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Polymer 47 (2006) 1812–1819

polymer

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Facile atom transfer radical homo and block copolymerization of higher alkyl methacrylates at ambient temperature using CuCl/PMDETA/quaternaryammonium halide catalyst system

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Received 21 September 2005; received in revised form 19 January 2006; accepted 20 January 2006
Available online 8 February 2006

Abstract

Controlled polymerization of higher alkyl methacrylates, e.g. lauryl methacrylate (LMA) and stearyl methacrylate (SMA) has been successfully achieved by atom transfer radical polymerization (ATRP) at ambient temperature using CuCl/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA)/tricaprylylmethylammonium chloride (Aliquat®336) as the catalyst system and ethyl 2-bromoisobutyrate or 2,2,2-trichloroethanol as the initiator. Although the bulk polymerization gives satisfactory control, the latter becomes better when anisole or THF is added into the system. Without AQCl the control was lost. A large deviation of molecular weight from theory has been observed which has been attributed to the very high-molecular weight of the dead polymers formed during the building-up of the persistent radical. The controlled polymers have been used as macroinitiators for block (di, tri and penta) ATR copolymerization with several methacrylates.

Keywords: Atom transfer radical polymerization; Living radical polymerization; Block copolymers

1. Introduction

The ATRP is a robust as well as a versatile living radical polymerization process for the controlled synthesis of polymers [1–3]. The copper mediated ATRP (CuBr/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) catalyst) of alkyl (meth)acrylates with large alkyl groups ($R=C_{12},C_{18}$) has been shown to require specially the addition of the deactivator (ca. 5 mol% of catalyst) to start with, in order to achieve satisfactory control [4–6]. This has been attributed to the very low-termination rate constants of polymer radicals with large α substituents [7,8] and consequently a weak build-up of the deactivator towards the equilibrium regime in the unaided system [9].

As regards the choice of ligands for the Cu-based catalyst, Matyjaszewski and co-workers tested PMDETA as a ligand for the ATRP of lauryl acrylate and found it to be unsuitable for solubility reasons even when solvents like anisole or acetone which serve well in the ATRP of MMA were used [4]. Although the systems were homogeneous to start with, the heterogeneity sets in through the precipitation of the Cu(II) complex and the polymer [4]. However, the use of the CuBr/dNbpy catalyst eliminates the heterogeneity problem from Cu(II) complex precipitation at an elevated temperature (90 °C) even without the use of a solvent [4]. This latter catalyst was successfully used also for the ATRP of stearyl methacrylate (SMA) and stearyl acrylate (SA) in xylene at 90 °C [5,6].

On the other hand, Xu et al. claimed satisfactory control in the ATRP of lauryl methacrylate (LMA) using the CuCl/PMDETA catalyst but without any added Cu(II) complex in various solvents which were added to keep the copper complexes in solution at 110 °C. However, the chain extension experiment showed bimodality and larger PDI in the chain extended polymer [10]. Raghunadh et al. also did not use any extraneously added deactivator and found that the CuBr/PMDETA catalyst does not provide satisfactory control, while the CuBr/N(*n*-propyl)2-pyridylmethanimine (PPMI) catalyst does [11]. But for the latter system they had to use a dilute solution of LMA (15% by volume) in toluene at 95 °C. Also, very recently, Street et al. reported that the CuBr/PPMI catalysed bulk ATRP of ODA at 95 °C is poorly controlled. However, the control improves significantly on increasing the alkyl group size in the methanimine catalyst from *n*-propyl to

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doi:10.1016/j.polymer.2006.01.068

n-octyl which increases the compatibility of the catalyst with such a highly non-polar monomer. Further improvement in control occurs on using an initiator having a large alkyl group which has been supposed to be more compatible with the monomer. Best control (PDI = 1.15) was reported when the non-polar character of the initiator was further increased by replacing the alkyl group with its perfluoro derivative, e.g. using zonyl-2-bromo-2-methyl propionate initiator [12].

Recently, we showed that cuprous halide/linear alkylamine catalysts are solubilized in MMA at ambient temperature by catalytic amounts of quaternaryammonium halides. The chloride-based catalyst CuCl/PMDETA/AQCl (AQCl = Aliquat®336 = tricaprylylmethylammonium chloride) used with ethyl 2-bromoisobutyrate (EBiB) initiator provides excellent control and that too at ambient temperature which is attractive due to lower side reactions (hence better product) and cost advantage [13].

We show here the efficacy of this catalyst system as well in the ATRP of LMA and SMA at ambient temperature without requiring any extraneous addition of the deactivator, or any special initiator. Moreover, the ATRP of LMA can be successfully performed without using any solvent. The facility of the method is demonstrated through the synthesis at ambient temperature of some block copolymers.

2. Experimental section

2.1. Materials

LMA (Aldrich, 96%), MMA (BDH) and *n*-butyl methacrylate (*n*BMA) (Acros Organics, 99%) were washed with 5% aqueous NaOH solution, dried over anhydrous $CaCl_2$, then vacuum distilled and stored under nitrogen at −15 °C. SMA (Aldrich) was dissolved in hexane and the solution passed through a basic alumina column in order to remove the inhibitor. The solvent was removed under reduced pressure. *t*-Butyl methacrylate (*t*BMA) (Aldrich, 98%) was passed through a neutral alumina column and then vacuum distilled and stored at −15 °C. PMDETA (99%), Aliquat®336, EBiB (97%), 2,2,2-trichloroethanol (TCE, 99+%) all Aldrich products were used as received. Tetrahydrofuran (THF) (GR, E. Merck, India) was dried over CaH_2 and distilled. Anisole (GR, E. Merck, India) was distilled and used. CuCl (98%, BDH) was purified by washing with 10% HCl in water followed by methanol and diethyl ether in a Schlenk tube under a nitrogen atmosphere. The difunctional initiator 1,2-bis(bromoisobutyryloxy)ethane (BiBE) was prepared according to a literature method [14].

2.2. Synthesis of a ω-chloro PLMA (PLMA–Cl)

In a nitrogen purged test tube (8×2.5 cm) provided with a B-19 standard joint and a stir bar were added AQCl (0.035 g, 0.086 mmol) and CuCl (0.0043 g, 0.043 mmol). Nitrogen purging was continued for 10 min following which the tube was closed with a rubber septum which was secured by a Cu wire. LMA (0.868 g, 3.42 mmol) previously purged with nitrogen was next introduced into the tube with a nitrogen purged gas-tight syringe. The mixture was stirred magnetically for 30 min to prepare a homogeneous solution. PMDETA (0.008 g, 0.043 mmol) followed by EBiB (0.008 g, 0.043 mmol) were then injected in. The polymerization was conducted at 35 °C with stirring. For kinetic studies, separate runs were performed for different times. After the desired time period, the contents of the tube were diluted with 1 ml THF and poured into 300 ml methanol. The separated polymer was isolated, redissolved in THF and reprecipitated into excess methanol. It was finally dried in a vacuum oven at 45 °C for 48 h, and weighed. The $M_{n(gpc)}$ and PDI of the polymer were 25,000 and 1.25, respectively, at 98% conversion.

2.3. Synthesis of a α,ω-dichloro PLMA (Cl–PLMA–Cl)

The procedure was similar to the above. The following recipe was used: AQCl = 0.028 g (0.068 mmol), CuCl (0.0034 g, 0.034 mmol), PMDETA (0.006 g, 0.034 mmol), LMA (1.736 g, 6.83 mmol), BiBE (0.0125 g, 0.034 mmol). After 8 h the conversion was 98% and the $M_{n(gpc)}$ and PDI were 41,000 and 1.24, respectively.

2.4. Synthesis of the triblock copolymer poly(MMA-b-LMA-b-MMA)

A one pot procedure was followed. In the pot containing the Cl–PLMA–Cl (macroinitiator) synthesized as above for 8 h was added by a gas-tight syringe MMA (0.752 g, 7.52 mmol) which was separately purged with N_2. The mixing was done using a vortex mixer. The mixture was then allowed to stand unstirred at 35 °C. After 20 h the polymer was isolated, purified and dried as described in the case of PLMA. The conversion of MMA was 81% and the $M_{n(gpc)}$ and PDI of the triblock copolymer were 56,000 and 1.17, respectively.

2.5. Synthesis of the pentablock copolymer poly(nBMA-b-MMA-b-LMA-b-MMA-b-nBMA)

The pentablock copolymer was prepared using the purified triblock Cl–PMMA-*b*-PLMA-*b*-PMMA–Cl as the macroinitiator (0.52 g, 0.009 mmol) in the polymerization of *n*BMA (0.53 g, 3.76 mmol). The mole ratios of the macroinitiator:CuCl:AQCl was 1:1:2. *n*BMA was previously purged with nitrogen before addition into a nitrogen purged septum sealed reaction vessel containing the macroinitiator, CuCl and AQCl. The macroinitiator was allowed to dissolve in *n*BMA for 24 h. PMDETA (0.0016 g, 0.009 mmol) was then injected into the tube and mixed with the solution with a vortex mixer. The polymerization was conducted at 35 °C unstirred. After 22 h the polymer was isolated, purified and dried as described in the case of PLMA. Conversion was 35%. The $M_{n(gpc)}$ and PDI values were 69,000 and 1.13, respectively.