RAFT Polymerization of *S*-(-)-α-methylbenzyl methacryloylamine and (*R,S*)-α-methylbenzyl methacrylate: A kinetic study by dilatometry

Soriano-Moro, J. G.[1†], Percino, J.[1], Chapela, V. [1], Guerrero-Santos, R.,[2]
[1]Centro de Química, Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla. Complejo de Ciencias Edif. 194, Ciudad Universitaria, Puebla, Puebla México.
[2]Centro de Investigación en Química Aplicada (CIQA). Blvd. Enrique Reyna 140. Saltillo, Coahuila México
[†]e-mail: memosoriano@hotmail.com

1. Abstract

It's reported the kinetic study by dilatometry of Reversible-Addition Fragmentation Transfer (RAFT) polymerization of two monomers: *S*-(-)-α-methylbenzyl methacryloylamine (*S*-(-)-α-MBMA) and *(R,S)*-α-methylbenzyl methacrylate (*(R,S)*-α-MBMA). Benzyl and (1-phenyl)ethyl dithiobenzoate were employed as control agents. Reactions were carried out in solution at 70º C initiated by AIBN. The effect of RAFT agent and initiator concentration on conversion was evaluated. Particularly, retardation in rate of polymerization was obtained, when the RAFT agent is added in the reaction, and raised with the increase of controlling agent. The average molecular weight number (M_n) was estimated by UV measurements using the extension molar coefficients of RAFT agents.

2. Introduction

Over the past few years, the ''living''/controlled free radical polymerization (LFRP) techniques have been rapidly developed, such as atom transfer radical polymerization (ATRP),[1, 2] the reversible addition-fragmentation chain transfer (RAFT) polymerization,[3] and nitroxyl radical mediated polymerization (NMP),[4] which provided a new set of robust methods for designed polymers that permitted very precise control over the polymerization process, while retaining much of the versatility of conventional free radical polymerization.[5] Particularly, RAFT polymerization represents a versatile LFRP polymerization technique,[6] because is compatible with a wide range of monomers, tolerated monomer functionality includes fluorine, tertiary amino, quaternary amino, carboxylic acid, betaine, hydroxyl, epoxy and thiirane.[7] Previously, our group reported the synthesis of several functional monomers,[8, 9] and now we are studying the free radical and LFRP polymerization of such monomers. However, results of ATRP polymerizations showed that deactivation of catalytic complex is responsible in the lost of

the control in the growing of the polymer chains. Thus, we decided evaluate RAFT polymerization as a technique to provide control in the polymerization of *S*-(-)-α-methylbenzyl methacryloylamine (*S*-(-)-α-MBMA) and *(R,S)*-α-methylbenzyl methacrylate (*(R,S)*-α-MBMA).

3. Experimental conditions

3.1 Synthesis

S-(-)-α-MBMA and *(R,S)*-α-MBMA were synthesized according to previous report.[8] *Benzyl* and *(1-phenyl)ethyl dithiobenzoate* (BDB and 1-FEBD, respectively) were synthesized as reported by Le *et al.*[10]. Molar extension coefficient of BDB and 1-FEDB was determinate by Lambert-Beer Law from a calibration curve in $CHCl_3$.

3.2 Polymerizations

Polymerizations were carried out in glass dilatometers, which are made up of 5 mL bulb, a capillary tube of 2 mm internal diameter and 10 cm length. A typical procedure of the polymerization is: A solution at 0.5 M of monomer in ethanol (to *S*-(-)-α-MBMA) or toluene (to *(R,S)*-α-MBMA), AIBN and RAFT agent was placed in a 5 mL flask. Solutions were bubbled with ultrahigh-purity argon for 20 min and after sealed with a rubber septum. Dilatometers were placed in water bath at 70 ºC (± 0.02). Monomer conversion was followed by volume contraction during polymerization. Reaction was stopped by cooling the dilatometer in ice-water bath. The polymer was precipitated in hexane (to *S*-(-)-α-MBMA) and ethanol (to *(R,S)*-α-MBMA) and drying in a vacuum.

3.3 Characterization

Monomers, RAFT agents and polymers were characterized by nuclear magnetic resonance (NMR) of ^1H and Infrared spectroscopy (FT-IR). NMR spectra were recorder on a 300 MHz Jeol spectrometer with tubes of 5 mm of diameter. The spectra were recorder at room temperature. FT-IR spectra were determined in a Bruker Vertex 70 spectrometer using Diffuse Reflectance accessory.

4. Results and Discussion

Figure 1 shows the conversion plots of *S*-(-)-α-MBMA polymerization in solution of ethanol and initiated with AIBN at 70 ºC carried out at two different molar ratios of initiator, with and without BDB (RAFT agent). When BDB is not present in the reaction (open symbols) the reaction proceed higher than when BDB is added to the reaction (close symbols). A similar effect is obtained when BDB is change by 1-FEDB. This effect denoted as retardation is typical in RAFT polymerization and is explained by the formation of adduct stable radical.[11] Figure 2 shows the UV spectra from original RAFT agent and the corresponding polymer synthesized under RAFT polymerization of MBMA (Figure 2a) and MBM (Figure 2b), the absorption at around 300 nm is attributed at the functionalized polymer by the thiocarbonylthio moiety. Such absorption, allows determinate the M_n. Polymers synthesized with out RAFT agents didn't show absorption at this wavelength.

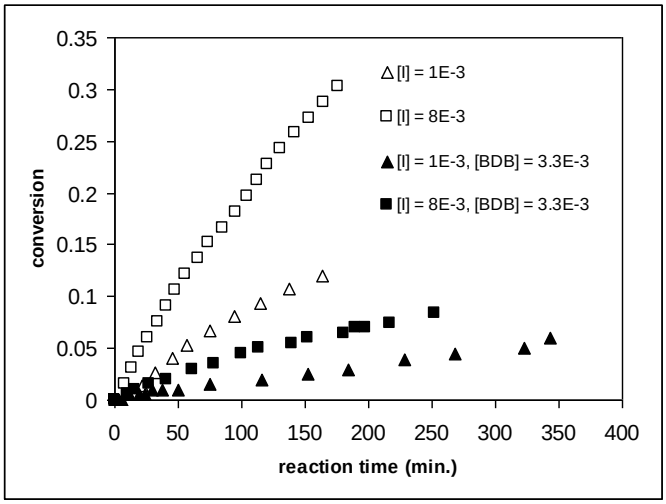

Figure 1.Profile Conversion vs. reaction time to the polymerization of MBMA initiated by AIBN at 70 ºC with out RAFT agent (close symbols) and with RAFT agent (close symbols).

5. Conclusions

Polymerizations of *S*-(-)-α-MBMA and *(R,S)*-α-MBMA were successfully synthesized under RAFT conditions, using two different RAFT agents. Reactions are retarded by the presence of RAFT agent. Through of the comparative evaluation between UV spectra of original RAFT agent and polymers synthesized in presence of RAFT agents were possible to affirm that the polymers chains contains the thiocarbonylthio moiety

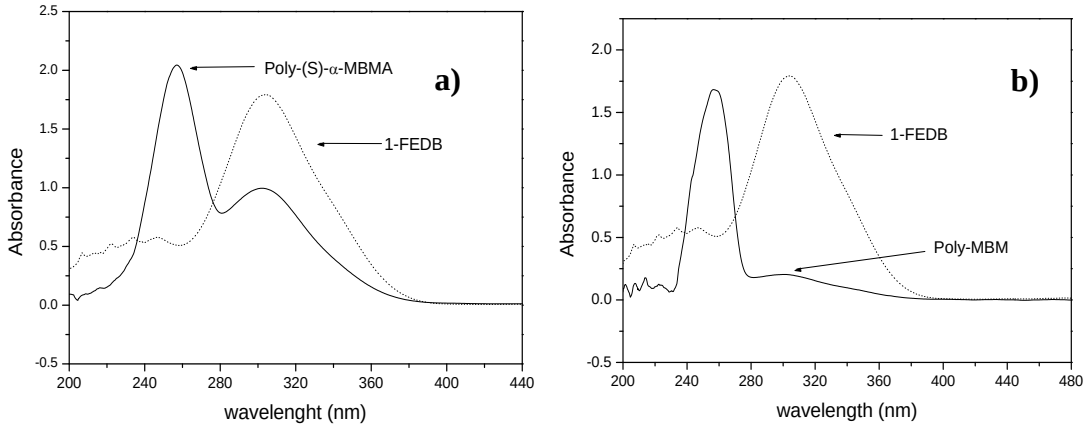

Figure 2.Comparative UV spectra of a) Poly-(S)-α-MBMA and b) Poly-(R,S)-MBM, synthesized in presence of 1-FEDB (solid line) and original UV spectrum of RAFT agent (dot line).

Acknowledgements: The authors acknowledge VIEP-BUAP for its financial support (project PEZM-NAT08-G) and CONACYT for the postdoctoral grant give to J. G. S. –M.

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