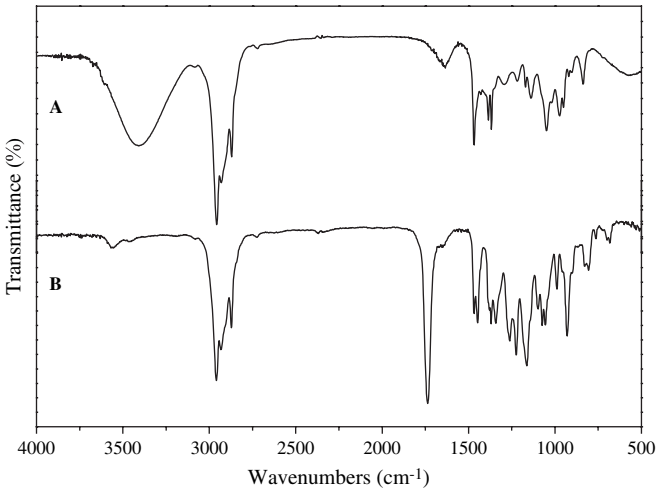


Fig. 1. FT-IR of PMHDO **2** (A) and PMHDO–Br **3** (Br% = 30.60%) (B).

The chemical structure of PMHDO homopolymer was examined by FT-IR, ^{1}H NMR and ^{13}C NMR, especially the signals of the double bonds. FT-IR spectrum of PMHDO **2** is shown in Fig. 1(A). The peaks of hydroxyl group and double bond appeared at 3403 and 1637 cm^{-1}, respectively. Fig. 2(A) depicts ^{1}H NMR spectrum of PMHDO **2**, it can be clearly seen a broad peak of the protons of the double bond appeared at around 5.39 ppm. Additionally, it was found that PMHDO **2** consisted of both 1,2- and 2,3-polymerized units (labelled as y and x in Scheme 1) from ^{1}H NMR spectrum. The ratio of 1,2-polymerized units to 2,3-polymerized units was calculated from the integration area ratio of the peak at 4.40 ppm to the peak at 3.70 ppm. The result is 60:40, which means PMHDO **2** contained 60% 1,2-polymerized units and 40% 2,3-polymerized units. The signals of the carbons of double bond appeared at 113.8 ppm, 132.6 ppm, 141.0 ppm and 147.3 ppm in ^{13}C NMR spectrum (Fig. 3(A)). All these evidences confirmed the structure of PMHDO homopolymer.

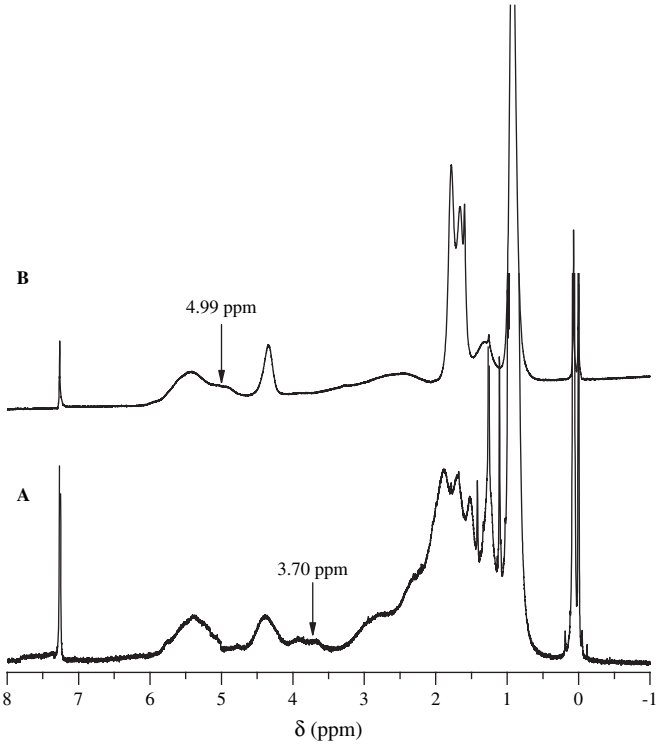


Fig. 2. ^{1}H NMR spectra of PMHDO **2** (A) and PMHDO–Br **3** (B) in $CDCl_3$.

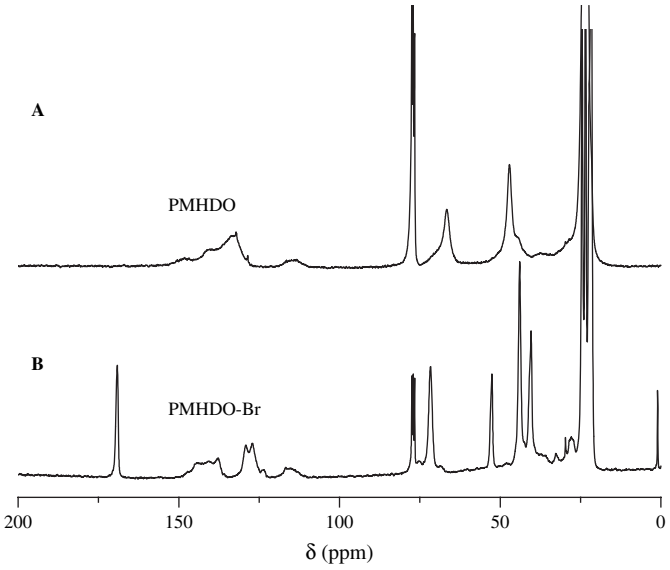


Fig. 3. ^{13}C NMR spectra of PMHDO **2** (A) and PMHDO–Br **3** (B) in $CDCl_3$.

PMHDO homopolymer can dissolve in common organic solvents such as THF, CH_2Cl_2, methanol, DMSO, acetone, etc. but it is insoluble in hexane and water.

The characteristic of nickel-catalyzed living coordination polymerization was demonstrated by the result of GPC since the molecular weight distribution of PMHDO homopolymer is as narrow as 1.15. We also have studied the evolution of the molecular weights with the feed ratios of the monomer to the initiator (Fig. 4). It was found that the molecular weights of PMHDO homopolymers increased linearly with the increase of the feed ratio and the molecular weight distributions remained narrow throughout the polymerization ($M_w/M_n < 1.23$). These results verified the living nature of the present polymerization system [7].

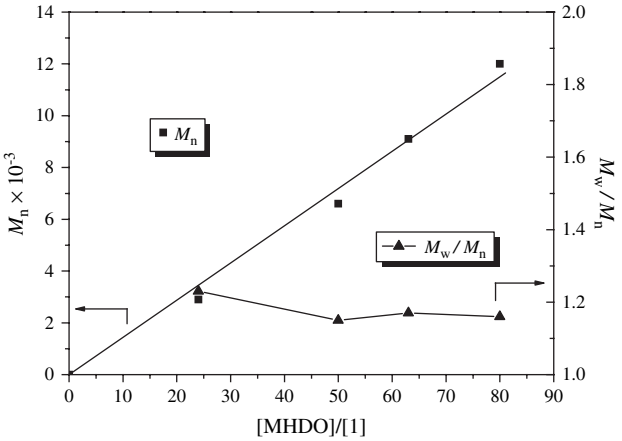


Fig. 4. Dependence of M_n and M_w/M_n of PMHDO on the feed ratio.

3.2. Synthesis and characterization of macroinitiator

The halogen-containing ATRP initiation groups were introduced into PMHDO backbone by the esterification of the pendant hydroxyl groups of PMHDO **2** with 2-bromopropionyl chloride. The formed macroinitiator was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR.

It was found that the stretching peak of the pendant hydroxyl group around 3403 cm^{-1} completely disappeared in FT-IR spectrum (Fig. 1(B)) after the reaction with 2-bromopropionyl chloride, which means the pendant hydroxyl groups of PMHDO **2** were all esterified. The existence of the carbonyl group can be demonstrated by a new strong peak at 1736 cm^{-1}. Also, the peak of double bond remained at 1638 cm^{-1}. ^{1}H NMR spectrum of PMHDO–Br **3** is shown in Fig. 2(B). The peak of the proton of >C*H*–OH of 2,3-polymerized units at 3.70 ppm disappeared and the new peak of the proton of >C*H*–OCO of 2,3-polymerized units overlapped with that of the proton of >C*H*–Br at 4.37 ppm. It was also found that a new peak attributed to the proton of >C*H*–OCO of 1,2-polymerized units appeared at 4.99 ppm. However, this peak overlapped with that of the protons of the double bond and thus it is difficult to calculate the esterification degree of the pendant hydroxyl groups from ^{1}H NMR spectrum. A new peak was found at 169.4 ppm in ^{13}C NMR spectrum of PMHDO–Br **3** as shown in Fig. 3(B). This peak was attributed to the carbon of the carbonyl (–O*C*OCH(CH$_3$)Br), which evidenced the introduction of bromopropionyl groups.

The molecular weight of PMHDO–Br **3** is higher than that of PMHDO **2** after the reaction with 2-bromopropionyl chloride due to the introduction of bromopropionyl groups. As we can see from Fig. 5, only a unimodal peak appeared in GPC curve of PMOMA–Br **3** after the reaction with 2-bromopropionyl chloride, which means the architecture of PMHDO polymer backbone was not altered.

The approximate grafted ATRP initiation group density was calculated from the data of bromine content of PMHDO–Br **3** [29]. The structure of PMHDO–Br **3** is as indicated in Scheme 2.

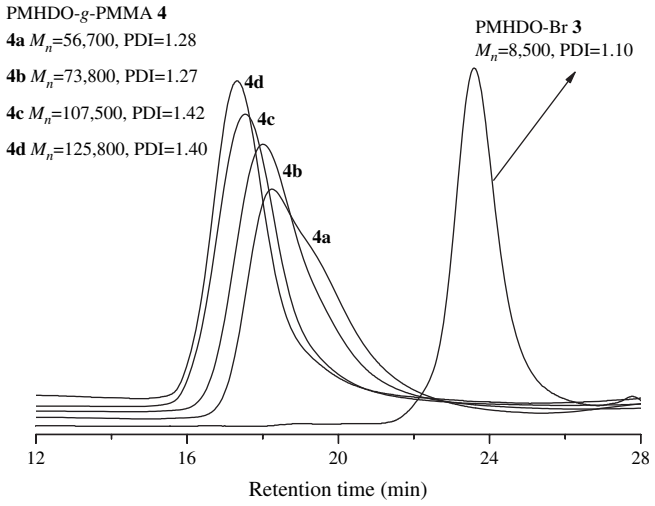
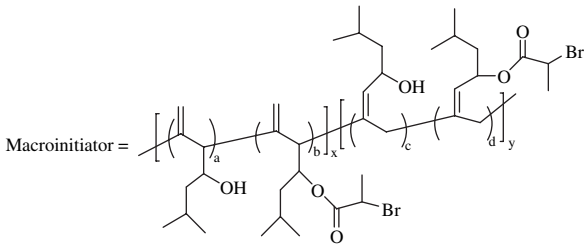


Fig. 5. GPC traces of PMHDO–Br **3** and PMHDO-*g*-PS **4** in THF.



Scheme 2. Chemical structure of PMHDO–Br macroinitiator.

The molecular weight of the parts "b" and "d" (incorporated with ATRP initiation group) is 261 and the molecular weight of the parts "a" and "c" (not esterified) is 126. The ratio of (a + c)/(b + d) was calculated to be 0.003/1 according to the following equation (Br% = 30.60%):

$$[80(b+d)]/[126(a+c)+261(b+d)] = 0.3060 \quad (1)$$

This result illustrated that the approximate grafted ATRP initiation group density was 1/1 (the denominator represents the total repeating units of PMHDO backbone and the numerator represents the repeating units which have been grafted by ATRP initiation group), which coincided with the result of FT-IR.

From the above results, we can conclude that PMHDO **2** was successfully converted to PMHDO–Br **3** macroinitiator and the halogen-containing ATRP initiation groups were introduced to every repeating unit of PMHDO backbone.

3.3. Synthesis of PMHDO-g-PMMA graft copolymer

ATRP of MMA was initiated by the totally esterified PMHDO–Br **3** macroinitiator ($M_n = 8500$, $M_w/M_n = 1.10$, Br% = 30.60%) at 50 °C as listed in Table 1. All the molecular weights of the resulting graft copolymers were much higher than that of PMOMA–Br **3** macroinitiator, which concludes that the polymerization of St was performed. The molecular weights of graft copolymers increased with the extending polymerization time, which is characteristic of ATRP.

From the data of conversion of methyl methacrylate listed in Table 1, the semilogarithmic plot of Ln([M]$_0$/[M]) *vs.* time was drawn in Fig. 6. It can be seen that the apparent polymerization rate is first order with respect to the concentration

Table 1
Synthesis of graft copolymers initiated by PMHDO **3** macroinitiator[a]

Copolymer	Time (h)	Conversion[b] (%)	M_n[c] (g/mol)	M_w/M_n[c]
4a	0.5	2.0	56,700	1.28
4b	1.0	3.0	73,800	1.27
4c	1.5	5.0	107,500	1.42
4d	2.0	7.0	125,800	1.40

[a] Initiated by PMHDO–Br **3** macroinitiator ($M_n = 8500$, $M_w/M_n = 1.10$, Br% = 30.60%, grafted ATRP initiation group density: 1/1) in bulk at 50 °C, [MMA]:[Br group]:[CuBr]:[PMDETA] = 500:1:1:2.
[b] Determined by ^{1}H NMR.
[c] Measured by GPC in THF at 35 °C.

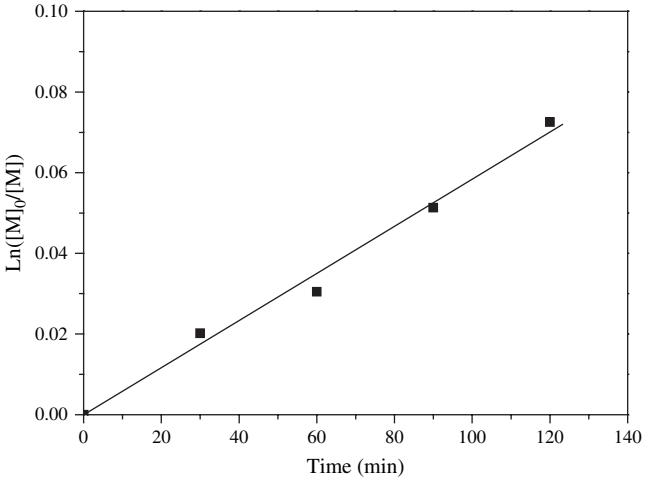


Fig. 6. Kinetic plot for ATRP of methyl methacrylate initiated by PMHDO–Br **3**.

of styrene. This phenomenon accorded with the characteristic of ATRP.

The resulting graft copolymer was characterized by ^{1}H NMR. Fig. 7 presents ^{1}H NMR spectrum of the graft copolymer in $CDCl_3$. The signals of the corresponding protons of PMHDO backbone and PMMA side chains were found in the spectrum. A new strong peak arose at 3.53 ppm, which was ascribed to the protons of $-OCH_3$ of PMMA side chains. The signal between 4.70 ppm and 6.00 ppm showed that the double bonds of the backbone were retained after ATRP.

Since ATRP initiation groups were introduced to every repeating unit of PMHDO backbone (the approximate grafted ATRP initiation group density was 1/1), the radical–radical coupling termination might occur more easily compared with the general ATRP [16,30]. To suppress the intermolecular coupling reactions, a high feed ratio of the monomer to the initiation group and a low conversion of MMA (<10%) were employed in our studies, which is a common method used in previous studies [12,16,30–32]. All graft copolymers showed unimodal and symmetrical GPC curves (Fig. 5) with narrow molecular weight distributions ($M_w/M_n \leq 1.40$), which are characteristic of ATRP [17] and also indicated that intermolecular coupling reactions could be neglected [30].

All the results confirmed that well-controlled ATRP of methyl methacrylate initiated by PMHDO–Br **3** macroinitiator was successful and resulted in the well-defined PMHDO-*g*-PMMA **4** graft copolymers.

3.4. Properties of graft copolymer

Solubility tests were run for PMHDO-*g*-PMMA **4** graft copolymers with different molecular weights in common solvents. The results showed that PMHDO-*g*-PMMA **4** graft copolymer exhibits excellent solubility in tetrahydrofuran, chloroform, dichloromethane and acetone. However, PMHDO-*g*-PMMA **4** graft copolymer is insoluble in diethyl ether, methanol and water.

DSC thermogram of PMHDO-*g*-PMMA **4** graft copolymer is shown in Fig. 8. Two different T_gs' were observed at 62.5 °C and 107.2 °C. The higher T_g at 107.2 °C was attributed to PMMA branches, which was similar with that of PMMA homopolymer [33]. Another T_g at 62.5 °C was attributed to PMHDO backbone, which was much lower than that of PMHDO **2** homopolymer [11] (92.3 °C, as shown in Fig. 8) since the hydroxyl groups of PMHDO **2** homopolymer were converted to the ester groups during the synthesis of PMHDO–Br **3** macroinitiator. Also, it is much lower than that of PMHDO–Br **3** macroinitiator (84.8 °C, as shown in Fig. 8) due to the shift of bromine atom to the end of PMMA branch after ATRP of MMA. This phenomenon is similar with that of the T_g difference between poly(vinyl alcohol) and poly(vinyl acetate). Also, the existence of two different T_gs' indicated a bulk micro-phase separation exists in the graft copolymer.

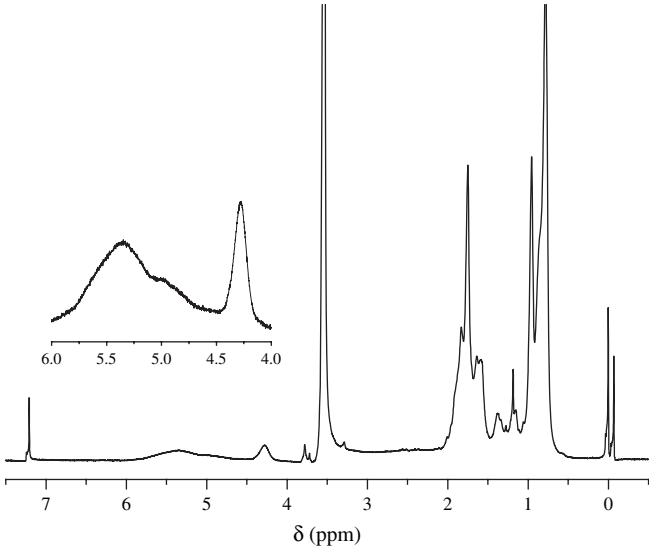


Fig. 7. ^{1}H NMR spectrum of PMHDO-*g*-PMMA **4** in $CDCl_3$.

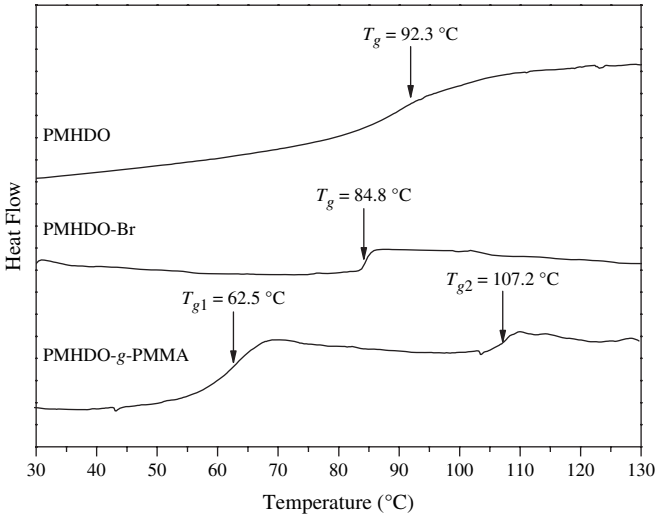


Fig. 8. DSC curves of PMHDO **2**, PMHDO–Br **3** and PMHDO-*g*-PMMA **4**.

4. Conclusion

A series of well-defined graft copolymers via 6-methyl-1,2-heptadien-4-ol and methyl methacrylate were synthesized by the combination of living coordination polymerization and ATRP. Narrow-dispersed poly(alcohol) with polyallene repeating units was firstly synthesized by living coordination polymerization. A further esterification of hydroxyl groups with 2-bromopropionyl chloride resulted in the macroinitiator. The final graft copolymer was obtained by ATRP of methyl methacrylate initiated by the macroinitiator. This kind of graft copolymer is the first example of graft copolymer via allene derivative and methacrylic monomer.

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