

Atom transfer radical polymerization of α -methylbenzylmethacrylate: kinetic study and characterization

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1. Abstract

It is reported the Atom transfer radical polymerization (ATRP) of monomer α -methylbenzylmethacrylate and its kinetic study by dilatometry. ATRP reactions were carried out at 48°C and at different molar ratios of the system $[M]/[I]/[M_{tr}-Y]/[L]$ where the initiator was ethyl 2-bromoisobutyrate, metal halide was copper bromide and the ligand was tris[2-(dimethylamino)ethyl]amine. The monomer concentration was raised in the following manner: 100, 200, 300 and 400 relative to the ratios of the other members of the system ([15]:[15]:15), to study the control of the polymerization. Size-exclusion chromatography (SEC) coupled with multi-angle light scattering (MALS) will be employed for the molar mass characterization of the bromide-terminated poly(α -methylbenzylmethacrylate).

2. Introduction

In recent years, Controlled Radical Polymerizations (CRP) have been successfully used to obtain polymeric materials with controlled molecular weights and low polydispersities for a wide range of monomers [1]. One of the CRP methods is Atom transfer radical polymerization (ATRP), which employs a multicomponent system including the monomer (M), an initiator (a molecule with one or more transferable atoms or groups, frequently a pseudohalide, R-X) and a transition metal catalyst (M_t^n-Y/L , where L is a ligand). In the activation step, the catalyst reacts reversibly with the initiator molecule and generates an oxidized transition metal halide complex ($X-M_t^{n+1}/L$) and a radical (R^*) [2]. The radical subsequently adds to the monomer before it is deactivated by the metal complex to form the dormant species P_mX . It is crucial for this kind of polymerization to reach an appropriate equilibrium between the activation process (generation of radicals, k_{act}) and the deactivation process (formation of alkyl halides, k_{deact}). The equilibrium between the two processes ($K_{eq} = k_{act}/k_{deact}$) determines the concentration of radicals and subsequently the rates of polymerization and termination [3].

The ATRP of the monomer S-(-)- α -methylbenzylmethacryloylamine has been studied previously in our group [4]. In this work we report the ATRP of the functionalized monomer α -methylbenzylmethacrylate and its kinetic study by dilatometry.

3. Experimental section

The initiators used for ATRP reactions were ethyl 2-bromoisobutyrate (EBIB) or methyl 2-chloropropionate. The catalytic system was composed by CuBr or CuCl and Tris[2-(dimethylamino)ethyl]amine (Me₆-TREN) as the ligand. All the reactions were performed using a mixture ethanol/toluene (60:40) as the solvent at different molar ratios of the system [M]/[I]/[M]_t-Y/[L]. The monomer concentration was raised in the following manner: 100, 200, 300 and 400 relative to the ratios of the other members of the system ([15]:[15]:[15]).

The ATRP reactions were carried out in a glass dilatometer containing a capillary following this general experimental procedure: an initiator solution was added into the dilatometer and degassed by purging with argon. A solution containing the monomer and the catalytic system was degassed too and was then added into the dilatometer using a syringe. The dilatometer was immersed in a water bath maintained at 48°C. The monomer conversion was followed measuring the volume contraction in the solution during polymerization.

All the products were purified and characterized by FT-IR and ¹H-NMR.

4. Results and discussion

Using EBIB and MCP as initiators in the ATRP of monomer α -methylbenzylmethacrylate, macroinitiators were obtained, this is, products containing an halide (Br or Cl, respectively) as a terminal chain group (Figure 1). These materials could be used in other ATRP reactions to produce copolymers.

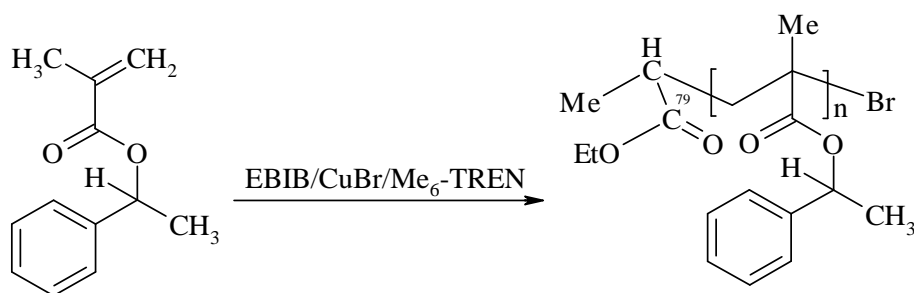


Figure 1. ATRP of monomer α -methylbenzylmethacrylate

Evidence of the initiator attached to the chains was found in the ^1H -NMR spectra of the materials obtained. For ATRP reactions where EBIB was used, a signal around 4 ppm was present, which corresponds to the two protons of the group $-\text{CH}_2-\text{O}-$ from the initiator (Figure 2). From the integration of this signal it was possible to calculate the molecular weights of the macroinitiator obtained. The values for the molecular weights obtained in this way went from around 2000 for the reaction where the lowest monomer initial concentration was used up to almost 7,000 g/mol for the macroinitiator prepared with the highest monomer concentration.

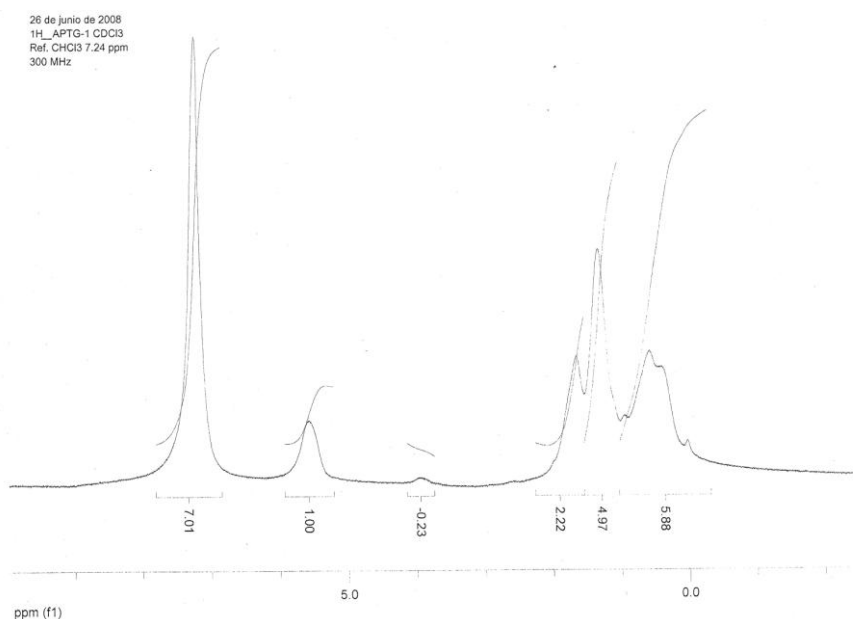


Figure 2. ^1H -NMR spectra of the macroinitiator from α -methylbenzylmethacrylate, system $[M]/[I]/[Mt]^n - Y]/[L] = 100:15:15:15$, using EBIB as an initiator

For ATRP reactions using MCP, a signal around 3.5 ppm appeared, corresponding to the three protons from the group $\text{CH}_3-\text{O}-$ of the initiator (Figure 3). Molecular weights were obtained from the integration of this signal (ranging from 4000 g/mol for the macroinitiator prepared with the lowest monomer initial concentration to almost 13,000 g/mol for the material prepared with the highest monomer concentration).

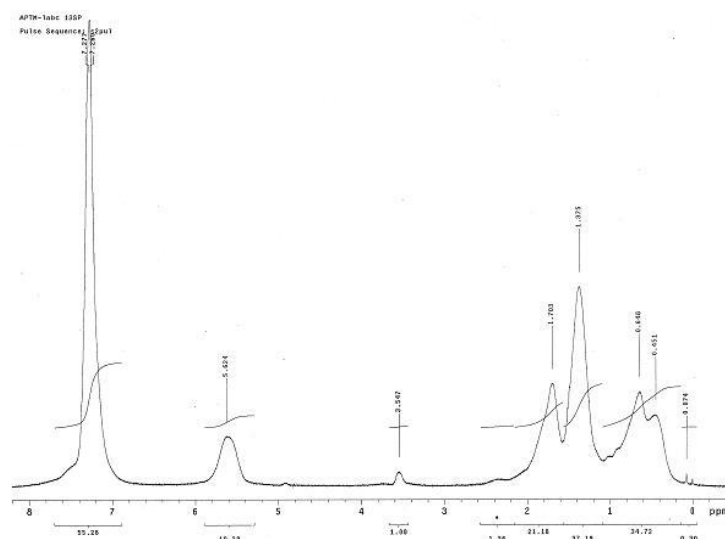


Figure 3. ^1H -NMR spectra of the macroinitiator from α -methylbenzylmethacrylate, system $[\text{M}]/[\text{I}]/[\text{Mt}]^n - \text{Y}]/[\text{L}] = 400:15:15:15$, using MCP as an initiator

5. Conclusions

Macroinitiators from the monomer α -methylbenzylmethacrylate with a bromide or chlorine chain-end were obtained using ATRP conditions. The kinetic data obtained from the dilatometric study is still being analyzed to confirm the control of the polymerization reactions. Size-exclusion chromatography (SEC) coupled with multi-angle light scattering (MALS) will be employed for the molar mass characterization of these materials and to obtain their polydispersities. Molecular weights (M_n) calculated from ^1H -NMR spectra will be compared with the results from SEC-MALS.

6. References

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