

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

Gang Li, Xiulin Zhu\*, Jian Zhu, Zhenping Cheng, Wei Zhang

*School of Chemistry and Chemical Engineering, Suzhou University, 1 Shizi Street, Suzhou, 215006 Jiangsu, China*

Received 9 May 2005; received in revised form 5 October 2005; accepted 6 October 2005

Available online 3 November 2005

## 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*-butyldithiocarbamate copper ( $\text{Cu}(\text{SC}(\text{S})\text{N}(\text{C}_4\text{H}_9)_2)_2$ ) 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 ( $M_w/M_n$ ).  $^1\text{H}$  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.

© 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Reverse ATRP; Glycidyl methacrylate; Copper (II) *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.  $\text{CuCl}_2$ ,  $\text{CuBr}_2$  and  $\text{Fe}(\text{SC}(\text{S})\text{NET}_2)_3$ ) 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  $\text{Mt}(\text{SC}(\text{S})\text{NR}_2)_n$  ( $\text{Mt} = \text{Fe}(\text{III})$ ,  $\text{Ru}(\text{III})$ ,  $\text{Cu}(\text{II})$ ;  $\text{R} = \text{ethyl}$  or  $\text{benzyl}$ ;  $n = 2$  or  $3$ ) [11]. Qiu et al. reported the living radical polymerizations of methyl

methacrylate and styrene in  $\text{Fe}(\text{SC}(\text{S})\text{NET}_2)_3$  [12],  $\text{Cu}(\text{I})(\text{SC}(\text{S})\text{NET}_2)/\text{bpy}$  [13,14], and  $\text{Cu}(\text{II})(\text{SC}(\text{S})\text{NET}_2)\text{Cl}/\text{bpy}$  [15,16] catalyst systems. It is noted that the polymers obtained above have an ultraviolet light sensitive  $\omega\text{-SC}(\text{S})\text{NR}_2$  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*-butyl dithiocarbamate copper ( $\text{Cu}(\text{SC}(\text{S})\text{N}(\text{C}_4\text{H}_9)_2)_2$ ) as the new catalyst [36]. This paper presents: (i) reverse ATRP of GMA without any extra ligand, using AIBN and  $\text{Cu}(\text{SC}(\text{S})\text{N}(\text{C}_4\text{H}_9)_2)_2$  as the initiating system, and (ii) synthesis

\* Corresponding author. Tel.: +86 512 651 11258; fax: +86 651 12796.  
E-mail address: [xlzhu@suda.edu.cn](mailto:xlzhu@suda.edu.cn) (X. Zhu).

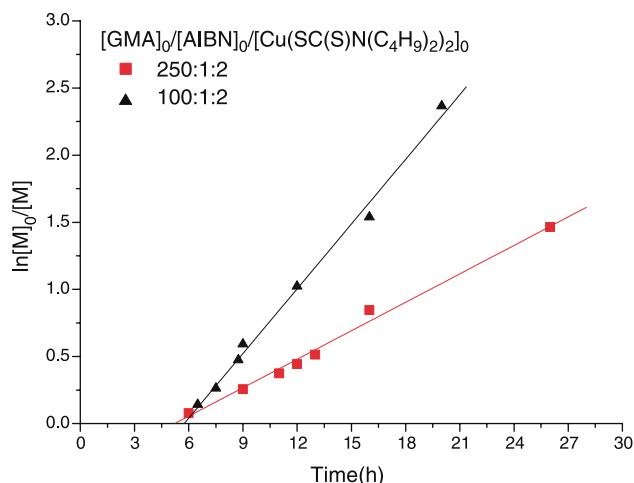


Fig. 1. Kinetics of reverse ATRP of GMA in bulk at different molar ratios of  $[GMA]_0/[AIBN]_0/[Cu(SC(S)N(C_4H_9)_2)_2]_0$  at 70 °C.

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.

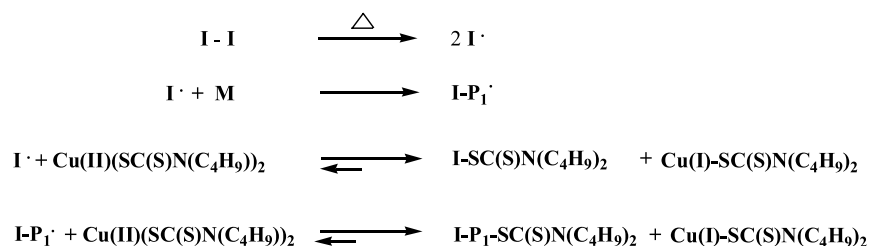
### 2.2. Characterizations

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<sup>-1</sup> at 30 °C. Monodispersed poly(methyl methacrylate) standards with a molecular weight range of 100–500,000 were used to generate the calibration curve. <sup>1</sup>H NMR spectra of the polymers were measured on an Inova 400-MHz NMR instrument with tetramethylsilane (TMS) as the internal standard in CDCl<sub>3</sub> 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<sup>-1</sup> in a nitrogen atmosphere (100 mL min<sup>-1</sup> of flow rate).

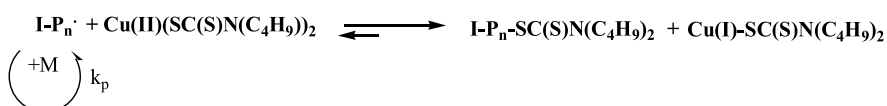
### 2.3. General procedure for the reverse ATRP of GMA

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



#### Propagation



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

Download English Version:

<https://daneshyari.com/en/article/5189676>

Download Persian Version:

<https://daneshyari.com/article/5189676>

[Daneshyari.com](https://daneshyari.com)