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Homogeneous reverse atom transfer radical polymerization of glycidyl methacrylate and ring-opening reaction of the pendant oxirane ring

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Abstract

The homogeneous reverse atom transfer radical polymerization (reverse ATRP) of glycidyl methacrylate (GMA) was carried out in bulk, using 2,2′-azobisisobutyronitrile (AIBN) as the initiator and *N*,*N*-*n*-butyldithiocarbamate copper ($Cu(SC(S)N(C_4H_9)_2)_2$) as the catalyst. The polymerization showed typical controlled/‘living’ polymerization behavior, i.e. first-order kinetics, well-controlled molecular weight (M_n) and narrow molecular weight distribution (M_w/M_n). ^{1}H NMR and IR spectra showed that the pendant epoxy groups in PGMA polymer remained intact throughout the polymerization of GMA. A phosphorated PGMA (PPGMA) polymer was obtained by phosphonation reaction of the pendant epoxy groups in PGMA with diphenylphosphinic chloride (DPPC). Thermal behavior of the PPGMA was studied by TG and DTG. A major DTG peak at 340 °C was observed for the PPGMA.

Keywords: Reverse ATRP; Glycidyl methacrylate; Copper (II) *N*,*N*-*n*-butyldithiocarbamate

1. Introduction

Atom transfer radical polymerization (ATRP) is an efficient method to synthesize polymers with well-controlled molecular weight, narrow molecular weight distribution and novel architecture. ATRPs of a wide range of vinyl monomers have been reported [1–8]. To overcome the drawbacks of normal ATRP, e.g. toxic halide initiators and easy oxidation of reduced-state metal catalysts, reverse atom transfer radical polymerization (reverse ATRP) was introduced [5,9,10]. In reverse ATRP, radical initiators (e.g. AIBN, BPO and C–C type thermal iniferter) and suitable oxidized transition-metal compounds (e.g. $CuCl_2$, $CuBr_2$ and $Fe(SC(S)NEt_2)_3$) were used to initiate the polymerizations of vinyl monomers. A great deal of excellent work on the reverse ATRP using transition-metal compounds as the catalyst systems has been reported [11–18]. Nishimura et al. reported a living polymerization of styrene using a halogen-free initiating system, which consists of AIBN and a transition metal dithiocarbamate $Mt(SC(S)NR_2)_n$ (Mt = Fe(III), Ru(III), Cu(II); R = ethyl or benzyl; $n = 2$ or 3) [11]. Qiu et al. reported the living radical polymerizations of methyl methacrylate and styrene in $Fe(SC(S)NEt_2)_3$ [12], $Cu(I)(SC(S)NEt_2)$/bpy [13,14], and $Cu(II)(SC(S)NEt_2)Cl$/bpy [15,16] catalyst systems. It is noted that the polymers obtained above have an ultraviolet light sensitive ω-$SC(S)NR_2$ group, and that the extra ligand is dispensable in the reverse ATRP systems [12].

Glycidyl methacrylate (GMA) is a useful monomer because the epoxy group can undergo ring-opening reaction with various nucleophiles [19–27]. Several types of controlled polymerizations, such as group transfer polymerization (GTP) [28], nitroxide-mediated polymerization (NMP) [29], ATRP [30], and reverse addition-fragmentation chain transfer (RAFT) [31], have been used in the polymerization of GMA. However, the ATRP of GMA in the presence of extra ligand (i.e. *N*-alkyl-2-pyridylmethanimine) was usually sensitive to the different components present in the polymerization mixture, such as the initiator, catalyst, ligand and solvent [32,33]. A ligand-free system may help to solve this problem.

Polymers with phosphonate or phosphate groups in the main chain or side chain attract great interest for their inherent flame resistance [34], and are also expected to be new functional ultraviolet (UV)-curable materials [35]. In our previous work, we reported the reverse ATRP of methyl methacrylate using *N*,*N*-*n*-butyl dithiocarbamate copper ($Cu(SC(S)N(C_4H_9)_2)_2$) as the new catalyst [36]. This paper presents: (i) reverse ATRP of GMA without any extra ligand, using AIBN and $Cu(SC(S)N(C_4H_9)_2)_2$ as the initiating system, and (ii) synthesis

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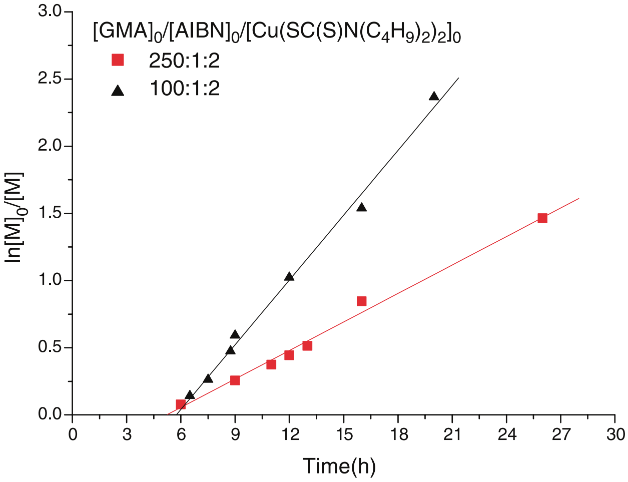


Fig. 1. Kinetics of reverse ATRP of GMA in bulk at different molar ratios of $[GMA]_0/[AIBN]_0/[Cu(SC(S)N(C_4H_9)_2)_2]_0$ at 70 °C.

of phosphorus-containing polymer via ring-opening reaction of the pendant epoxy groups in the well-defined PGMA with diphenylphosphinic chloride (DPPC).

2. Experimental section

2.1. Materials

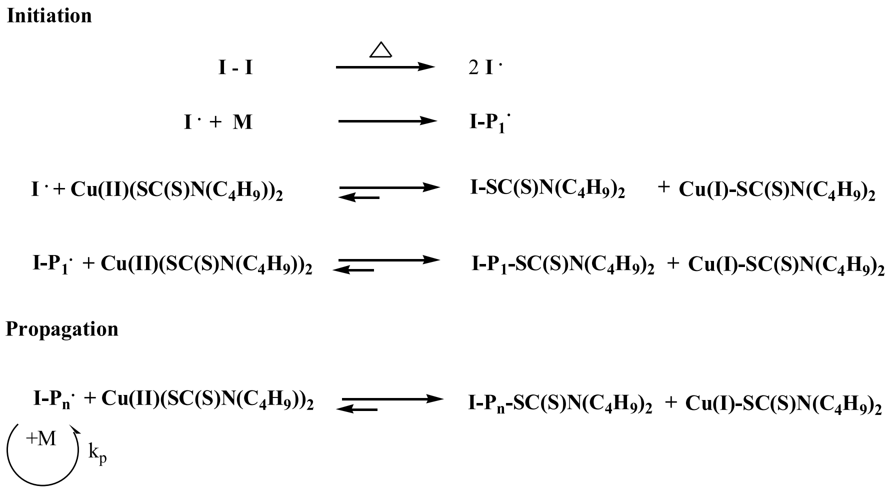
Glycidyl methacrylate (GMA, 98%, Jihua Suzhou Anli Chemicals Co. Ltd, China) was distilled under reduced pressure before use. 2,2′-Azobisisobutyronitrile (AIBN, 99%, Shanghai Chemical Reagent Co. Ltd, China) and Copper(II) *N*, *N*-*n*-butyl dithiocarbamate copper, ($Cu(S_2CN(C_4H_9)_2)_2$), 96%, Wuxi Chemical Factory, China) were recrystallized twice in ethanol and dried under reduced pressure at room temperature. Diphenylphosphinic chloride (DPPC, 98%, Aldrich), tetrahydrofuran (THF, analytical reagent), tetra-*n*-butylammonium bromide (TBAB, 99%, Shanghai Chemical Reagent Co. Ltd, China), petrol ether, methanol and *n*-hexane (commercially available) were used as received. All other chemicals and solvents (technical grade) were used after standard purification procedures.

2.2. Characterizations

Conversion of monomer was determined gravimetrically. The number-average molecular weights and molecular weight distributions of the polymers were measured on a Waters 1515 gel permeation chromatography (GPC), equipped with refractive-index detector and HR1, HR3 and HR4 columns. THF was used as the eluent at a flow rate of 1.0 mL min^{-1} at 30 °C. Monodispersed poly(methyl methacrylate) standards with a molecular weight range of 100–500,000 were used to generate the calibration curve. ^{1}H NMR spectra of the polymers were measured on an Inova 400-MHz NMR instrument with tetramenthylsilane (TMS) as the internal standard in $CDCl_3$ at ambient temperature. The Fourier transfer infrared (FT-IR) spectra were measured on a Perkin–Elmer 2000 FT-IR spectrometer. Thermogravimetric analysis was carried out on a TA instrument SDT 2960 system at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere (100 mL min^{-1} of flow rate).

2.3. General procedure for the reverse ATRP of GMA

The reverse ATRP of GMA was carried out in bulk. A typical procedure of bulk polymerization was as follows. A dry ampule was filled with $Cu(SC(S)N(C_4H_9)_2)_2$ (0.1436 g, 0.3042 mmol), GMA (2.16 g, 15.21 mmol) and AIBN (0.0249 g, 0.1518 mmol). The contents were purged with argon for 15 min to eliminate the dissolved oxygen. The ampule was then flame-sealed and placed in an oil bath thermostated at the desired temperature. After the desired time, the ampule was quenched in ice water and opened. The contents were diluted with a little THF and precipitated into about 250 mL of petrol ether. The polymer was dried at room



Initiation

$$I\text{-}I \xrightarrow{\triangle} 2\,I^{\cdot}$$

$$I^{\cdot} + M \longrightarrow I\text{-}P_1^{\cdot}$$

$$I^{\cdot} + Cu(II)(SC(S)N(C_4H_9))_2 \rightleftharpoons I\text{-}SC(S)N(C_4H_9)_2 + Cu(I)\text{-}SC(S)N(C_4H_9)_2$$

$$I\text{-}P_1^{\cdot} + Cu(II)(SC(S)N(C_4H_9))_2 \rightleftharpoons I\text{-}P_1\text{-}SC(S)N(C_4H_9)_2 + Cu(I)\text{-}SC(S)N(C_4H_9)_2$$

Propagation

$$I\text{-}P_n^{\cdot} + Cu(II)(SC(S)N(C_4H_9))_2 \rightleftharpoons I\text{-}P_n\text{-}SC(S)N(C_4H_9)_2 + Cu(I)\text{-}SC(S)N(C_4H_9)_2$$

Scheme 1. Mechanism of reverse ATRP of GMA using $AIBN/Cu(SC(S)N(C_4H_9)_2)_2$ as the initiation system.

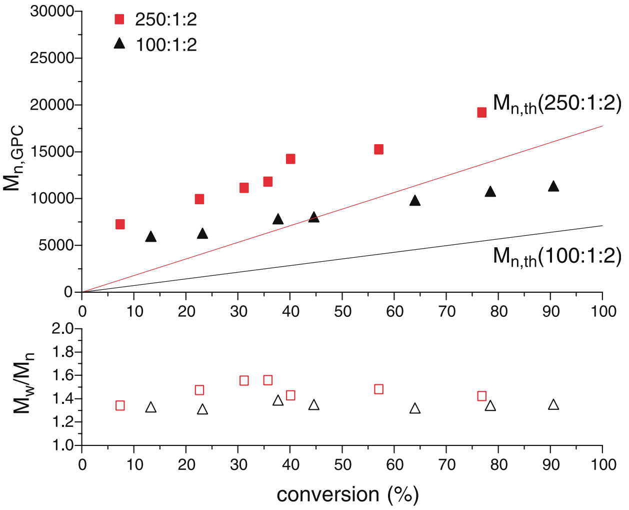


Fig. 2. The dependence of M_n and M_w/M_n on the monomer conversion at different molar ratios of $[GMA]_0/[AIBN]_0/[Cu(SC(S)N(C_4H_9)_2)_2]_0$. Conditions: bulk, 70 °C.

temperature under reduced pressure until a constant weight was obtained.

2.4. Phosphonation of PGMA

PGMA (1.00 g, 7.04 mmol epoxy ring) and tetra-*n*-butylammonium bromide (TBAB) (0.11 g, 0.35 mmol) were dissolved in 15 mL of THF when being stirred, then diphenylphosphinic chloride (DPPC) (1.67 g, 7.04 mmol) was added. The mixture was stirred for 24 h under reflux. At the end of the reaction, the reaction mixture was precipitated into a large amount of water. The crude product was then precipitated twice. The crude polymers were first dissolved in THF, precipitated into a large amount of methanol and then precipitated again in n-hexane. Finally, the purified polymers were dried under reduced pressure at room temperature until a constant weight was obtained. The yield was 1.96 g (73%).

3. Results and discussion

3.1. Reverse ATRP of GMA in the presence of AIBN and $Cu(SC(S)N(C_4H_9)_2)_2$

The reverse ATRP of GMA was carried out in bulk at 70 °C, using AIBN as the initiator and $Cu(SC(S)N(C_4H_9)_2)_2$ as the catalyst. The kinetic plots at two molar ratios, 250:1:2 and 100:1:2 ($[GMA]_0/[AIBN]_0/[Cu(SC(S)N(C_4H_9)_2)_2]_0$), are shown in Fig. 1. They both showed first-order for the polymerizations of GMA, indicating that the propagating radical concentrations were almost constant during the polymerizations. The polymerization rate increased significantly, as expected, with an increase of AIBN concentration. As shown in Fig. 1, an induction period of about 5.5 h in both cases was observed. It might be attributed to the fact that the establishment of equilibrium between active species and dormant species (Scheme 1) required a certain period of time in the presence of the higher initial Cu(II) concentration. Thus, at the beginning of the polymerization, $Cu(SC(S)N(C_4H_9)_2)_2$ was in great excess compared to the radicals generated by the decomposition of AIBN. As a result, the polymerization was retarded/inhibited during the induction period. The induction period was also found in the ATRP of MMA when Cu_2Y (Y = O, S, Se and Te) [37] and $CuBr_2$ [10] were used as catalysts.

The dependence of molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers on the monomer conversion is shown in Fig. 2. The molecular weights increased

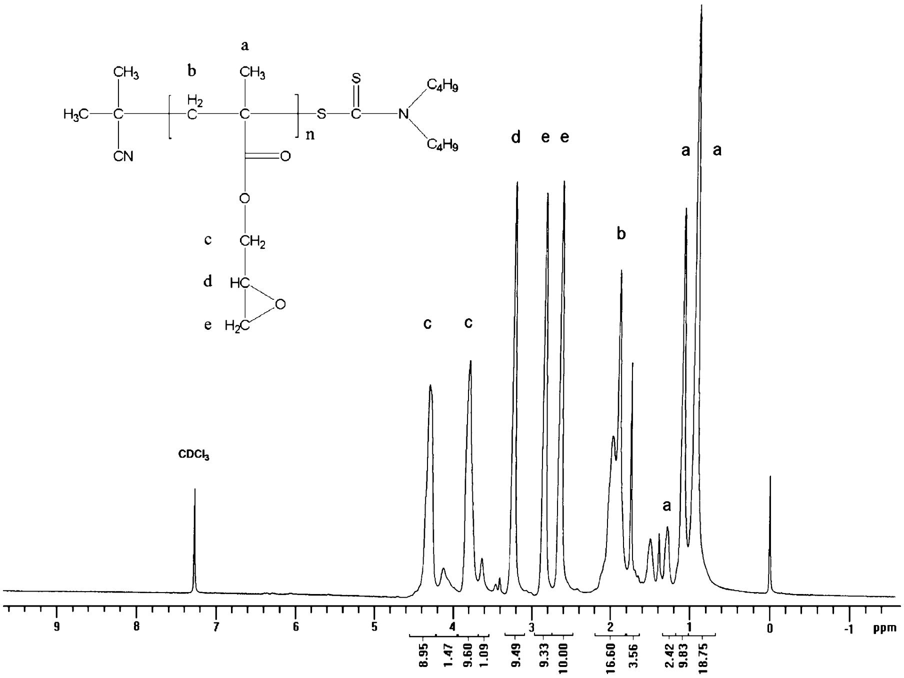
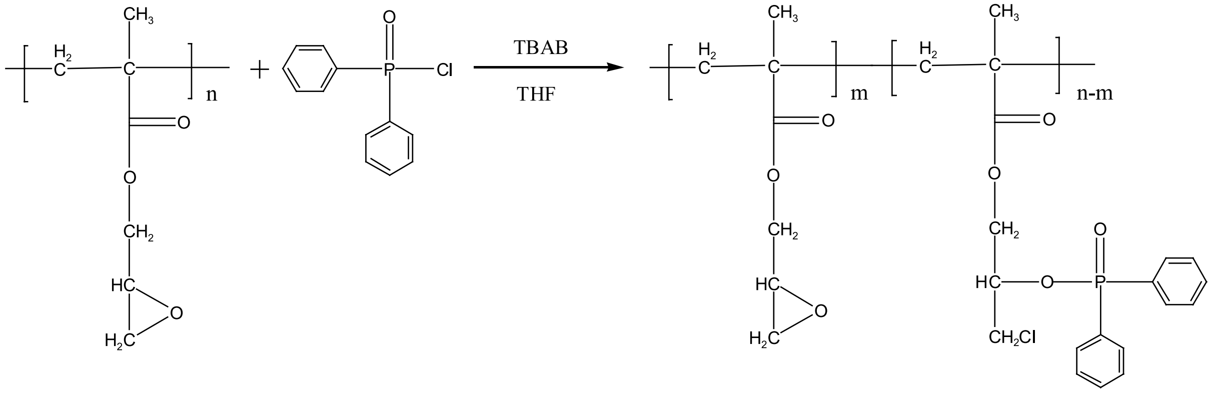


Fig. 3. ^1H NMR spectrum of PGMA (M_n = 6100, M_w/M_n = 1.29).



Scheme 2. Phosphonation of PGMA.

linearly with monomer conversion. However, they were higher than the corresponding theoretical values, determined by Eq. (1) on the assumption that one initiating radical from the thermal decomposition of AIBN generated one growing polymeric chain. It should be attributed to the lower thermal decomposition efficiency (about 0.6) of AIBN. Moreover, the corresponding M_w/M_n remained relatively narrow ($M_w/M_n = 1.29$–1.48).

$$M_{n,\mathrm{th}} = \left(\frac{[\mathrm{GMA}]_0}{2[\mathrm{AIBN}]_0}\right) \times \mathrm{MW}_{\mathrm{GMA}} \times \mathrm{conversion} \qquad (1)$$

3.2. ^{1}H NMR analysis of PGMA

The structure of PGMA was characterized by ^{1}H NMR spectroscopy, as shown in Fig. 3. The chemical shifts at $\delta = 0.94$, 1.09 and 1.29 ppm (a) can be assigned to the protons of the methyl, which splits into three peaks, i.e. isotactic, heterotactic and syndiotactic triads, respectively [38]. The chemical shift at $\delta = 1.75$ ppm (b) was attributable to the methylene group. Those at $\delta = 3.80$ and 4.31 ppm can be assigned to the –O–CH$_2$– group (c). The peaks at $\delta = 3.24$ ppm (d) and $\delta = 2.63$ and 2.84 ppm (e) can be assigned to the protons of the oxirane ring. Furthermore, the ratio of peak area of a, d and e is about 3:1:2. These results indicated that the epoxy groups in the PGMA remained intact throughout the polymerizations of GMA.

3.3. Phosphonation of PGMA

The epoxy groups in the PGMA reacted successfully with DPPC as described in Scheme 2. A 73% of conversion was

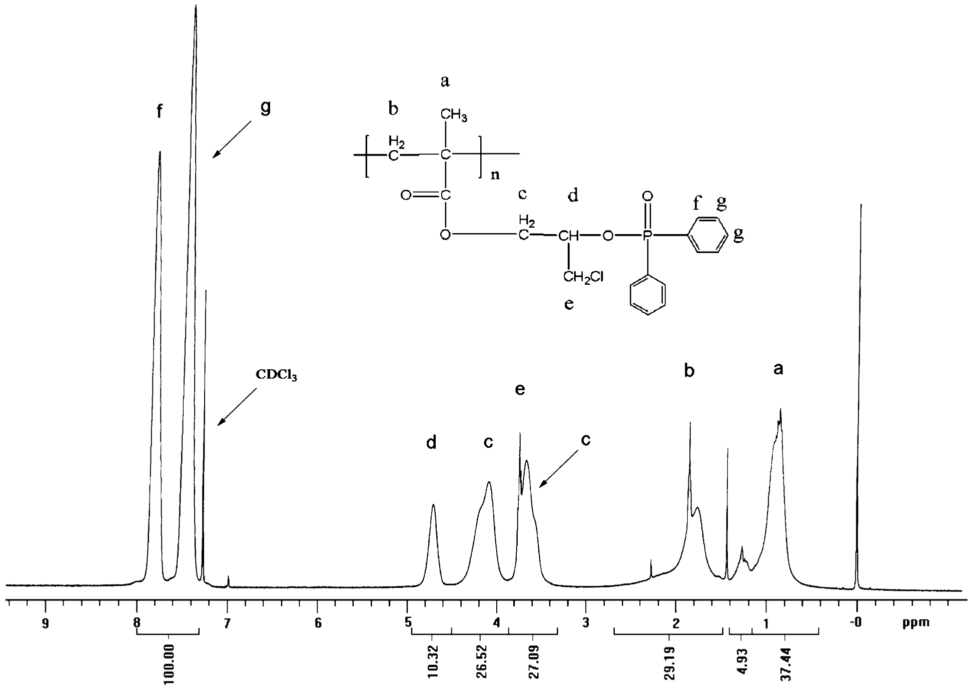


Fig. 4. ^{1}H NMR spectrum of PPGMA.

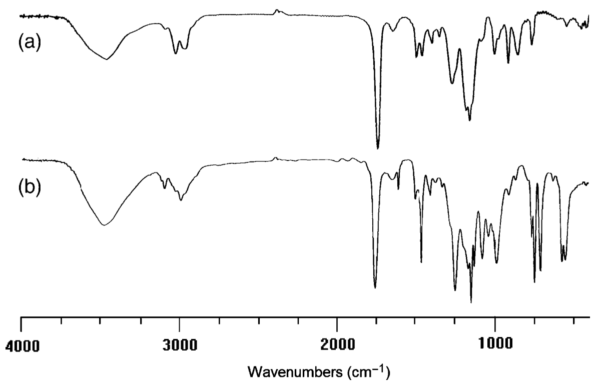


Fig. 5. IR spectra of (a) PGMA ($M_n = 6900$, $M_w/M_n = 1.33$) and (b) PPGMA.

obtained. The ratio of reacted oxirane rings can be calculated from ^{1}H NMR spectroscopy result (Fig. 4). The ratio of the aromatic protons to methyl group protons (a) was about 50:21, which indicated that approximately 71% of oxirane rings were opened by DPPC after phosphonation, in good agreement with the conversion (73%) of DPPC.

Structure of the resulting phosphorated polymer (PPGMA) was confirmed by ^{1}H NMR spectrum and IR spectrum. Fig. 4 shows the ^{1}H NMR spectrum of PPGMA. The proton peaks of the oxirane ring (2.85 ppm and 3.24 ppm) almost disappeared and new peaks appeared at about 3.75 ppm (e), 4.71 (d) ppm and 7.43, 7.80 ppm (aromatic protons f and g), respectively, which was consistent with a previous report [39]. Fig. 5 shows the IR spectra of the PGMA (a) and PPGMA (b). In Fig. 5(a), the absorption peaks at 1260 and 1730 cm^{-1} were associated with the presence of the oxirane ring and carbonyl group (O–C=O) in the PGMA, respectively. In Fig. 5(b), the strong absorption peak of the oxirane ring (1260 cm^{-1}) weakened significantly, and the new absorption peaks at 752 cm^{-1} (–CH_2Cl), 972 cm^{-1}, 1061 cm^{-1} (P–O–C), 1131, 1230 cm^{-1} (P=O), 1439 cm^{-1} (P-phenyl), 1592 cm^{-1} (C=C, aromatic) and 3058 cm^{-1} (C–H, aromatic) appeared, which indicated the presence of the PPGMA [39–41].

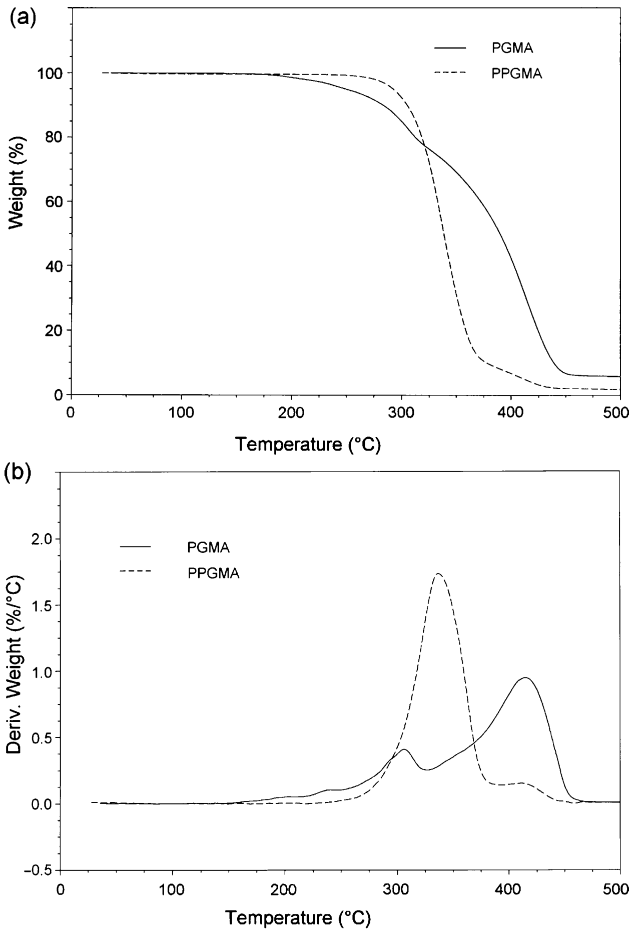


Fig. 6. TG (a) and DTG (b) thermograms for PGMA and PPGMA. Conditions: 10 °C min^{-1}, nitrogen atmosphere, 100 mL min^{-1}.

3.4. Thermal stability of the polymers

Fig. 6(a) and (b) shows the respective TG and DTG thermograms of PGMA and PPGMA. The PGMA prepared by AIBN/$Cu(SC(S)N(C_4H_9)_2)_2$ system showed a two-step degradation mode at 160–320 °C and 320–460 °C, respectively. Compared to the thermal degradation of PGMA, PPGMA functionalized by phosphorus-containing molecules showed a different thermal behavior. The PPGMA exhibited a major DTG peak at about 340 °C, which indicated that the resulting PPGMA had potential flame retardant properties. This may be due to some weak points introduced in the polymeric chains during phosphonation reaction, which led to thermal degradation at a lower temperature [42].

4. Conclusions

The homogeneous reverse ATRP of GMA were successfully carried out in bulk, using AIBN/$Cu(SC(S)N(C_4H_9)_2)_2$ as the initiating system without additional ligand and well-defined PGMA was obtained. The epoxy groups in the PGMA remained intact throughout the polymerization of GMA. Furthermore, PPGMA with pendent phosphonate groups could be obtained by ring-opening reaction of the epoxy groups with DPPC.

Acknowledgements

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