



Trade Science Inc.

# Macromolecules

*An Indian Journal*


---

**Full Paper**

MMAIJ, 3(3), 2007 [000-000]

## Synthesis Of Furan End-Capped Poly(Methyl Methacrylate)s Via Atom Transfer Radical Polymerization With Two Different Initiators

B.Filiz Senkal, Zulfiye Ilter, M.Fatih Coskun, Kadir Demirelli\*, Idris Cakmak  
 Department of Chemistry, Faculty of Science and Arts, University of Firat, Elazig, (TURKEY)

E-mail : [kdemirelli@firat.edu.tr](mailto:kdemirelli@firat.edu.tr)

Tell : 0424 2370000/3698 ; Fax: 0424 2330022

Received: 30<sup>th</sup> August, 2007 ; Accepted: 4<sup>th</sup> August, 2007

### ABSTRACT

The synthesis of benzofuran and naphthafuran end-capped poly(methyl methacrylate)s via atom transfer radical polymerization (ATRP) is reported. Methyl methacrylate (MMA) was polymerized in bulk at different temperatures (90°C, 100°C and 110°C) via ATRP using a new benzofuran and naphthafuran initiators (2-acetyl bromine benzofuran and 2-acetyl bromine naphthafuran) in the presence of CuBr/2,2'-bipyridine (bpy) as the catalyst. With this new initiating systems, a successful ATRP of MMA was carried out, and benzofuran and naphthafuran end-capped polymers with predetermined molecular weights and polydispersities were obtained at desired polymerization temperature. The linear proportionality of the molecular weights to the conversions and straight lines observed in  $\ln(M_0/M)$  (where  $M_0$  and  $M$  are the monomer contents at the beginning and any time, respectively) versus time plots indicate typical controlled polymerization characteristics. Poly(methyl methacrylate)s as a macroinitiator were used to synthesize the poly(MMA-b-St) block copolymer, which allowed a demonstration of its living character.

© 2007 Trade Science Inc. - INDIA

### KEYWORDS

2-Bromoacetyl benzofuran;  
 1-Bromomethyl-1-(naphthabenzofuran-2-yl);  
 Atom transfer radical polymerization;  
 Polymerization.

### INTRODUCTION

Atom transfer radical polymerization (ATRP) has proved to be effective for the living radical polymerization (LRP) of a variety of monomers such as styrene, (meth)acrylates, acrylonitrile, and (meth)acrylamides<sup>[1]</sup>. It works on the "persistent radical effect" principle, according to which a transition metal complex of a higher oxidation state acts as the persistent radical to reversibly deactivate a growing polymer radical to form a

dormant polymer molecule with a labile carbon halogen bond at the chain end<sup>[2-5]</sup>. Appropriate ligands and transition metal salts may suitably adjust the equilibrium position of reversible deactivation so that the polymer radical concentration becomes good enough for a reasonably fast ATRP.

The development of "living"/controlled free radical polymerization systems in the last years has highly increased the tools for the achievement of polymers with low polydispersity, tailored molar mass and controlled

structures<sup>[6-8]</sup>. Among these systems, ATRP (atom transfer radical polymerization) is particularly attractive for the synthesis of novel and complex architectures<sup>[9-12]</sup> in rather straightforward operating conditions.

Alkyl halogenides, especially  $\alpha$ -keto chlorides and bromides, are common initiators in ATRP. Alkyl halogenides with  $\alpha$ -hydrogens are not preferred because of HX elimination as a side reaction. Obviously, the carbonyl group connecting with the halomethyl group prevents  $\beta$ -elimination and makes it easier to cleave the carbon-halogen bond. Since the pioneering study of Wang and Matyjaszewski on copper mediated ATRP<sup>[6,7]</sup> many halogenides<sup>[8]</sup>, including sulfonyl chloride<sup>[9,10]</sup> were studied as initiator components in polymerization.

Although R-Br/CuBr-L couples were found to be superior to the R-Cl/CuCl-L system<sup>[11]</sup> cross systems of R-Br/CuBr-L were demonstrated to work successfully<sup>[12]</sup>.

The incidence of fungal infection has increased significantly in the past 25 years. The growing number of immunocompromised patients as a result of cancer chemotherapy, organ transplantation, and HIV infection are the major factors contributing to this incidence. It is reported that the presence of the spacer between the heterocyclic substituent and the benzofuran nucleus may be essential for the biological activity<sup>[13]</sup>. The benzofuran inhibitors have been reported to be fungal Nmt inhibitors<sup>[14-16]</sup>. Some of the benzofuran inhibitors showed high selectivity over human and exhibited antifungal activity *in vivo*.

In this work, the benzo, and naphthafuran ring end-capped poly(methyl methacrylate)s (PMMA) were synthesized via ATRP by using a new functional initiator bearing furan ring (2-acetylbromine benzofuran and 2-acetylbromine naphthafuran), and the properties of ATRP of methyl methacrylate (MMA) with this new initiators were investigated under the different conditions.

## EXPERIMENTAL

### Materials

2-Hydroxynaphthaldehyde, salicylaldehyde, chloro acetone, bromine, potassium carbonate, acetonitrile and ethylalcohol were obtained from Fluka (Switzerland) and used without further purification.

### Characterization techniques

Infrared spectra were obtained on a Mattson 1000 FTIR spectrometer. The NMR spectra were recorded on a NMR (300MHz and 90MHz) spectrometer at room temperature in  $\text{CDCl}_3$ . Gel permeation Chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump with Agilent 1100 system equipped with a vacuum degasser, a refractive index dedector. The tetrahydrofurane (THF) was the carrier solvent at a flow rate of 1 mL/min and at room temperature. The instrument was calibrated with linear polystyrene (PSt) standards.

### Preparation of benzofuran

The preparations of the products were performed according to previously reported procedures<sup>[13]</sup>.

### Synthesis and characterization of 2-bromoacetyl benzofuran (BrBF) and 1-bromomethyl-1-(naphthabenzofuran-2-yl) (BrNF)

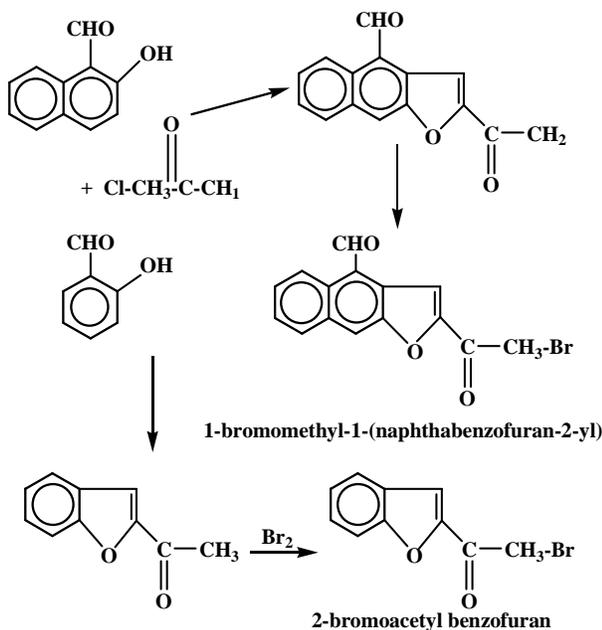
The initiators were synthesized and characterized by using FT-IR and  $^1\text{H-NMR}$  spectroscopy.

### Typical procedure was given as follows

Into a three-necked 500 mL flask equipped with magnetic stirring were placed (0.1 mol) of 2-bromoacetyl benzofuran was dissolved in 60 mL of glacial acetic acid. Then 0.1 mol of bromine in 50 mL glacial acetic acid was added drop wise at 15°C for 1 h. The mixture was stirred for 1 h at room temperature. The product was poured into excess of cold water, filtered, washed with excess of water and dried under vacuum at 40°C for 24 h. 2-bromoacetyl benzofuran was recrystallized from ethylalcohol to get yellow crystals.

### Polymerization procedure

The polymerizations were carried out in bulk polymerization conditions by using MMA monomer at 90°C, 100°C and 110°C. A typical procedure was to use a 100-mL three-necked, round-bottom flask equipped with a reflux condenser, a dropping funnel, and a nitrogen inlet into which were placed 25.4 mL (0.25 mol) of MMA, 0.78 g (5 mmol) of bipyridine, and 0.36 g (2.5 mmol) of CuBr under a nitrogen flow. The flask was mounted in a silicon oil bath and the mixture was stirred until all the CuBr dissolved (10 min). The reaction content was heated and kept at a constant temperature



SCHEME 1 : The structure of new initiators

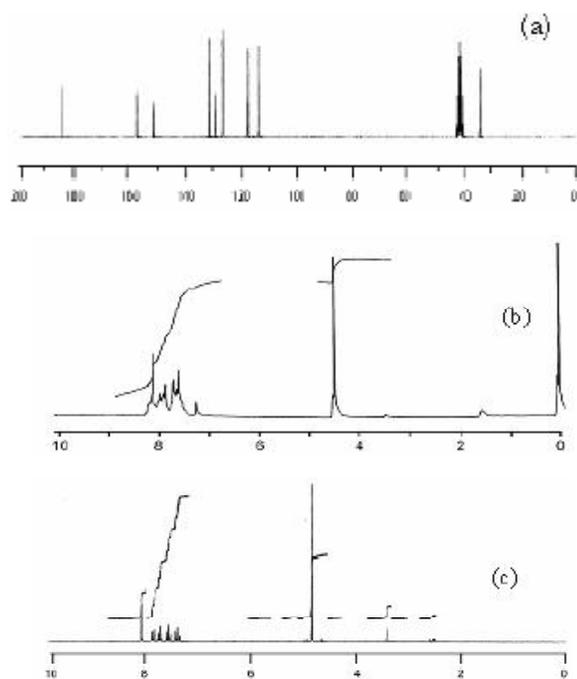


Figure 1 (a) :  $^{13}\text{C}$ -NMR spectrum and (b)  $^1\text{H}$ -NMR spectrum of (b) 2-bromoacetyl benzofuran (BrBF), (c)  $^1\text{H}$ -NMR spectrum of 1-bromomethyl-1-(naphthalenyl)acetone (BrNF)

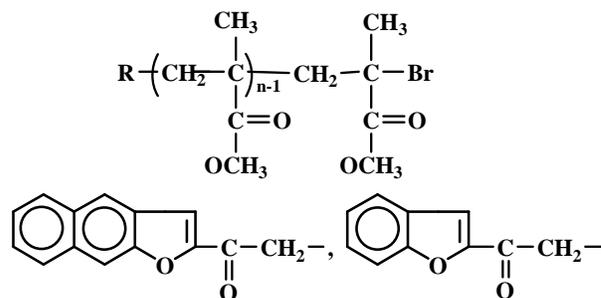
with stirring. Then 0.60g(2.5mmol) of 2-bromoacetyl benzofuran was added to the reaction mixture. The solution became brownish-green within 20min. The kinetics of the reaction was followed by aliquots taken at appropriate time intervals.

## RESULTS AND DISCUSSION

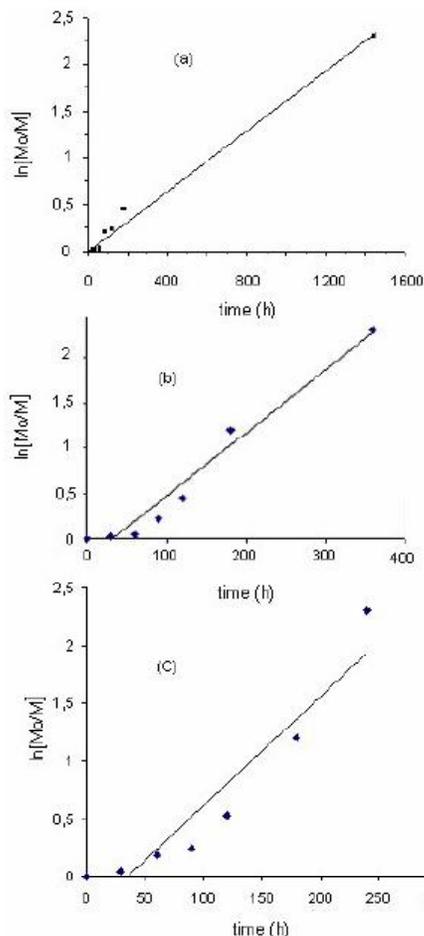
2-Bromoacetyl benzofuran (BrBF) and 1-bromomethyl-1-(naphthalenyl)acetone (BrNF) could be easily obtained with high yield via the reaction of chlorineaceton with 2-hydroxynaphthaldehyde, salicylaldehyde in the presence of bromine referring to a similar procedure in literature<sup>[13]</sup>. BrBF and BrNF are a kind of furan ring compound containing alkyl bromide group, so it can be used for ATRP as initiator. The structure of new initiators is illustrated in SCHEME 1.

The proton on the furan ring appeared at 8.1 ppm, while the aromatic protons were observed at 7.4 ppm and 7.90 ppm. In the  $^{13}\text{C}$ -NMR spectrum of the initiator BrBF (Figure 1a), it is characteristic for ketone,  $\text{C}=\text{O}$ , signal at  $\delta=184$  ppm and the other signals are a good agreement with structure of BrBF. The structure of the new initiators was also characterized by using  $^1\text{H}$ -NMR and FT-IR spectra. In the  $^1\text{H}$ -NMR spectrum of the BrBF (Figure 1b), all the signals corresponding to the proposed structure of BrBF were observed in  $\text{CDCl}_3$ .  $^1\text{H}$ -NMR spectrum of BrNF, Figure 1c, showed at 4.5 ppm the methylene protons next to the bromine. Based on all these signals of  $^1\text{H}$ -NMR, the product was confirmed to be BrNF exactly. The FT-IR spectra of BrBF and BrNF showed the  $\text{C}=\text{O}$  stretch in  $1686\text{cm}^{-1}$  and  $1660\text{cm}^{-1}$ , respectively. The structure of benzo or naphtha end capped poly(MMA) is illustrated in SCHEME 2.

The dependences of  $\ln[\text{M}_0/\text{M}]$  on time for polymerization of MMA at  $90^\circ\text{C}$ ,  $100^\circ\text{C}$ ,  $110^\circ\text{C}$  initiated with BrNF/CuBr/2,2'-bpy and are plotted in figure 2a, 2b, 2c, respectively. The polymerization proceeds very fast in the beginning of the reaction then stabilizes. The dependence of  $\ln[\text{M}_0/\text{M}]$  on the polymerization time shows



SCHEME 2 : The structure of benzo or naphtha end capped poly(MMA)



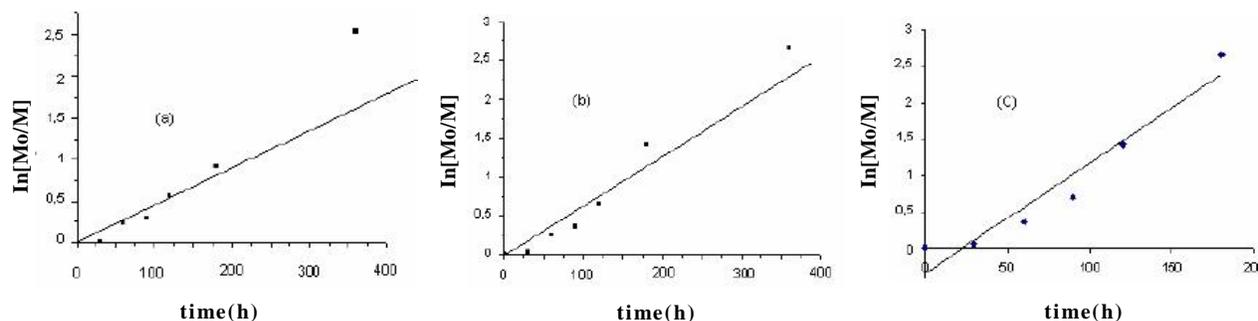
**Figure 2 :** The plots of  $\ln[M_0/M]$  vs. time for the polymerization of methyl methacrylate at (a) 90°C, (b) 100°C, (c) 110°C initiated with BrNF/Cu(I)Br/bpy

a linear relationship when the polymerization is stable. The linearity of the plot of  $\ln[M_0/M]$  versus time indicates that the polymerization follows the first kinetics with respect to the monomer concentration and the concentration of growing chain species remains constant.

The kinetics plot of MMA polymerization at 100°C and 110°C initiated with BrNF/CuBr/2,2'-bpy is shown in figure 3a, 3b and 3c, respectively. Contrary to the MMA polymerization with a fast initiation stage, there is an induction period during the polymerization process of MMA. After induction period, the dependence of  $\ln[M_0/M]$  on the time is approximatively linear.

$M_n$  of PMMA produced at 90°C, 100°C and 110°C initiated with BrBF/CuBr/2,2'-bpy as a functions of monomer conversion are shown in figure 4a, 4b and 4c, respectively. GPC data showed that  $M_n$  value of poly(PAMA) obtained for polymerization of MMA at 90°C initiated with BrBF/CuBr/2,2'-bpy for 30min was 14900 ( $M_w/M_n=1.91$ ). On the other hand,  $M_n$  of PMMA produced at 100°C and 110°C initiated with BrNF/CuBr/2,2'-bpy as a functions of monomer conversion are shown in figure 5a, and 5b, respectively. The obtained polymers in presence of both initiators have broad polydispersities. This means that the bulk polymerization of MMA is not well controlled under the conditions that were used. This might be because of the following reasons: the fast initiation that could not be balanced by a relatively slow bromine transfer reaction and the excess viscosity of the reaction mixture, which leads to difficulty in controlling it<sup>[16]</sup>. It is known that well-defined polymers with molecular weights ranging from 1.000 to 250.000 have been successfully synthesized<sup>[17,18]</sup>. Thus, narrow  $M_w/M_n$  is usually the feature of living or well-controlled polymerization.

The <sup>1</sup>HNMR spectrum of PMMA-Br in figure 6 showed that naphthafuran and bromine group had been introduced to the end of polymers. It was clear that the signals which appeared at 7.75, 7.66, 7.57 and 7.25ppm were consistent to the protons of the



**Figure 3 :** The plots of  $\ln[M_0/M]$  vs. time for the polymerization of methyl methacrylate at (a) 90°C, (b) 100°C, (c) 110°C initiated with BrBF/Cu(I)Br/bpy

## Full Paper

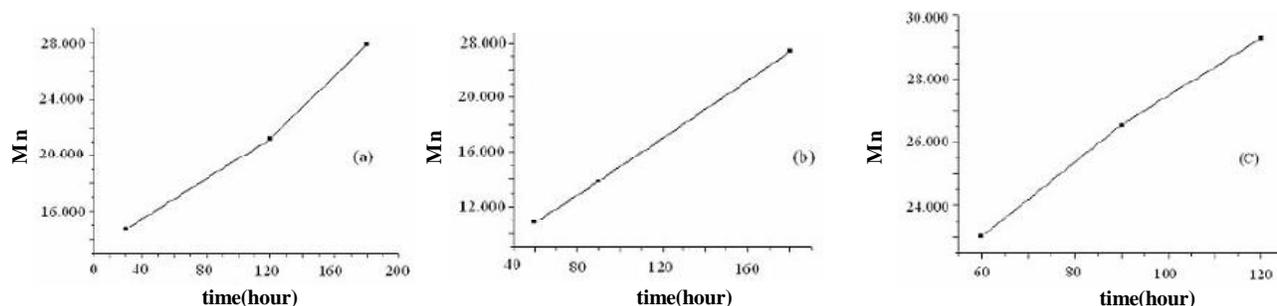


Figure 4 : The plots of Mn vs. time for the polymerization of methyl methacrylate at (a) 90°C, (b) 100°C, and (c) 110°C initiated with BrBF/Cu(I)Br/bpy

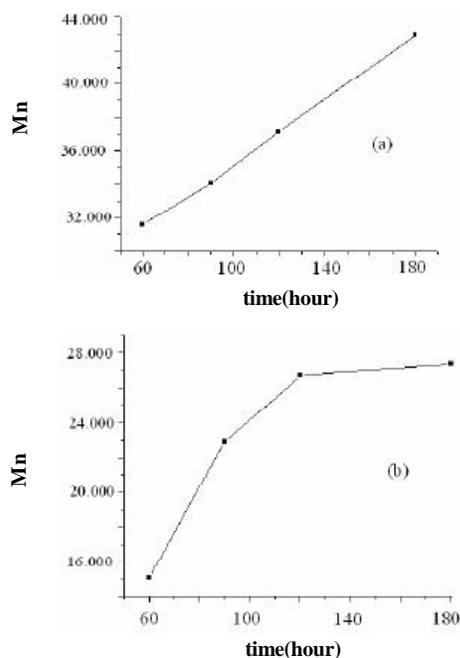


Figure 5 : The plots of Mn vs. time for the polymerization of methyl methacrylate at (a) 100°C, (b) 110°C initiated with BrNF/Cu(I)Br/bpy

naphthafuran, and the other signals corresponded to the protons of other PMMA moiety except one signal ( $\delta=7.25$ ppm) for  $\text{CDCl}_3$ .  $^1\text{H}$  NMR experiments on the same polymers detected low levels of a naphthafuran end group are also present. The  $^1\text{H}$  NMR spectrum showed that there were 0.01 naphthafuran end groups per 100 polymerised MMA units. The molecular weight ( $M_n$ ) of the polymer sample could be estimated from the relative intensity of the MMA moiety and naphthafuran resonances. The signals in question are those arising from alkyl protons in the  $\text{CH}_3\text{OCOCCH}_2$  ( $\text{CH}_3$ ) moiety in the repeat unit and the naphthafuran group in the initial unit of the chain. The number average molecular weight ( $M_n$ ) was then calculated from the

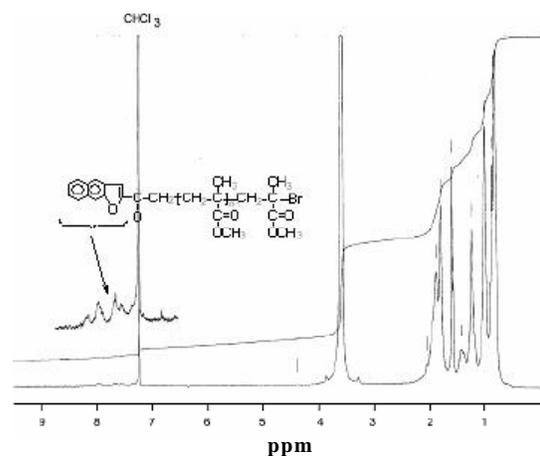


Figure 6 :  $^1\text{H}$ -NMR spectrum of naphtha end-capped PMMA in  $\text{CDCl}_3$

following equation:

$$M_n = I_r / 8 \times 7 / I_i \times M_r(\text{MMA}) + 289$$

where  $I_r$  and  $I_i$  are the integrals for the MMA resonances in the repeat unit and initial unit, respectively, and  $M_r(\text{MMA})$  is the molecular weight of MMA. The value of 289 is simply the molecular weight of the initiator. Data for the poly(MMA) studied indicated that the number average molecular weights was approximately 10900. This is in good agreement with that of the GPC ( $M_n=12000$ ).

To ensure that the obtained polymers retained their activity, consequently, virtually released from transfer and termination reactions, with conventional ATRP technique<sup>[19]</sup>, the chain extension was carried out a chain-extension polymerization of St with the isolated both benzofuran and naphthafuran end-capped poly(methyl methacrylate)s, PMMA, macroinitiator. For this purpose, CuBr as a catalyst and 2,2'-bpy as a ligand. The polymerization temperature was kept at 90°C. Figure 7 shows  $^1\text{H}$ -NMR spectra of benzo and naphtha end-capped PMMA-b-PSt copolymer in  $\text{CDCl}_3$ . The 6.7-

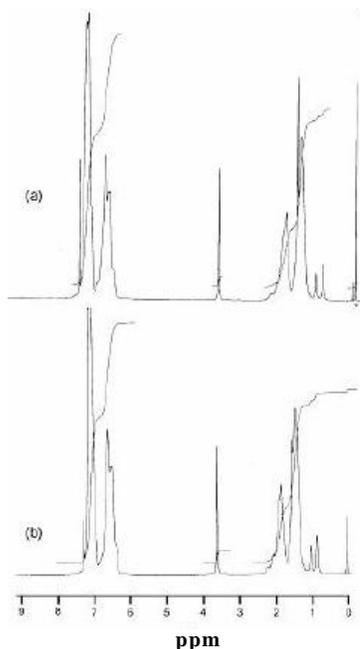


Figure 7 :  $^1\text{H-NMR}$  spectra of (a) benzo and (b) naphtha end-capped PMMA-b-PSt copolymer in  $\text{CDCl}_3$

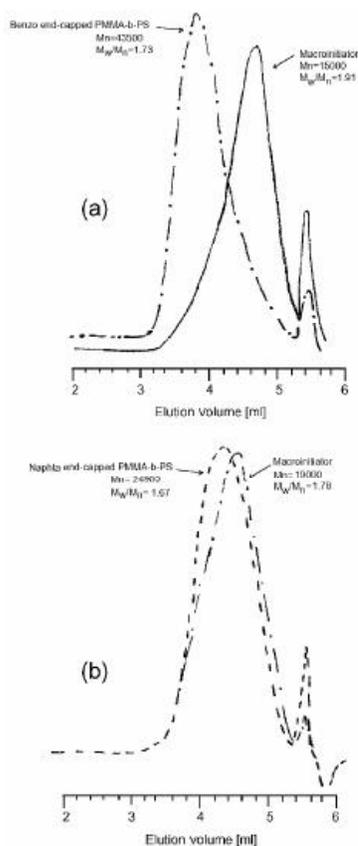


Figure 8 : Molecular weight distributions of (a) benzo-end capped PMMA macroinitiator and (b) naphtha-end capped PMMA macroinitiator and PMMA-b-PSt diblock copolymer at  $90^\circ\text{C}$

7.3ppm signals in  $^1\text{H-NMR}$  spectrum of both copolymers showed that styrene units had been introduced to block copolymers. As shown in figure 8a and 8b, the block copolymer showed an increase in  $M_n$ . From the GPC curves of benzofuran end-capped PMMA before and after chain extension in figure 8a, it could be easily observed that the increase in molecular weight was evidenced from PMMA ( $M_n=15000$ ) to chain-extended PMMA-b-PS ( $M_n=43500$ ). The polydispersity changed from 1.91 to 1.73. As seen in figure 8b, it could be easily observed that the increase in molecular weight was evidenced from naphthafuran end-capped PMMA ( $M_n=19000$ ) to chain-extended PMMA-b-PS ( $M_n=24900$ ). The polydispersity changed from 1.78 to 1.67. Therefore, all of the above results presented the macroinitiators, (Br-PMMA)s are “living” polymer. This showed a good blocking efficiency of Br-PMMA prepared by both initiators by ATRP and a complete Br functionalization of the macroinitiator. In a typical ATRP,  $M_w/M_n$  of polymer is narrow because both initiation and deactivation rates are much higher than the propagation rate, allowing for all the chains to begin growing at the same time<sup>[20]</sup>. As a multicomponent system, ATRP is composed of a monomer, an initiator and a catalyst. Sometimes an additive is used. For a successful ATRP, other factors, especially such as solvent and temperature, must be taken into consideration<sup>[21]</sup>. So during our research, the effect of temperature and time on the polymerization of MMA was investigated. For this purpose, the polymerization temperature was changed from  $90^\circ\text{C}$  to  $110^\circ\text{C}$  for desired time. In the polymerization of MMA initiated with both initiators,  $M_w/M_n$  is some broad, when the equilibrium between the active carbon of propagation chain and the Cu(II) complex is well established after initial stage, the calculated rate constant of chain propagation of MMA is less than  $10^{-2}\text{ s}^{-1}$ .  $k$  values for polymerization of MMA at different temperatures initiated with BrBF or BrNF/CuBr/2,2'-bpy are given in TABLE 1.

TABLE 1 :  $k$  values for polymerization of MMA at different temperatures initiated

System	$90(^\circ\text{C})$	$100(^\circ\text{C})$	$110(^\circ\text{C})$
The polymerization of MMA initiated with BrNF	0.00159	0.00695	0.00939
The polymerization of MMA initiated with BrBF	0.00724	0.00789	0.01528

## Full Paper

This indicates that might be a consequence of the undesirable side reactions such as transfer and termination reactions. Thus, it is known that termination and other side reactions are also present in ATRP, and they become more prominent as higher molecular weight polymers are targeted<sup>[22]</sup>.

### CONCLUSIONS

The controlled polymerization of MMA at 90°C, 100°C and 110°C with two different monofunctional initiators was achieved. From the results mentioned above, it can be concluded that the combination of benzo and naphthafuran end-capped poly(methyl methacrylate)s and Cu(I)Br/2,2'-bpy as a new initial system is effective for the polymerization of MMA and St. The naphthafuran or benzofuran group and bromine atom are at the ends of resultant polymers. For the polymerization of MMA, the dependence of  $\ln[Mo/M]$  on time follows linearity after the initial stage and molecular weight of produced polymer ( $M_n$ ) increases linearly with the monomer conversion.  $M_n$  increases nonlinearly with monomer conversion. In addition, well-defined diblock copolymers were synthesized and they demonstrated the preservation of the end-group functionality.

### REFERENCES

- [1] (a) For a review see K.Matyjaszewski Xia, *J.Chem. Rev.*, **101**, 2921-2990 (2001).  
(b) V.Coessens, T.Pintauer, K.Matyjaszewski; *Prog. Polym.Sci.*, **26**, 337-377 (2001).
- [2] (a) J.S.Wang, K.J.Matyjaszewski; *Am.Chem.Soc.*, **117**, 5614-5615 (1995).  
(b) *Macromolecules*, **28**, 7901-7910 (2001).
- [3] M.Kato, M.Kamigaito, M.Sawamoto, T.Higashimura; *Macromolecules*, **28**, 1721 (1995).
- [4] V.Percec, B.Barboiu; *Macromolecules*, **28**, 7970 (1995).
- [5] H.Fischer; *J.Polym.Sci.Polym.Chem.Ed*, **37**, 1885 (1999).
- [6] N.M.Hadjichristidis, S.Pitsikalis, Pispas, H.Iatrou; *Chem.Rev.*, **101**, 3747 (2001).
- [7] C.J.Hawker, A.W.Bosman, E.Hart; *Chem.Rev.*, **101**, 3661 (2001).
- [8] K.Matyjaszewski; *Macromol.Symp.*, **195**, 25 (2003).
- [9] K.Matyjaszewski, J.Xia; *J.Chem.Rev.*, **101**, 2921 (2001).
- [10] M.Kamigaito, T.Ando, M.Sawamoto; *Chem.Rev.*, **101**, 3689 (2001).
- [11] K.Matyjaszewski; *Polym.Int.*, **52**, 1559 (2003).
- [12] J.Pyun, T.Kowalewski, K.Matyjaszewski; *Macromol. Rapid Commun*, **24**, 1043 (2003).
- [13] S.M.Rida, S.A.M.El-Hawash, H.T.Y.Fahmy, A.A.Hazzaa, M.M.M.El-Meligy; *Archives of Pharmacal. Research*, **29**, 826 (2006).
- [14] H.Ebiike, M.Masubuchi, P.Liu, K.Kawasaki, K.Morikami, S.Sogabe, M.Hayase, T.Fujii, K.Sakata, H.Shindoh, Y.Shiratori, Y.Aoki, T.Ohtsuka, N.Shimma; *Bioorg.Med.Chem.Lett*, **12**, 607 (2002).
- [15] T.Ando, M.Kato, M.Kamigaito, M.Sawamoto; *Macromolecules*, **29**, 1070 (1996).
- [16] J.Jiang, K.Zhang, H.Zhou; *J.Polym.Sci.Part A: Polym.Chem.*, **42**, 5811 (2004).
- [17] K.Matyjaszewski, J.H.Xia; *Chem.Rev.*, **101**, 2921 (2001).
- [18] J.Pietrasik, H.Dong, K.Matyjaszewski; *Macromolecules*, **39**, 6384 (2006).
- [19] H.Ma, X.Wan, X.Chen, Q.F.Zhou; *Polymer*, **44**, 5311 (2003).
- [20] J.H.Xia, K.Matyjaszewski; *Macromolecules*, **32**, 5199 (1999).
- [21] K.Matyjaszewski; *ACS.Symp.Ser.*, **768**, 2 (2000).
- [22] H.Shinoda, P.J.Miller, K.Matyjaszewski; *Macromolecules*, **34**, 3186 (2001).