

# Controlled Polymerization of Polymethylmethacrylate with Sulfone Containing Initiator

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**Abstract** -The synthesis of polymethylmethacrylate (pMMA) was realized with newly synthesized difunctional initiator, bis[4-(β-(2-bromopropanoate) ethoxy)phenyl]sulphone (BrEPS) in the presence of copper bromide (CuBr) and N, N, N', N'', N'''-pentamethyl-diethylenetriamine (PMDETA) by using atom transfer radical polymerization (ATRP). Sulphone group containing initiator was prepared by esterification of bis[4-(β-hydroxyethoxy)phenyl] sulfone (HEPS). Both initiator and polymers were characterized by <sup>1</sup>H-NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The ATRP was supported by an increase in the molecular weight of the forming polymers and also by their monomodal molecular weight distribution. Pendulum hardness tests on films of synthesized polymers indicated higher degree of hardness than that of pure pMMA.

**Keywords:** ATRP, initiator, polymethylmethacrylate, sulfone containing

## 1. Introduction

The incorporation of functional groups in the polymer using ATRP can be achieved by use of initiators containing functional groups such as vinyl, hydroxyl, epoxide, cyano (Hutson, L., et al., 2004), (Kamigaito, M., T. Ando, M. Sawamoto, 2001), (Hegewald, J., et al., 2009), fluoro (Çanak, T.C., et al., 2012), amide, N-carboxy anhydride, carboxylic acid, acetophenone formaldehyde resin, cyclohexanone formaldehyde resin, amino acid, norbornenyl, and amino adamantine.

A number of investigations showed that sulfone containing polymers such as polyethers, epoxy resins, polyesters and polyarylates, display good physical, mechanical and thermal properties. Gaynor and Matyjaszewski developed a novel strategy to prepare ABA block copolymers having polysulfone segment via the atom transfer radical polymerization (ATRP) technique, using a difunctional polysulfone as macroinitiator (Matyjaszewski et al., 1997). Also two kinds of novel amphiphilic ABA copolymers, which contain hydrophobic polysulfone block and hydrophilic poly[poly(ethylene glycol) methyl ether methacrylate] segments, by ATRP using a bromo-terminated difunctional polysulfone as macroinitiator was designed and synthesized successfully (Wang, J., 2008). Liaw and Chang previously reported the synthesis of bis[4-hydroxyethoxy]phenylsulfone (HEPS) and they used to synthesize HEPS containing polycarbonates by melt transesterification (Liaw, D.-J. and P. Chang, 1997), polyamides (Liaw, D.-J. and P. Chang, 1999) and polyesters by direct polycondensation, and polyurethanes (photolysis investigation), polyimides. Also amorphous copolyesters, and poly(ethylene terephthalate) copolymers, polyurethane-ureas which contain BHEPS were synthesized and presented previously (Tsai, Y., 2009). Some other macroinitiators were also used for the controlled growth via ATRP (Agudelo, N. A., 2014). To the best of our knowledge, there is no report on the synthesis of sulfone containing polymers with controlled molecular weight using bis[4-hydroxyethoxy]phenylsulfone functionalized initiator by ATRP technique. The objective of this study is to design and synthesize chain-end sulfonated polymers and to investigate the effect of this sulfone group to the polymer surface and thermal properties.

For this, a novel sulfone containing polymer with well-defined structure was successfully synthesized via ATRP technique, using a bromo-terminated difunctional sulfone as initiator. The

difunctional sulfone initiator was prepared by esterifying the -OH end groups of sulfone to  $\alpha$ -haloester. This initiator was then used to initiate the polymerization of methyl methacrylate monomer. The efficiency of the synthesized initiator is evaluated and discussed on the basis of the molecular weight and polydispersity of the polymers. Synthesized initiator was characterized by FT-IR, and  $^1\text{H-NMR}$ . Obtained sulfone containing polymers were also characterized by  $^1\text{H-NMR}$ , GPC and the thermal properties were examined by DSC and TGA methods. Thin films of these polymers were prepared by spin coating to investigate the hardness behavior of the polymers.

## 2. Results and Discussion

In this study sulphone group containing polymethylmethacrylate was synthesized via ATRP technique. For this purpose, bis[4-( $\beta$ -hydroxyethoxy)phenyl]sulfone (HEPS) used for the preparation of BrHEPS. Reaction of bis(4-hydroxyphenyl)sulfone with ethylene carbonate in the presence of  $\text{Na}_2\text{CO}_3$  gave HEPS in 90 % yield. Then sulphone group containing bifunctional ATRP initiator was synthesized by esterification of HEPS with 2-bromopropionylbromide.

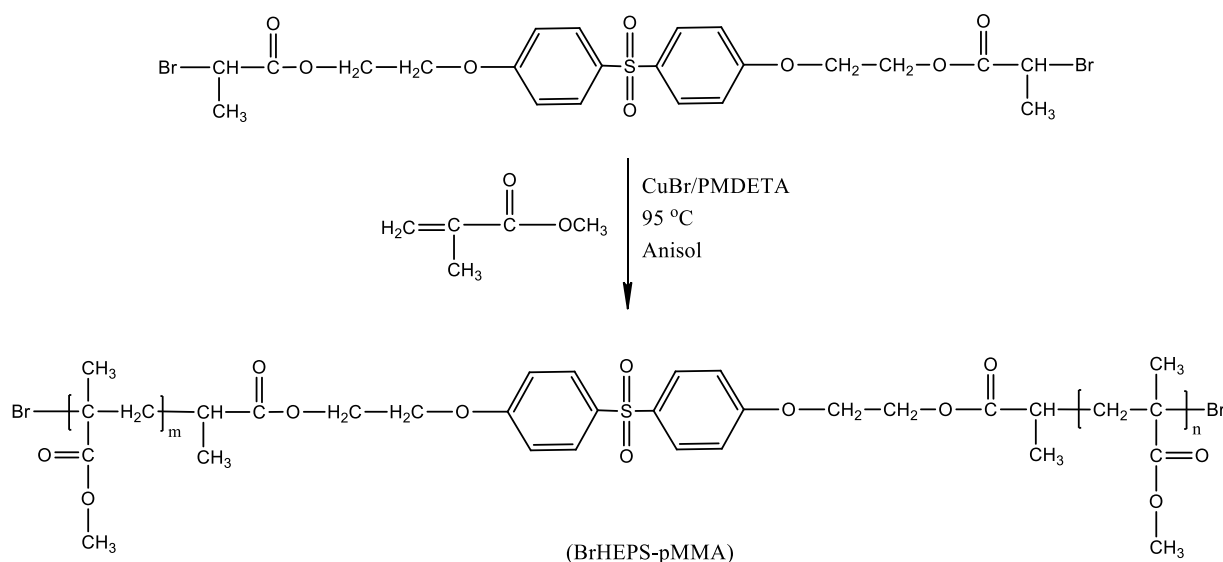


Fig. 1. Synthesis of BrHEPS-pMMA

The structure of the product BrHEPS was confirmed by spectroscopic investigations. FT-IR spectrum showed no signal corresponding to  $-\text{OH}$  groups of the bis[4-( $\beta$ -hydroxyethoxy)phenyl]sulfone (HEPS) at  $3416\text{ cm}^{-1}$  and shows the characteristic  $\text{C}=\text{O}$  ester band at  $1735\text{ cm}^{-1}$  and  $\text{C-Br}$  band at  $696\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  spectrum recorded in  $\text{CDCl}_3$  evidenced resonance signals of  $-\text{CH}_3$ ,  $-\text{CH}_2$ ,  $-\text{OCH}_2$ ,  $-\text{CH-Br}$  protons of relative intensities corresponding to the number and type of protons. The peak observed at 4.38 ppm corresponded to  $\text{CH-Br}$  protons and spectrum indicated the presence of  $-\text{OCH}_2$  protons at 4.24 and 4.51 ppm, aromatic protons at 6.97, 7.85 ppm and  $\text{CH}_3$  protons at 1.80 ppm. The BrHEPS initiator with two bromine group was used to initiate the ATRP of methylmethacrylate (MMA) to obtain sulphone containing polymer. Typical results concerning the polymerization are presented in Table 1.

As shown in Table 1 as the conversion increased with the time, polydispersities decreased during the polymerizations. It can be said that an acceptable agreement of theoretical,  $M_n$ , th, and experimental,  $M_n$ , exp, number-average molecular weight and polydispersity index were obtained. For synthesized polymers,  $M_n$ , exp, is more than two times higher than  $M_n$ , th although the polydispersity index is still low. This can be explained by investigations of imperfections such as slow initiation, termination, transfer, and slow exchange and their effects on kinetics, molecular weight, and polydispersities of "living" chain growth polymerization. During the polymerization initiating efficiency is decreasing, this could be due to some chains in polymer lost its active end during the polymerization because of the

termination reactions. Very reactive initiators may produce too many radicals, which will terminate at early stages. This will reduce efficiency of initiation, produce too much of the deactivator. Table 1. shows the increase of monomer conversion with time, which is a basic requirement for living systems. Figure 2 shows the semi-logarithmic kinetic plot of  $\ln ([M]_0/[M]_t)$  versus time,  $t$ , where  $[M]_0$  is the initial concentration of the monomer, and  $[M]_t$  is the monomer concentration at any time and also plots of  $M_n$  and polydispersity indexes ( $M_w / M_n$ ) as a function of conversion. The linearity of the plot indicates that the concentration of growing radicals is constant and polymerizations of MMA monomer proceed in a controlled and living manner.

Table. 1. Polymerization Characteristics of Sulfone Containing Polymethylmethacrylates.

Run	Time(h)	Conv.(%) <sup>b</sup>	$M_n$ , th <sup>c</sup>	$M_n$ , exp <sup>d</sup>	$M_w/M_n$ <sup>d</sup>
BrHEPS-pMMA1	4	15	2692	8434	1.30
BrHEPS-pMMA2	8	22	4400	9436	1.22
BrHEPS-pMMA3	16	26	5220	11795	1.22
BrHEPS-pMMA4	20	37	7380	14565	1.19
BrHEPS-pMMA5	24	40	8000	18657	1.18

<sup>a</sup>  $[I]_0 : [CuBr]_0 : [PMDETA]_0 : [Monomer]_0 = 1 : 2 : 4 : 200$  in anisole at 95 °C, <sup>b</sup> Determined gravimetrically, <sup>c</sup> Calculated by  $M_n, th = ([M]_0 / [I]_0) \times (\text{conversion } \%) \times M_{monomer}$ , <sup>d</sup> Determined by means of GPC calibrated with pMMA standards.

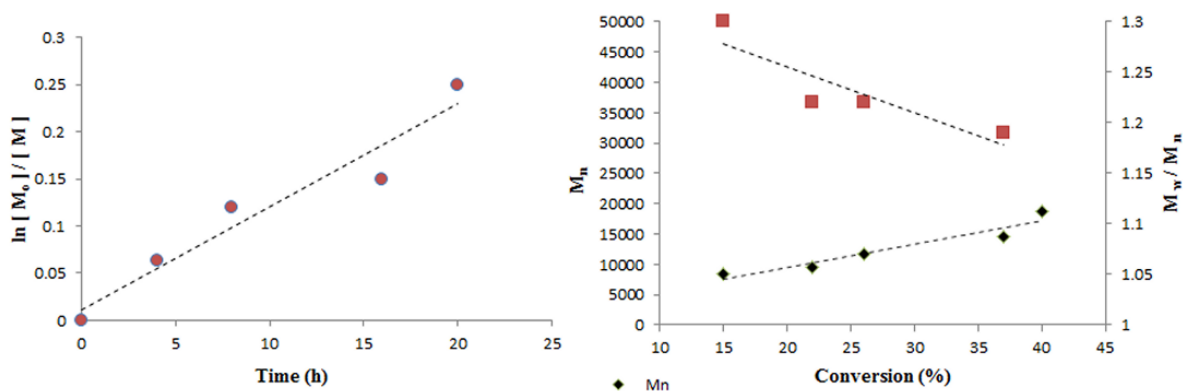


Fig. 2. First-order kinetic plots for the polymerization of MMA in anisole at 95 °C .

The bands at 0.76, 1.00, and 1.20 ppm in the <sup>1</sup>H-NMR spectrum of pMMA represented the resonance of syndiotactic, atactic, and isotactic methyl (-CH<sub>3</sub>) groups. The methylene proton (-CH<sub>2</sub>) of pMMA resonances between 1.4 and 2.3 ppm. The signals observed at 3.59 ppm corresponded to the methyl (-OCH<sub>3</sub>) of the ester group of MMA. The complete disappearance of initiator CH-Br signals at 4.38 ppm indicated that Br functions took part in initiating the pMMA chain growth. Thermal behaviours of polymers were checked with DSC and TGA measurements.

DSC measurements were conducted with a heating rate of 10 °C/min. In all cases, the  $T_g$ 's could be easily measured in the second heating traces of DSC. The thermal stability measurements were evaluated by TGA under nitrogen at a heating rate of 20 °C/min. The thermal behavior data for all polymers are listed in Table 2.

The  $T_g$  values of the pMMAs were in the range of 114–121 °C/min depending on the molecular weight increase. In the range of 8000-11000 molecular weights  $T_g$  values did not change much, after 14000 they increased with increasing molecular weight. Thermal effect of sulfone group on the polymers was examined. To make a comparison, the  $T_g$  and TGA of standard pMMA which has a number average molecular weight ( $M_n$ ) of 11550 g/mol, were measured. The  $T_g$  of the standard PMMA is 122.5 °C and

the weight loss is 98.8 %. So the results show us that sulfone containing pMMA have lower T<sub>g</sub> and the char yield is higher than the standard PMMA. That is because of the narrow polydispersity of pMMAs due to the one sulfone group within each chain of the polymer. The low molecular weight, the free volume of sulfone groups, bromine end functionalized groups, and also the etheric groups which give flexibility to chains probably effected to decrease the T<sub>g</sub> value of pMMA. The introduction of sulfone groups into pMMA polymers was expected to improve their thermal stability. As observed from TGA, weight loss begins at around 230 °C and then gives another weight loss at about 315 °C, to result in a two-stage weight loss. At 500 °C higher char yields were obtained indicating that sulfone containing polymers exhibited better thermal stability than that of standard pMMA as a result of all the chains have the bromine end function and sulfone group.

Table 2. DSC and TGA results for polymers BrHEPS-pMMA.

Polymers	T <sub>g</sub> ( °C )	T <sub>%50</sub> ( °C )	Residue at 500 °C (%)
BrHEPS-pMMA1	116.5	404.5	1.0
BrHEPS-pMMA2	115.8	404.4	1.0
BrHEPS-pMMA3	114.2	398.3	1.2
BrHEPS-pMMA4	117.9	399.1	3.3
BrHEPS-pMMA5	121.0	402.9	6.2
STD-pMMA	122.5	393.6	1.2

Thin polymer films were spin-coated (1000 rpm for 30 s) using a SCS P6700 spin coater onto a clean and dried glass substrate using solutions of the synthesized polymers with concentrations of 30 mg in 2ml of dichloromethane. After spin-coating the polymer films were annealed for 2 h at 80 °C in an oven. By this procedure glass substrate was completely covered with the polymers. König pendulum hardness tests were applied to all coated glass plates. As shown in Table 3 spin coated film of pure pMMA showed hardness value of 160 könig while sulfone containing pMMA films had hardness values between 163-172. The pendulum hardness increased with increase in molecular weight as the number of chains having rigid phenyl sulfone groups increase.

Table 3. Pendulum Hardness Results of Sulfone Containing Polymethylmethacrylates.

Run	Hardness König
STD-pMMA	160
BrHEPS-pMMA1	163
BrHEPS-pMMA2	167
BrHEPS-pMMA3	167
BrHEPS-pMMA4	171
BrHEPS-pMMA5	172

### 3. Conclusions

A new ATRP initiator, bis[4-(β-(2-bromopropanoate) ethoxy)phenyl]sulphone (BrHEPS) having sulphone group was synthesized and used to carry out ATRP of methylmethacrylate in the presence of CuBr/PMDETA.

The structures of the initiator and polymers were thoroughly characterized and confirmed using NMR spectroscopy. A linear relationships between both ln[M]<sub>0</sub>/[M] vs time and molecular weight vs conversion indicated controlled/living polymerization of MMA using BrHEPS as ATRP initiator. The DSC results correlate well with the results of standard pMMA polymer. Introducing the sulphone group into the polymer gave higher residue in the TGA analysis.

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