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Simple process for preparation of optically active methacrylates polymer with controlled molecular weight

Xing Juan Chen · Min Zhao · Shan Shan Gu

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Abstract Novel optically active methacrylates polymer with controlled molecular weight have been prepared simply by opening ring reaction of poly(glycidyl methacrylate) and S-(−)-α-methylbenzylamine. The structure of the novel optically active methacrylates polymer was characterized by FT-IR, and chiroptical properties of the polymer were characterized by polarimeter and circular dichroism spectrum. Thermogravimetry analysis and differential scanning calorimetry were employed to examine the thermal properties of the polymer. This preparation process was simple and the racemization of optically active monomers in preparation can be avoided. The molecular weight of optically active methacrylates polymer could be controlled by molecular weight of poly(glycidyl methacrylate) prepared by atom transfer radical polymerization.

Keywords Atom transfer radical polymerization · Optically active methacrylates polymer · Poly(glycidyl methacrylate) · Simple process for preparation

Introduction

Glycidyl methacrylate (GMA) is a commercially interesting functional monomer with a wide range of industrial applications. This monomer has been used to prepare homogeneous and heterogeneous polymer networks, which play an important role in polymer chemistry and technology, for example, in coatings, matrix resins, and adhesives [1–4]. Poly(glycidyl methacrylate) (PGMA) is of great interest, since the pendant oxirane ring can be opened and a range of functionalities could be introduced with subsequent reactions. In addition, such polymers have recently

X. J. Chen (✉) · M. Zhao · S. S. Gu
College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin, China
e-mail: xjchen23@yahoo.com.cn

gained special interest due to their superior performance in more specific applications such as drug and biomolecule binding [5].

The optically active polymers carrying chiral group moieties have the important potential applications as biocompatible materials, optical, and chemical functional materials [6, 7] and so on. The optically active polymers have generally been synthesized by radical polymerization or polycondensation of the corresponding optically active monomers, prepared in turn from optically active precursors [8–15]. But the racemization of optically active monomers occurred easily in the process for preparation of the monomers.

We reported here a simple approach toward the synthesis of optically active methacrylates polymer with controlled average-number molecular weight (M_n). The PGMA was synthesized first by atom transfer radical polymerization (ATRP). The novel optically active methacrylates polymer was synthesized by opening ring reaction of the epoxide group in the PGMA and S-(−)-α-methylbenzylamine. The results of the study are presented.

Experimental section

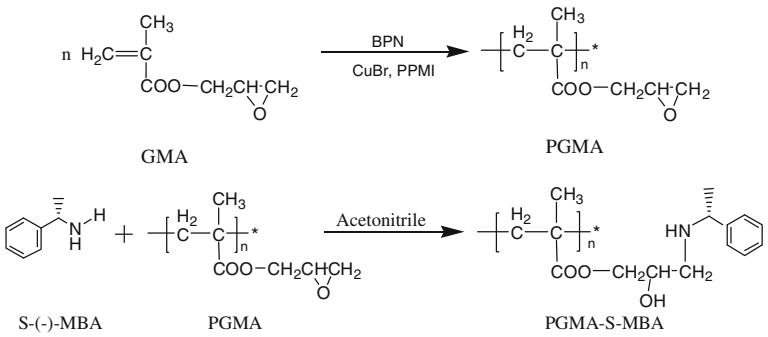
Materials

Glycidyl methacrylate (GMA, Aladdin reagent, China, 97%) was purified by vacuum distillation under reduced pressure and stored in a refrigerator under a nitrogen atmosphere. *n*-Propylamine (Tianjin Guangfu reagent, China, 98%), Pyridine-2-carboxaldehyde (Aldrich, 99%), Initiators 2-bromopropionitrile (BPN, Aldrich, 97%), Cuprous bromide (CuBr, Aldrich, 98%), Acetonitrile (Tianjin Kemiou reagent, China), and S-(−)-α-methylbenzylamine (S-(−)-MBA, Aladdin reagent, China, 98%) were all used as received. Diphenyl ether (Aladdin reagent, China) was dried over molecular sieves and stored in a nitrogen atmosphere. All other chemicals and solvents were purchased from commercial sources and used after standard purification procedures.

The preparation of optically active methacrylate polymer with controlled molecular weight

The PGMA with controlled molecular weight was first prepared by ATRP of GMA monomer. The ATR polymerization of GMA was carried out according to references [16, 17] by using Cu(I)Br complexed with *N*-*n*-propyl-2-pyridylmethanimine (PPMI) ligand as catalyst system and BPN as initiators in diphenyl ether solvent at an ambient temperature (30 °C). Ligand PPMI was prepared by *n*-propylamine and pyridine-2-carboxaldehyde according to references [18, 19].

The optically active methacrylate polymer with controlled molecular weight was prepared by opening ring reaction of epoxy group in PGMA and S-(−)-MBA. The synthesis of the optically active methacrylate polymer with controlled molecular weight is shown in Scheme 1.



Scheme 1 Synthesis of the optically active methacrylate polymer with controlled molecular weight

The general procedure of the opening ring reaction of epoxy group in PGMA and S-(−)-MBA is as follows:

A solution of PGMA was prepared by dissolving 0.50 g of the PGMA [M_n (GPC) = 10,497, M_w/M_n = 1.113, epoxy group 3.48 mmol] in 40 mL of acetonitrile. Then, 0.90 mL (6.99 mmol) of S-(−)-MBA was added in. The reaction mixture was degassed by three freeze–pump–thaw cycles and then heated at an appropriate temperature in an oil bath with stirring. The reaction was carried out for 24 h in N_2 atmosphere. The acetonitrile in reaction mixture was removed and raw product was poured into THF, the final product was isolated by precipitation into petroleum ether and filtered. Then, it was washed several times, filtered, and dried under reduced pressure at room temperature.

Characterization

The structures of ligand PPMI and polymer PGMA were determined by ^{1}H-NMR on a Bruker AVANCE-500 spectrometer operating at 500 MHz in $CDCl_3$ solvent with over 15,000 scans and a relaxation delay of 1 s. Chemical shifts are given in ppm from tetramethylsilane (TMS) as the internal reference. The conversion of GMA was determined by ^{1}H-NMR of polymer solution.

Molecular weights and molecular weight distributions of PGMA were measured by gel permeation chromatography (GPC). The GPC setup consisted of a Waters Delta 600 LC pump and a Waters 2414 differential refractive index detector. Calibration was based on linear polystyrene standards. The GPC eluent was HPLC grade THF at a flow rate of 1.0 mL/min. The instrument was set at 35 °C before starting the analysis.

The Fourier transform infrared (FT-IR) spectra of ligand PPMI and optically active methacrylate polymer with controlled molecular weight were recorded with Perkin Elmer SP 100 spectrometer onto KBr disks.

Specific rotation measurements were made on Perkin Elmer Model 341 polarimeter. Circular dichroism (CD) spectra were carried out at 25 °C in THF solutions on a JASCO J-815 dichrograph, using the cell path lengths of 1 cm for the 200–400 nm and solution concentrations of 0.6 mg/mL.

Thermal stabilities of the polymer were examined with utilizing TA instrument Q50 thermogravimetric analyzer (TGA). The samples (8–10 mg) were heated from room temperature to 800 °C under N_2 atmosphere at a scanning rate of 20 °C/min. Differential scanning calorimetry (DSC) measurements were carried out on a TA instrument DSC Q200 thermal analyzer system in crimped aluminum pans under N_2 atmosphere. The samples were heated to 150 °C and kept for 3 min at this temperature to eliminate the influence of thermal history, then cooled down to −30 °C, and then reheated to 150 °C, all at a rate of 10 °C/min. The actual values for the glass transition temperatures (T_g) were estimated as the temperatures at the midpoint of the line drawn between the temperature of the intersection of the initial tangent with the tangent drawn through the point of inflection of the trace and the temperature of the intersection of the tangent drawn through the point of inflection with the final tangent.

Results and discussion

The confirmation of structures on PPMI, PGMA and process of controlled/"living" radical polymerization

The structure of ligand PPMI and polymer PGMA prepared by ATRP was confirmed by ^{1}H-NMR and FT-IR.

^{1}H-NMR ($CDCl_3$, ppm) of ligand PPMI: δ 8.63 (m, 1H), 8.38 (s, 1H), 8.00 (m, 1H), 7.69 (m, 1H), 7.28 (m, 1H), 3.63 (t, 2H), 1.73 (m, 2H), 0.96 (t, 2H). FT-IR (KBr disk, cm^{-1}): 3,059–2,840, 1,647 (C=N), 1,592, 1,564, 776, 741. These results corresponded to Ref. [18].

^{1}H-NMR ($CDCl_3$, ppm) of PGMA: δ 0.94–1.10 (t, 3H), 1.95 (s, 2H), 2.65 (s, 1H), 2.86 (s, 1H), 3.25 (m, 1H), 3.81 (s, 1H), 4.32 (s, 1H). FT-IR (KBr disk, cm^{-1}): 2,992–2,840, 1,737 (C=O), 1,376, 912 (epoxy group). These results corresponded to references [16, 17].

Polymerization of GMA was carried out in diphenyl ether at 30 °C where GMA:BPN:CuBr:PPMI = 150:1:1:2 (mol ratio), and solvent:monomer = 1:1 (v/v). the results of linear first-order kinetic plots of ln $[M]_0/[M]$ versus time, an linear increase in the number-average molecular weight (M_n) versus conversion and relatively narrow polydispersities ($M_w/M_n < 1.22$) indicated that the polymerization was controlled/"living" radical polymerization [16, 17]. The GPC curve of the PGMA obtained is shown in Fig. 1. Figure 1 showed that when the conversion of GMA was 57% the M_n of PGMA was 10,497, the M_w/M_n was 1.113.

The characterization of optically active methacrylate polymer with controlled molecular weight

The FT-IR spectra of the optically active polymer prepared from PGMA and S-(−)-MBA are shown in Fig. 2. The peaks about 3,000–2,840 cm^{-1} are attributed to stretching vibration of CH_3 and CH_2 in PGMA. The peak at 1,370 cm^{-1} is attributed to CH_3 and CH_2 bending vibration. The peak at 1,734 cm^{-1} is attributed

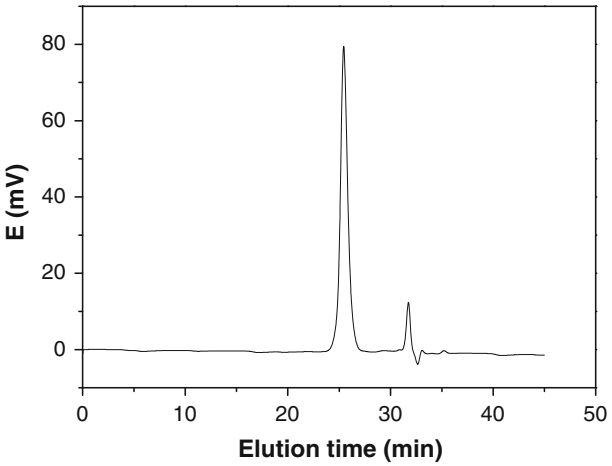


Fig. 1 The molecular weight distribution curve of PGMA prepared by ATRP

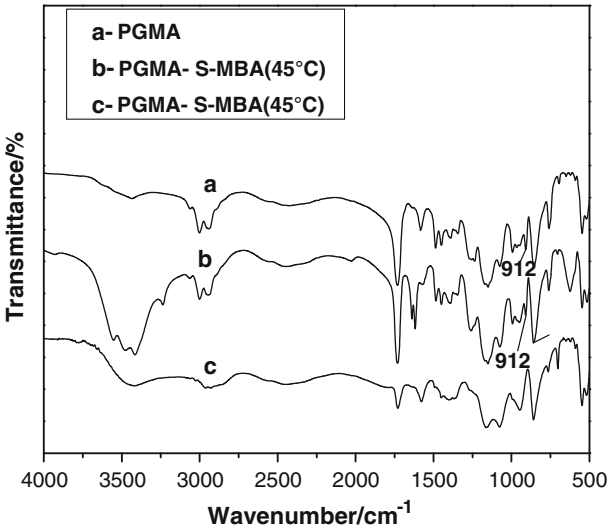


Fig. 2 FT-IR spectra of the optically active methacrylates polymer from PGMA and S-(−)-α-methylbenzylamine

to C=O stretching vibration in PGMA. The strong, broad peak at 3,440 cm^{-1} is attributed to a combination of O–H and N–H stretching vibration in Fig. 2b, c. The peaks at 1,580 and 1,451 cm^{-1} are attributed to C=C stretching modes for benzenoid rings. The peaks at 767 and 708 cm^{-1} are attributed to =C–H bending vibration for monosubstituted benzenoid rings in Fig. 2c. The peak at 912 cm^{-1} is attributed to the pendant epoxy group of PGMA in Fig. 2a. The peak at 912 cm^{-1} disappeared in Fig. 2c and there was weak absorption in Fig. 2b. It has

demonstrated that the pendant oxirane ring in PGMA had opened and the optically active polymer had been prepared when reaction temperature was 90 °C. The pendant oxirane ring had not opened completely at 45 °C.

Chiroptical properties of the optically active methacrylate polymer with controlled molecular weight

Table 1 shows specific rotation of S-(−)-MBA and opening ring reaction products (PGMA-S-MBA) of S-(−)-MBA and PGMA. When the reaction temperature was 90 °C, grafting degree of PGMA was 79.5%, and specific rotation $[\alpha]_D^{25} = -30.4°$ ($c = 0.6$ mg/mL, THF). When the reaction temperature was 45 °C, grafting degree was only 15.2%, and specific rotation was near 0°. The results of specific rotation indicated that when reaction temperature was higher (90 °C), opening ring reaction of epoxy group could occur and grafting degree of PGMA was higher, specific rotation of PGMA-S-MBA was higher. Figure 3 showed CD spectra of S-(−)-MBA and opening reaction products PGMA-S-MBA. The CD spectrum of S-(−)-MBA shows a positive band at 261 nm in Fig. 3a. When the reaction temperature was

Table 1 Specific rotation of S-(−)-α-methylbenzylamine and opening reaction products of PGMA and S-(−)-α-methylbenzylamine

Samples	Temperature (°C)	Grafting degree[a] (%)	$[\alpha]_D^{25}$ (°)
S-(−)-MBA	–	–	−38 (neat)
Products 1	45	15.2	−1.0
Products 2	90	79.5	−30.4

[a] The actual mass of PGMA-S-MBA/theoretical mass of PGMA-S-MBA

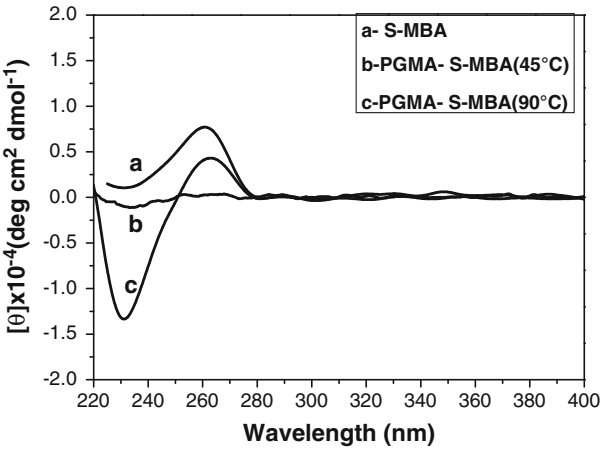


Fig. 3 CD spectra of S-(−)-α-methylbenzylamine and opening reaction products of PGMA and S-(−)-α-methylbenzylamine

45 °C the PGMA-S-MBA has not cotton effect in Fig. 3b. When the reaction temperature was 90 °C PGMA-S-MBA shows a negative band at 231 nm and a positive one at 262 nm in Fig. 3c. The CD spectra and specific rotation have both demonstrated that the optically active methacrylate polymer had been prepared when reaction temperature was 90 °C.

Thermal stability of optically active methacrylate polymer with controlled molecular weight

Thermogravimetric analysis method was employed to understand the thermal behavior of PGMA and its graft copolymer PGMA-S-MBA. Typical weight loss (TG) and derivative of weight loss (DTG) curves of PGMA and PGMA-S-MBA are shown in Figs. 4 and 5. From the TG curves initial and final degradation temperatures were determined. From DTG curves, the maximum temperature of weight loss was also noted. The mass loss of PGMA begins at 309 °C and reaches to maximum at 348 °C. The TG curve of PGMA indicates one reaction stage (Fig. 4a) which is reflected as single peak in the DTG curve (Fig. 5a). Initial degradation temperature of PGMA showed that the degradation was due to random chain

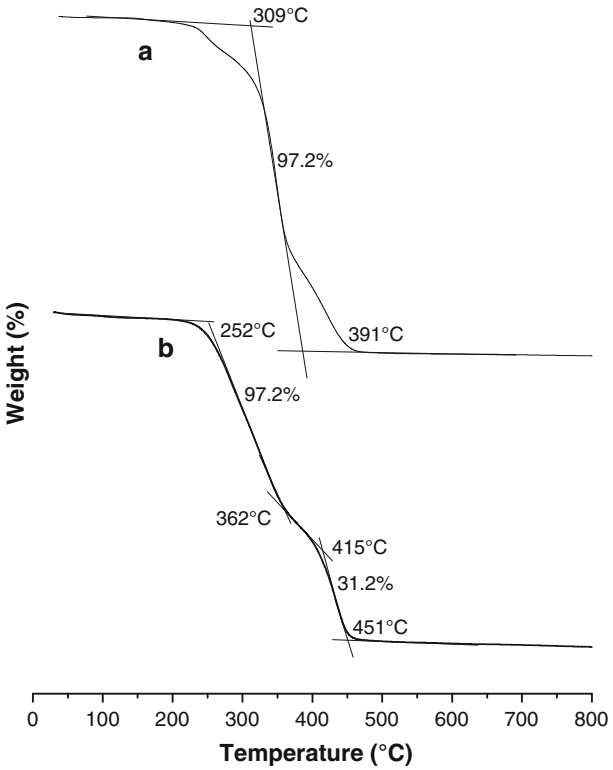


Fig. 4 TGA thermograms of (*a*) PGMA and (*b*) PGMA-S-MBA under N_2 atmosphere at a heating rate of 20 °C/min

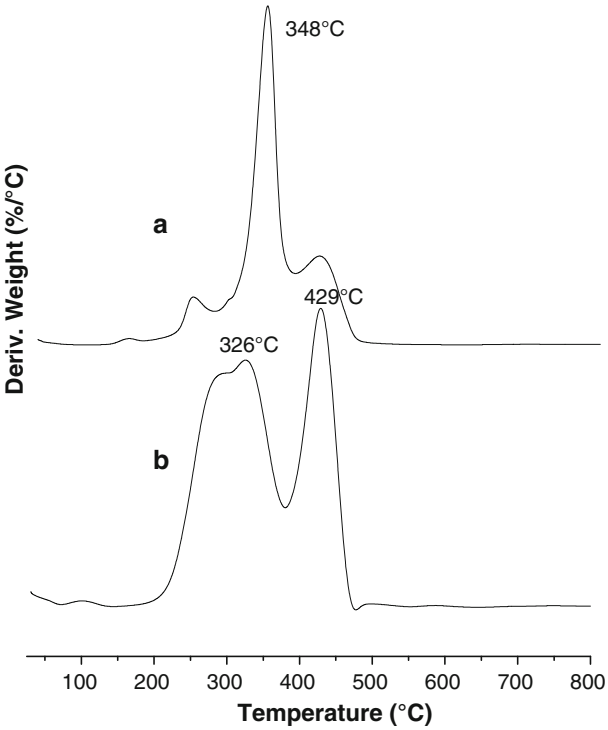


Fig. 5 DTG thermograms of (*a*) PGMA and (*b*) PGMA-S-MBA under N_2 atmosphere at a heating rate of 20 °C/min

scission [17]. On the other hand, the PGMA grafted (PGMA-S-MBA) degrade in two steps. This is evidenced by the appearance of distinct peaks in DTG thermograms. Grafting of PGMA with S-(−)-MBA seems to impart thermal stability to the base material since both the onset of degradation and maximum degradation temperatures were shifted to lower temperatures, Fig. 5b. Stepwise degradation of PGMA-S-MBA indicated that the functional group introduced on the trunk polymer had different thermal stability giving rise to the appearance of distinct, separate derivative peaks [20, 21].

Figure 6 shows the DSC thermograms of PGMA and PGMA-S-MBA. The T_g of the homopolymer PGMA was reported to be near 74 °C [22]. The T_g of PGMA prepared by ATRP via CuBr/BPN initiating system has a T_g of 54 °C, while graft copolymer, PGMA-S-MBA has a T_g of 68 °C. The T_g of PGMA-S-MBA has increased 14 °C. The increase in T_g of the graft copolymer can be attributed to formation of side chains as well as strong hydrogen bonding which may restrict the cooperative segmental relaxation. The presence of single T_g confirms the homogeneity of the graft copolymer [23]. The thermoanalysis data of these polymers are summarized in Table 2. The temperature of 5% weight loss for PGMA and PGMA-S-MBA was 244 and 242 °C, the temperature of 10% weight loss was 271 and 261 °C, respectively.

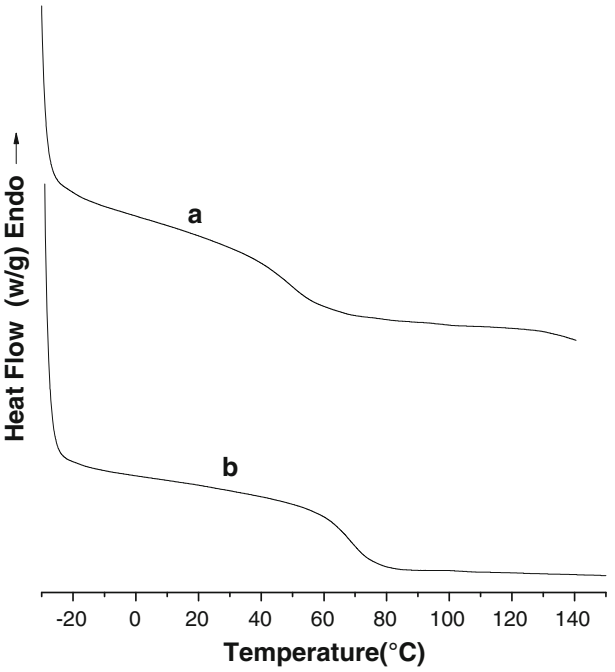


Fig. 6 DSC traces of (*a*) PGMA and (*b*) PGMA-S-MBA recorded under N_2 atmosphere at a heating rate of 10 °C/min

Table 2 Thermal properties of PGMA and PGMA-S-MBA

Polymer code	T_5^a (°C)	T_{10}^b (°C)	T_g^c (°C)
PGMA	244	271	54
PGMA-S-MBA	242	261	68

[a] Temperature at which 5% weight loss was recorded by TGA at heating rate of 20 °C/min under N_2 atmosphere

[b] Temperature at which 10% weight loss was recorded by TGA at heating rate of 20 °C/min under N_2 atmosphere

[c] The glass transition temperature recorded by DSC at heating rate of 10 °C/min under N_2 atmosphere

Conclusions

The novel optically active methacrylates polymer with controlled molecular weight had been synthesized from PGMA prepared by homogeneous ATRP of GMA and S-(−)-α-methylbenzylamine, and characterized by FT-IR, polarimeter, CD spectra, TGA, and DSC. The results of FT-IR, polarimeter, and CD spectra indicated that when the reaction temperature was higher, the degree of opening ring for epoxy group was higher, and grafting degree of polymer PGMA was higher, specific rotation of PGMA-S-MBA was higher. The results of thermal analysis indicated that

PGMA-S-MBA degrade in two steps. This result demonstrated that the functional group introduced on the trunk polymer had different thermal stability giving rise to the appearance of distinct, separate derivative peaks. The T_g of PGMA-S-MBA has increased 14 °C compared with PGMA, which can be attributed to formation of side chains as well as strong hydrogen bonding which may restrict the cooperative segmental relaxation.

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