

A New Star Polymethylmethacrylates by Atom Transfer Radical Polymerization

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Abstract

In this paper, a new high molecular weight 4-arm star polymethylmethacrylates (PMMA) is synthesized by a "core-first" method. The process is as follows: tetra-functional initiator is synthesized by esterification reaction of ethylenediamine-*N,N,N',N'*-tetra-2-propanol. The reaction creates a new core that is used as an initiator and employed in the homogenous atom transfer radical polymerization (ATRP) of MMA monomer. The ATRP process is carried out in presence of CuBr as a catalyst and 2,2'-bipyridine ligands to synthesize star polymers with high conversion, low polydispersity and nearly monomodal molecular distributions.

Keywords: ATRP; Star polymers; TEM; Living polymerization

Introduction

Star polymers have attracted lots of attention due to their unique properties in bulk and solution [1-7]. Their synthesis are classified as: "arm first" and the "core first" methods [8,9]. In the arm first approach, preformed arms was prepared by living polymerization, reacted with a multifunctional coupling agent as the core [10,11], but in the core first method, a multifunctional core/initiator, initiate living polymerization to produce star polymer [12,13].

In the past, star polymers were mainly synthesized by living anionic [14,15] and cationic polymerization [16-18], but the strict reaction conditions and monomer selections, limit their application [14,19]. Significant attempts have been devoted to developed living/controlled polymerization based on free radical chemistry, among them controlled radical polymerization (CRP) methods [20] have been demonstrated as an effective route for preparing new polymers such as star polymers.

ATRP is probably the most robust and efficient CRP to produce well-defined polymers with controlled topology, composition and functionality [21-24].

This polymerization method is an effective technique for the design and preparation of multifunctional, nanostructured materials for a variety of applications in biology and medicine [25].

ATRP is a particularly successful CRP that has attracted commercial interest [26] because of its easy experimental setup, use of readily accessible and inexpensive catalysts, [27] and simple commercially available or easily prepared initiators.

Control of Alkyl bromides as ATRP initiators for acrylates, was gained through metal-mediated halogen atom transfer [28].

In this article, we report that the synthesis of 4-arm star polymers using new initiator based on ethylenediamine-*N,N,N',N'*-tetra-2-propanol, esterified with 2-bromopropionyl bromide for the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) in the presence of Cu(I)Br and 2,2'-bipyridine. All polymers

have been characterized by FT-IR, ¹H-NMR, elemental analysis and GPC.

The purpose of this paper is the synthesis of star polymers for specific characteristics such as spherical shape, small size, large surface, high mobility and the stability and uniformity of these polymeric materials. We synthesize a new initiator by esterification of ethylenediamine-*N,N,N',N'*-tetra-2-propanol, with 2-bromopropionyl bromide. Then this core, as a bromide initiator, initiates the polymerization of MMA monomers in the presence of Cu(I)Br and 2,2'-bipyridine ligands to produce PMMA polymers.

The multi-dentate nitrogen-based ligands are very useful in the copper-mediated atom transfer radical polymerization for bonding constant and electronic effects.

However, In other paper, substituent 2,2'-bipyridines were investigated for atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) [29].

Experimental Section

Reagents and apparatus

Solvents and chemical materials were purchased from Fluka (Switzerland) and Merck (Germany) chemical companies. Methyl methacrylate, was passed through a basic activated alumina column, extracted 3 times with 5% wt NaOH (aq), washed with deionized water and dried by using anhydrous MgSO₄, and finally distilled from CaCl₂ just before use.

The ¹H-NMR and ¹³C-NMR spectra were recorded on Bruker Avance 500 MHz spectrometer. Chemical shifts (δ) are listed in ppm against internal references. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (PDI=M_w/M_n) were determined by gel permeation chromatography (GPC) with linear polystyrene standards using an Agilent 1100 instrument and THF as the eluent at 30°C at 1 ml/min. FT-IR spectra were obtained as KBr pellets with a 680 plus-JASCO. SEM analyses were obtained using Philips XL30. TEM analyses were obtained using Philips CM10, with 100KB high-tension.

Synthesis of initiator

Ethylenediamine-*N,N,N',N'*-tetra-2-propanol (14.7 mmol, 4.3 g), triethylamine (36.8 mol, 8.73 ml), and CH_2Cl_2 (100 ml), were charged into dry 250 ml three-neck round-bottom reaction flask and stirred at 0°C under N_2 for 1hr, immediately 2-bromopropionyl bromide (0.015 mmol, 8 ml), was added, and the solution was stirred at room temperature overnight, then filtered and extracted with saturated Na_2CO_3 (aq) and CH_2Cl_2 , 2 times; the organic phase was dried over anhydrous magnesium sulfate. The solution was concentrated and vacuum-dried to produce colorless liquid. Yield: 84%; $R_f = 0.89$ (60/40 cyclohexane / ethylacetate).

FT-IR (KBr): $\nu = 2979, 2932, 2827, 2386, 2316, 2048, 1735, 1528, 1447, 1378, 1331, 1268, 1226, 1162, 1051, 987, 924, 880, 832, 763, 738, 681, 655, 591 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.23$ (d, 12H, CH_3 , $J = 5.54$ Hz), 1.821 (d, 12H, CH_3 , $J = 6.865$ Hz), 2.59 (brs, 4H, $-\text{NCH}_2\text{CH}_2\text{N}-$), 2.71 (brs, 8H, CH_2), 4.35 (t, 4H, CH), 5.08 (brs, 4H, CH) ppm; $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 170.14$ (C=O group), 71.33 ($-\text{CH}$ in CH-O-C=O), 59.36 ($-\text{CH}$ in CH-C-CH_3), 40.93 (CH_2 in $-\text{N-CH}_2\text{-CH}_2\text{-N-}$), 18.02 (CH_3 group in $-\text{O-CH-CH}_3$), 37.61 ($-\text{CH}$ in CH-Br), 22.03 (CH_3 group in $\text{CH}_3\text{-CH-Br}$) ppm; Elem. Anal.: $\text{C}_{26}\text{H}_{44}\text{N}_2\text{O}_8\text{Br}_4$ (Calcd.): C, 37.52%; H, 5.67%; Br, 38.40%; N, 3.37%; O, 13.38%; Found: C, 37.14%; H, 5.67%; N, 3.28%.

General procedure for the synthesis of star polymer by ATRP

CuBr (1.08 mmol, 0.106 g), 2,2'-bipyridine (2.04 mmol, 0.832 g), initiator (0.255 mmol, 0.21 g), xylene (20 ml), water (1 ml) and MMA (204 mmol, 21.7 ml) were added into a nitrogen purged dry glass tube (25 ml) with a magnetic stirrer. The tube was then sealed with a rubber septum, cooled, evacuated and back-filled three times with ultra-high pure nitrogen. The reaction flask was immersed into an oil bath at 110°C and was stirred for 17 hr. Then, the mixture was, purified by passing through an alumina column two or three times, concentrated and precipitated in methanol. The product was filtered, washed with methanol and dried in vacuum oven for 24 hr at 50°C to obtain white 4-arm star PMMA powder ($[\text{M}]_0:[\text{I}]_0$ of 800:1); Yield: 51%.

FT-IR (KBr): $\nu = 2994, 2950, 2842, 1730$ (C=O), 1482, 1448, 1386, 1268, 1240, 1192, 1149, 989, 966, 840, 751 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.886$ (s, CH_3), 1.057 (s, CH_3), 1.247 (s, CH_3), 1.849 (2H, CH_2), 3.635 (3H, OCH_3) ppm.

Higher molecular weight polymer ($[\text{M}]_0:[\text{I}]_0$ of 16000:1), also have been synthesized, in the same method; Yield: 70%.

FT-IR (KBr): $\nu = 2996, 2951, 1730$ (C=O), 1632, 1484, 1449, 1385, 1269, 1241, 1193, 1148, 990, 840, 751 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.88$ (s, CH_3), 1.05 (s, CH_3), 1.24 (s, CH_3), 1.84 (2H, CH_2), 3.63 (3H, OCH_3) ppm.

Hydrolysis of star polymers

Star PMMA (0.5 g) was dissolved in a mixture of methanol (25 ml) and KOH solution (5%, 3 ml). The mixture was refluxed for 72 hr at 60°C . The organic phase was extracted with chloroform and dried over anhydrous magnesium sulfate. The polymer was precipitated in methanol, filtered and washed with water to obtain hydrolysate arms of star PMMA.

Results for hydrolysis of low molecular weight star polymer ($[\text{M}]_0:[\text{I}]_0$ of 800:1); FT-IR (KBr): $\nu = 2950, 1733$ (C=O), 1633, 1451, 1387,

1262, 1144, 990, 748 cm^{-1} ; M(calcd): 20000, GPC: M_n : 1.6546×10^4 , M_w : 1.7018×10^4 , PDI=1.028.

Results for hydrolysis of high molecular weight star polymer ($[\text{M}]_0:[\text{I}]_0$ of 16000:1); FT-IR (KBr): $\nu = 2951, 1734$ (C=O), 1636, 1450, 1388, 1264, 1148, 991, 751 cm^{-1} ; M(calcd):400000, GPC: M_n : 2.5617×10^5 , M_w : 3.7865×10^5 , PDI=1.47.

Results and Discussion

In this study, two star PMMAs were synthesized via ATRP. Figure 1 outlines the synthesis of a tetrafunctional initiator, and its use in the preparation of 4-arm star PMMA. The initiator was synthesized by esterification reaction of ethylenediamine-*N,N,N',N'*-tetra-2-propanol with 2-bromopropionyl bromide.

4-arm star PMMA were successfully synthesized by ATRP using ethylenediamine-*N,N,N',N'*-tetra-2-propanol tetrakis (2-bromopropionyl bromide) as the initiator, CuBr as the catalyst, and 2,2'-bipyridine as the ligand at 110°C in xylene (Figure 1).

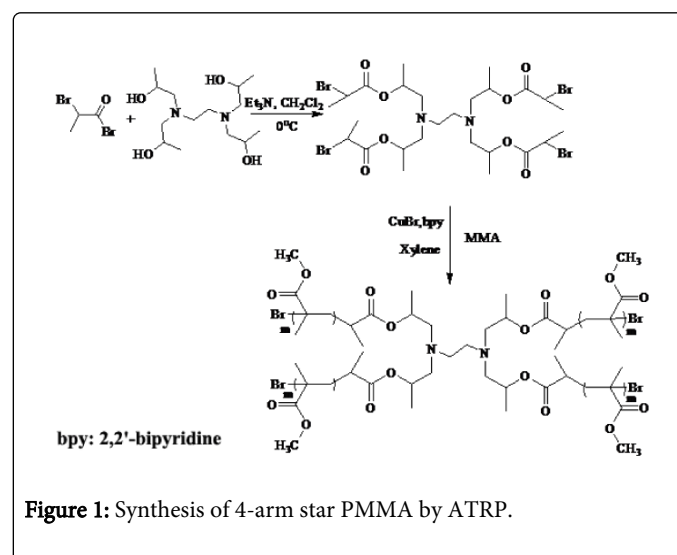


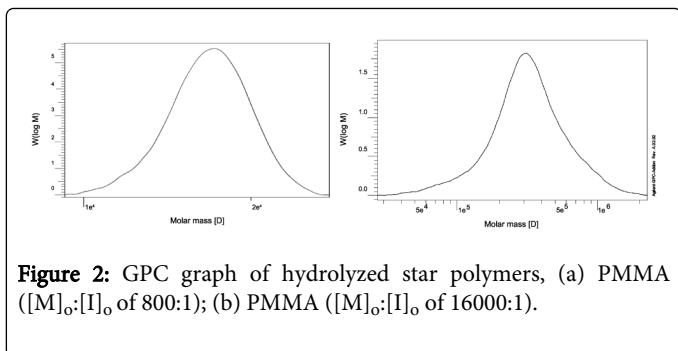
Figure 1: Synthesis of 4-arm star PMMA by ATRP.

The reaction must be operated in inert atmosphere to avoid termination of living polymerization due to CuBr oxidation.

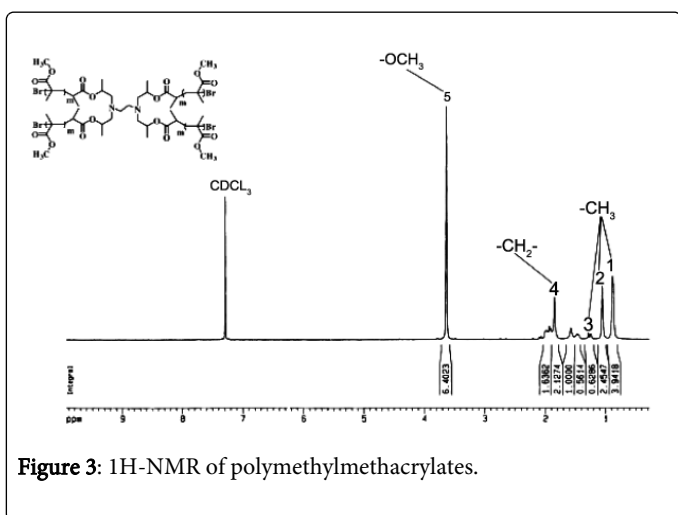
Figure 2a and 2b shows the GPC traces of hydrolyzed star polymers. The M_n of the hydrolyzed star polymers is about 1/4 times as much as that of original 4-arm star PMMA. The M_w s were close to theoretical values, and the polymers had very narrow PDI. Since, GPC traces achieved from hydrolyses of star polymers and the standards in GPC calculation are polystyrene with different molecular weights, some logical difference can be seen in the quantities of M_n and M (calcd). Both GPC traces were monomodal and indicate that the ATRP of MMA has controlled/living characteristics (Table 1).

PDI	M_w	M_n	M (calcd)	Polymer
1.028	1.7018×10^4	1.6546×10^4	20000	PMMA ₁ (Hyd)
1.47	3.7865×10^5	2.5617×10^5	400000	PMMA ₂ (Hyd)

Table 1: GPC data for hydrolyzed PMMA



The NMR spectra and GPC analyses demonstrated the formations of 4-armed star polymer. The $^1\text{H-NMR}$ is employed to analyze the structure of star PMMA (Figure 3). The signals at 0.88-1.24, 1.84-3.63 ppm, represented methyl groups, methylene groups, and methoxy groups, respectively.



It should be noted that the characteristic carbonyl band is clearly detected by FT-IR spectroscopy due to the polymer chain.

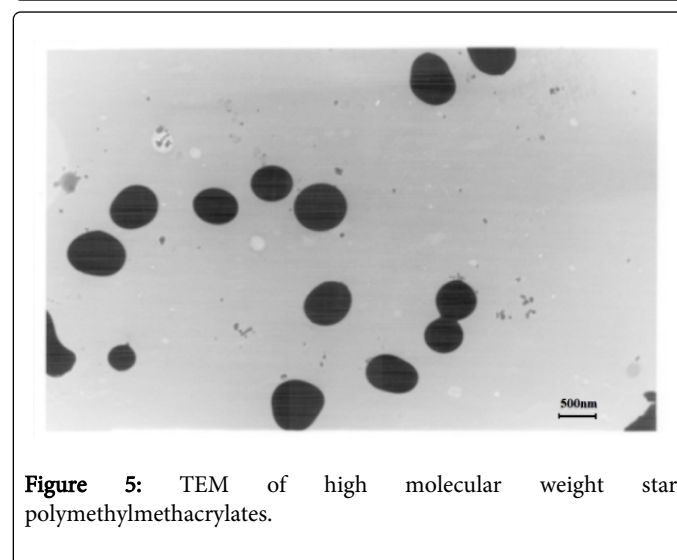
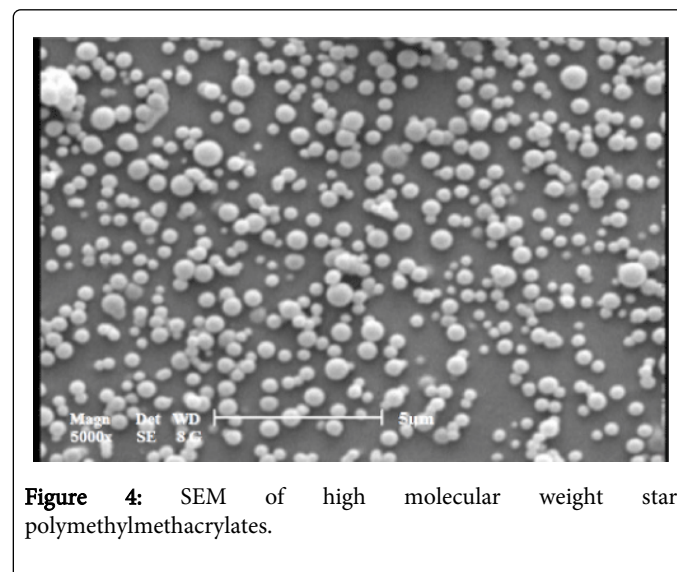
Finally, (Figures 4 and 5) depict SEM and TEM micrographs of high molecular weight star PMMA. Particle morphology is confirmed to be spherical and near mono-disperse in particle size, as expected. Therefore, due to the size and size distribution of the polymer, they could be used as mono-sized polymer additive for lots of the applications [30].

Conclusion

Because the important role of initiator in ATRP, we used the new initiator (Core) with α -haloester units because of its selective and quick halide radical immigration in the ATRP polymerization reaction. Also, because of suitable bonding constant and electronic effects of bidentate nitrogen-base ligand (2,2'-bipyridine), it successfully stabilizes transition metal salts (copper catalysts) in organic phase of the ATRP of MMA monomers. So, Multifunctional new initiator containing α -bromo-ester units as the core were synthesized and initiated atom transfer radical polymerization of MMA, for the synthesis of star polymers with well-defined structures.

Star polymers have special characteristics such as: due to spherical shapes and high surface of these polymers, they are very useful like

erosive materials that have many usages in drug delivery and various other applications.



In this paper, high MW 4-arm star PMMA with a narrow MW distribution was synthesized by a "core-first" method. The star polymers were characterized by $^1\text{H-NMR}$, SEM, TEM and GPC. Formation of star polymers was confirmed by spherical ingredients in SEM and TEM pictures. In the SEM picture, spherical particles show the same arms on every side of star polymer and the formation of the circle limits around the core. GPC of the hydrolyzed star polymers were mono-modal which are the characteristics of living systems. The molecular weights of these linear polymers were near 1/4 of molecular weights of star polymers.

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