

## Synthesis of Star-like Random Copolymers from Resorcinarene-Based Octa-Functional Alkoxyamine Initiator *via* Nitroxide Mediated Free Radical Polymerization

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**Abstract:** An octa-functional alkoxyamine initiator, with the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) free radical, was synthesized based on resorcinarene, with its efficiency to initiate the nitroxide-mediated free radical copolymerization of styrene and methyl methacrylate (MMA) described. A difunctional analogue of this initiator was also synthesized, using resorcinol as the core molecule. The structures of the resulting initiators were confirmed by homolysis studies based on electron spin resonance spectroscopy and molecular modeling. The polymerization behavior and characteristics of the polymers obtained using these two initiators were also compared. Well-defined star-shaped and linear random copolymers, with low polydispersities and controlled molecular weights, were prepared. The efficiencies of these initiators towards copolymerization, as well as the parameters permitting the formation of well-defined polymers, were also investigated. The reactivity ratios were  $r_a = 0.42$  ( $a = \text{styrene}$ ) and  $r_b = 0.33$  ( $b = \text{MMA}$ ) for the octa-functional initiator system and  $r_a = 0.45$  and  $r_b = 0.39$  for the difunctional initiator system.

**Keywords:** controlled polymerization, methyl methacrylate, nitroxide-mediated radical polymerization, random copolymer, star polymer, styrene.

### Introduction

A feasible method for the random copolymerization of vinyl monomers yielding well-defined macromolecules possessing new and/or improved properties has long been a desire of synthetic polymer chemists. Many traditional methods such as anionic,<sup>1</sup> cationic,<sup>2</sup> or group transfer procedures<sup>3</sup> are not well suited for the preparation of well-defined random copolymers from vinyl monomers like styrenics and acrylates. Later nitroxide-mediated free-radical polymerization (NMRP), which emerged in the past decade as a powerful tool for macromolecular engineering, exhibits promising ability to achieve the goal and is still utilizing for the preparation of random copolymers leading to advanced materials.<sup>4-6</sup> The living free radical polymerization using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a mediating counter radical produce well-defined random copolymers with functional end groups and required characteristics for applications. Random copolymers of styrenics and acrylates has an increasing demand due to its ability to control the interfacial energies and wetting behavior towards solid surfaces and its fascinating ability to form microphase-separated structures leading to nano-materials.<sup>6,7</sup>

Recently, star shaped polymers have a significant attention due to their tunable properties which aroused from the highly branched structure.<sup>8</sup> They have been widely employed as model branch-polymer in order to sketch out the structure-property relationship in polymer science.<sup>8,9</sup> Commonly, atom transfer radical polymerization (ATRP) was employed for the synthesis of star polymers either by 'core-first'<sup>10</sup> or by 'arm-first'<sup>11</sup> approach.<sup>12</sup> There are also reports regarding dendrimer<sup>13</sup> like star polymers and milktoarm stars<sup>14</sup> prepared by the combination of ring opening polymerization and ATRP.<sup>15</sup> Recently resorcinarene-centered star polymers have also been synthesized successfully using ATRP.<sup>16</sup> Recently, there are many reports regarding the synthesis of acrylates<sup>17</sup> and methacrylates<sup>18</sup> by ATRP by modified catalyst systems.<sup>19</sup> A modular approach for the preparation of functionalized star polymers by NMRP is also reported recently.<sup>20</sup>

This paper discusses the ability of an octa-functional alkoxyamine to bring about the controlled polymerization of styrene and methyl methacrylate producing eight-arm star copolymers. The synthesis and characterization of an octa-functional alkoxyamine initiator using resorcinol as the core-molecule is described in detail. In order to compare its initiation efficiency, a resorcinol based difunctional alkoxyamine initiator was also prepared. The characteristics of the

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obtained linear and star polymers were evaluated comparatively. The initiators were characterized by NMR and elemental analysis (EA). The structural confirmation and orientation of the star alkoxyamine was carried out by molecular modeling and 2D-ROESY NMR spectroscopy. The C-O bond homolysis of the alkoxyamines and the generation of the mediating radical were monitored by ESR spectroscopy. The linear and star shaped polymers were characterized by gel permeation chromatography (GPC) and NMR. Monomer conversion studies were carried out by GC analysis. The efficiency of these initiators and the conditions that allows the formation of well-defined star polymers is also investigated in detail. The copolymer composition was determined by NMR and DSC and the reactivity ratio was calculated by Fineman-Ross linearization method.<sup>21</sup>

## Experimental

**Materials.** Styrene and methyl methacrylate (MMA) was obtained from Aldrich and was purified by standard process. Resorcinarene were synthesized according to the previously reported procedure.<sup>22</sup> 2-Bromopropionyl bromide (97%), triethylamine (TEA, 99.5%), copper bromide (99.99%), and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) free radical (98%) were purchased from Aldrich and were used as received. 2,2'-bipyridine (99%) was obtained from Fluka. All solvents used were purified by standard purification methods prior to use. All manipulations were carried out under purified nitrogen using standard Schlenk techniques and glove box. Purification of the synthesized initiator was carried out with a Combi-Flash (Companion) auto-column machine. <sup>1</sup>H-NMR spectrum of initiators (in CDCl<sub>3</sub>) and polymers (in THF) were recorded on a Varian Unity Plus-300 (300 MHz) spectrometer at 293 K, using tetramethylsilane as the internal reference. The <sup>13</sup>C-NMR spectra were also taken on the same machine operating at 75.5 MHz. ESR spectrum of the alkoxyamine initiator was recorded using a Bruker EMX 300 spectrometer. Elemental analysis of the initiators was done using a Vario EL-Elemental Analyzer. Molecular weight (MW) and PDI of the star polymers were estimated by GPC using a Hewlett Packard Model 1100 series system and <sup>1</sup>H-NMR spectroscopy, respectively. The DSC analysis was carried out at a heating rate of 4°C/min using a Q100, TA instrument. Monomer conversion during the polymerizations was determined with a Hewlett Packard 5890 gas chromatograph equipped with FID detector.

**Synthesis of 2-Bromopropionyl Derivatives.** Resorcinarene (13.6 g, 25 mmol) was dissolved in 250 mL dry THF in a three-necked flask. TEA (20.73 g, 205 mmol) was added in to this solution and was vigorously stirred. The reaction mixture was then cooled to 0°C, and a THF solution of 2-bromopropionyl bromide (44.3 g, 205 mmol) was added drop wise over a period of 2 h. The solution was then

stirred continuously for 2 days at 25°C. The white precipitate of (Et<sub>3</sub>N)Br formed was removed by filtration and the product was concentrated by solvent evaporation. It was then redissolved in diethyl ether and washed with aq. K<sub>2</sub>CO<sub>3</sub> solution. Finally the ether layer was washed with water, dried, evaporated to isolate the crude product. Upon purification using the auto column machine, a light yellow solid was obtained (24 g, yield = 59.4%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 293 K, δ): 1.32, 1.48, 1.66, 1.81 (16H, CH<sub>3</sub> in CH(CH<sub>3</sub>)Br), 3.43, 3.67, 3.79 (4H, CH in macro-cycle ring), 4.46, 4.5 (8H CH in CH(CH<sub>3</sub>)Br), 6.52, 6.97, 7.48, 7.57 (Ar-H, upper and lower) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, 293 K, δ): 16.46, 21.07, 38.74, 43.62, 115.83, 126.7, 128.8, 134.83, 147.37, 169.47 ppm.

The same process was carried with a solution of resorcinol (5.51 g, 50 mmol), triethylamine (10.62 g, 105 mmol), and 2-bromopropionyl bromide (22.7 g, 105 mmol) in THF solution for a reaction time of 30 h. The crude product obtained was purified using an auto column machine giving pure compound as a pale yellow semi-solid (13 g, yield = 68.8%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 293 K, δ): 1.83 (6H, CH<sub>3</sub> in CH(CH<sub>3</sub>)Br), 4.45 (2H CH in CH(CH<sub>3</sub>)Br), 7.04, 7.13, 7.15, 7.47 (Ar-H) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, 293 K, δ): 21.77, 42.76, 116.26, 119.32, 131.17, 147.64, 167.72 ppm.

**Synthesis of Alkoxyamines (Initiators II and I).** In a suitable Schlenk flask, 4.9 g (3 mmol) of resorcinarene derivative (n = 4) was taken and dissolved in 200 mL of CH<sub>2</sub>Cl<sub>2</sub>. To this solution CuBr (3.45 g, 24 mmol) and 2,2'-bipyridine (7.8 g 50 mmol) was added and stirred well until the complex is formed. TEMPO (4.4 g, 28 mmol) free radical was then added and stirred for 2 days at room temperature. After the reaction is completed the mixture was filtered, washed with aq. CuSO<sub>4</sub> solution and the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product was isolated as yellow oil. It was then purified by auto column to form a pale yellow solid (initiator II, yield = 48.8%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 293 K, δ): 1.03-1.32 (96H, TEMPO CH<sub>3</sub>), 1.303-1.392 (24H CH<sub>3</sub> in CH(CH<sub>3</sub>)Br), 1.42-2.34 (24H TEMPO ring), 4.33-4.67(8H CH in CH(CH<sub>3</sub>)Br), 6.07, 6.87, 7.02, 7.17, 7.44 (Ar-H) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, 293 K, δ): 16.7, 17.67, 18.03, 25.18, 27.32, 38.1, 41.58, 47.32, 73.21, 115.11, 126.17, 134.37, 148.1, 149.72, 171.12 ppm. Anal. Calcd for C<sub>128</sub>H<sub>200</sub>N<sub>8</sub>O<sub>24</sub>: C, 68.79; H, 9.02; N, 5.01. Found: C, 68.32; H, 8.96; N, 5.06.

The similar procedures described above was followed with resorcinol derivative (n = 1) to afford initiator I as a pale yellow oil (yield = 72%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 293 K, δ): 1.04-1.24 (24H, TEMPO CH<sub>3</sub>), 1.37 (6H CH<sub>3</sub> in CH(CH<sub>3</sub>)Br), 1.33-1.58 (6H TEMPO ring), 4.27-4.52 (2H CH in CH(CH<sub>3</sub>)Br), 6.78, 6.91, 7.02, 7.23, 7.47 (Ar-H) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, 293 K, δ): 16.7, 17.67, 18.03, 25.18, 27.32, 38.1, 41.58, 47.32, 73.21, 115.11, 126.17, 134.37, 148.1, 149.72, 171.12 ppm. Anal. Calcd for

**Table I. Polymerization of Styrene and Methyl Methacrylate at 125 °C Using the Di- (I) and Octa-functional (II) Alkoxyamines with Various Feed Ratios**

Run no.	Ini. <sup>a</sup>	$f_a$ ([St] in feed)	$F_a$ ([St] in polymer) <sup>b</sup>	Conv. (%) <sup>c</sup>	$M_{n,THEO}$	$M_{n,NMR}$ <sup>d</sup>	$M_{n,GPC}$ <sup>d</sup>	$PDI_{GPC}$ <sup>e</sup>
1	I	0.8	0.72	83	14,000	12,100	13,700	1.18
2	II	0.8	0.71	64	50,000	51,100	44,100	1.43
3	I	0.67	0.69	77	13,200	13,700	13,100	1.17
4	II	0.67	0.70	67	52,500	56,100	42,400	1.47
5	I	0.5	0.58	70	12,400	10,100	12,100	1.24
6	II	0.5	0.56	58	44,800	43,700	40,000	1.46
7	I	0.33	0.42	77	13,500	9,000	10,500	1.23
8	II	0.33	0.41	63	46,500	40,100	27,700	1.51
9	I	0.2	0.28	76	13,300	9,800	10,100	1.26
10	II	0.2	0.30	53	42,500	46,100	33,700	1.63

<sup>a</sup> Initiator conc. of I is  $9.8 \times 10^{-3}$  & II is  $2.45 \times 10^{-3}$  mol. <sup>b</sup> Mole fraction of styrene in copolymer obtained after 4 h of polymerization, calculated from NMR spectrum. <sup>c</sup> Conversion after 60 h of polymerization. <sup>d</sup> Number average MW values ( $M_n$ ) of copolymers obtained after 60 h polymerizations measured by NMR and GPC. <sup>e</sup> Polydispersity of copolymers obtained after 60 h polymerizations measured by GPC.

$C_{38}H_{48}N_2O_6$ : C, 67.64; H, 9.08; N, 5.26. Found: C, 67.71; H, 9.12; N, 4.99.

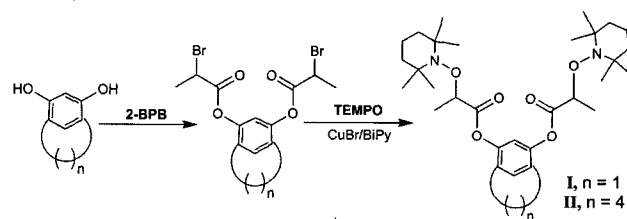
**Polymer Synthesis.** The typical polymerization procedures with the synthesized initiators are as follows. A mixture of styrene, MMA, and initiator was taken in a Schlenk flask and degassed three times with dry nitrogen. A small amount of TEMPO free radical (0.15 eq.) was also added in the reaction flask which protects the growing radicals and prevents termination reaction. The flask was then immersed in an oil bath thermostated at 125 °C. The monomers were allowed to polymerize for about 60 h with continuous stirring. At the end of the reaction the polymer was dissolved in THF and precipitated in methanol/water mixture. The reactions were carried out with different feed ratios of monomers. The experimental conditions and copolymerization results are tabulated in Table I.

## Results and Discussion

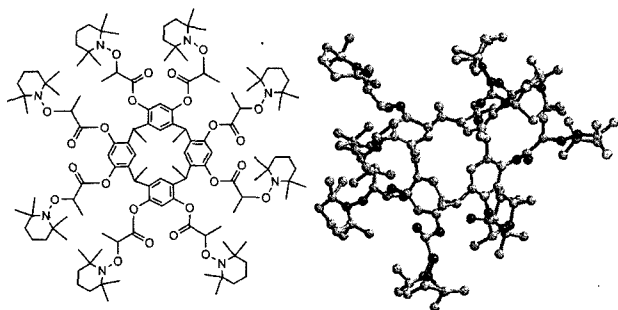
**Synthesis of Initiators.** Octa-functional alkoxyamine was synthesized with resorcinarene as the core molecule. Resorcinarene is a macro cycle compound containing free phenolic hydroxyl groups at the upper and lower rim which exists in various conformations.<sup>22</sup> The hydroxyl groups of resorcinarene were firstly acylated with 2-bromopropionyl bromide and further it was coupled with TEMPO free radical. Resorcinarene contains strain free hydroxyl groups which has little role with the intramolecular hydrogen bonding and an easier initial acylation reaction is possible. After complete acylation, the intramolecular hydrogen bonds are all ruptured and the molecule becomes very flexible. The investigations regarding the conformational changes of the resorcinarene ring due to the acylation of hydroxyl groups is reported recently.<sup>16</sup> The extend of acylation reaction was verified and confirmed by NMR analysis.

Commercially available TEMPO free radical was further coupled with this acylated resorcinarene by a halogen abstraction reaction using a CuBr/BiPy catalytic system. Difunctional alkoxyamines were also prepared by using resorcinol as the core molecule and coupled with similar nitroxides. This was intended to compare the initiation efficiency and to evaluate the characteristics of obtained linear and star polymers. Partially functionalized molecules were removed by flash column chromatography using the auto column machine. The purity of the synthesized alkoxyamines was confirmed by NMR spectroscopy and elemental analysis. The general schematic representation of the synthesis of the alkoxyamine initiators is depicted in Scheme I.

**Conformational and Stability Analysis.** The molecular conformations of the octa-functional initiator were studied by molecular modeling using Hyperchem<sup>TM</sup> program<sup>23</sup> (7.01 package) running on a Windows PC workstation. Geometry optimizations were done at the Restricted Hartree-Fock level. The minimum energy conformation of the macrocyclic ring without any substituents was calculated first and was observed to be in good agreement with the *crown* conformation stabilized by intramolecular hydrogen bonds. The molecular structure and one of the lowest energy conformations of the octa-functional initiator are shown in Figure 1.



**Scheme I.** Synthesis of resorcinarene-based 2- and 8-arm alkoxyamine initiators.

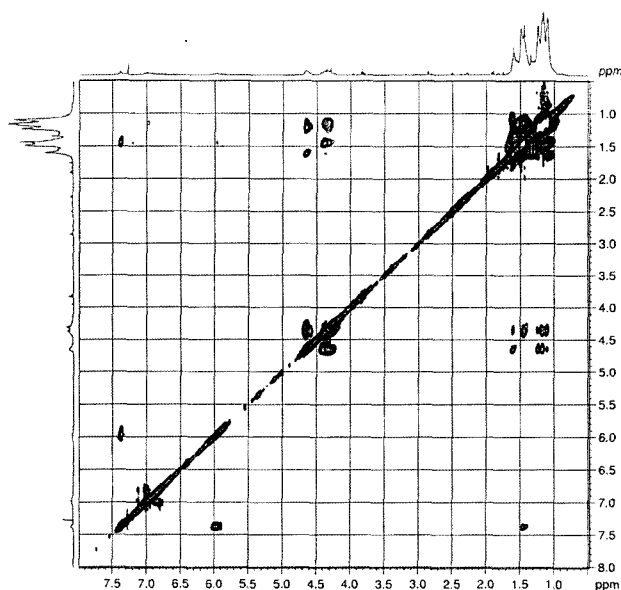


**Figure 1.** Molecular structure (left) and energy-minimized structure (right) of initiator **II**.

While conjugating with the substituents through the acylation and derivatization reactions at their hydroxyl groups, the hydrogen bonds which holds the *crown* conformation break and it shifts to either boat or chair conformation. It was observed that the initiator exist in *boat* form with a minimum energy within 215 kJ/mol at its lowest energy conformation.

The conformational studies of the star alkoxyamine were further carried out by 2D-ROESY NMR spectroscopy. In the 2D spectrum, the appearance of cross peaks corresponding to the aromatic macro cyclic protons indicates their  $C_2$ -symmetric conformation. Also, the absence of the cross peaks for the aromatic lower rim protons indicate that these protons are more equatorially positioned. Figure 2 shows the ROESY NMR spectrum of initiator **II**.

The stability of the initiators was studied by ESR in methylenechloride solution and the evolution of ESR signals was monitored as a function of time. Both the star and linear ini-



**Figure 2.** ROESY Spectrum of octa-functional initiator **II** in  $CDCl_3$ . The cross peaks of aromatic protons are visible.

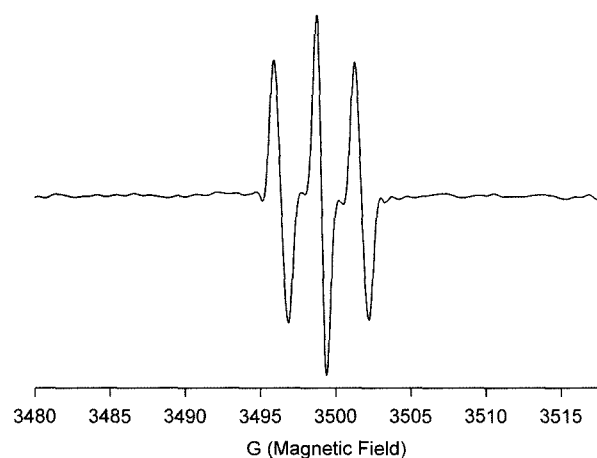
tiators were found to be stable compounds which could be isolated and stored either neat or in solution. The C-O bond homolysis was observed between 115 to 130 °C for both the initiators. Oxygen was used to scavenge the styryl radical and the concentration of the released nitroxide was measured by ESR spectroscopy.<sup>24</sup> The cleavage rate constants  $k_d$  were calculated using the following equation and the activation energy  $E_a$  was calculated from the rate constant using  $A = 2.4 \times 10^{14} \text{ s}^{-1}$ .

$$\ln\left(\frac{[\text{nitroxide}]_\infty - [\text{nitroxide}]_t}{[\text{nitroxide}]_\infty}\right) = -k_d t \quad (1)$$

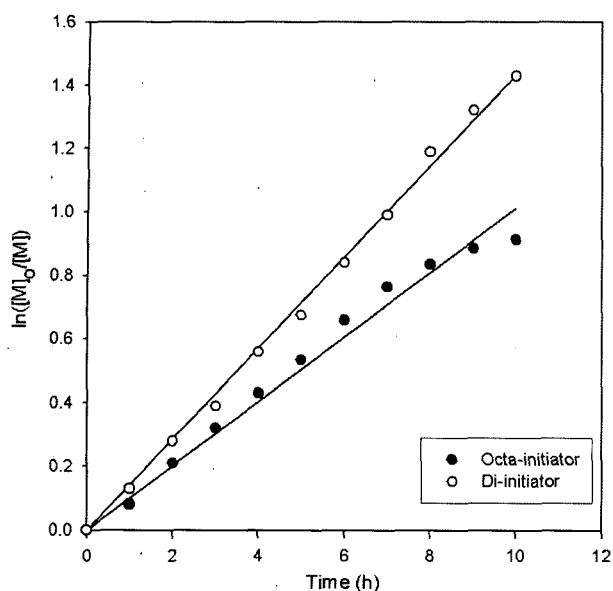
The  $k_d$  values of alkoxyamines **I** and **II** were obtained as  $6.56 \times 10^{-4}$  and  $5.52 \times 10^{-3} \text{ s}^{-1}$  and the  $E_a$  values 132.1 and 124.4 kJ/mol respectively. The typical ESR spectrum of star initiator is shown in Figure 3.

**Synthesis and Characterization of Copolymers.** Eight arm star polymers possessing various molecular weights and compositions were synthesized using the multi site initiator at 115 °C. Purified monomers were allowed to polymerize in an inert oxygen free atmosphere for about 60 h. The characteristic features of all synthesized copolymers are summarized in Table I.

The polymerizations were carried out with a variety of monomer feed ratios. It is observed that polymers obtained with high styrene ratios shows excellent agreement between the observed and theoretical molecular weights. As a typical example, polymerization of styrene and MMA with a feed ratio 4 : 1 at 115 °C (Run 1) for 60 h resulted in 64% yield of polymer with  $M_n$  of 51,100 and PDI of 1.43. Polymerization were conducted with  $[\text{styrene}]/[\text{MMA}]$  molar feed ratios of 4 : 1, 2 : 1, 1 : 1, 1 : 2, and 1 : 4. The star copolymers exhibit a higher PDI than the linear analogues. This may mainly due to the chain coupling reactions between chain arms and the formation of independent arms with different



**Figure 3.** ESR spectrum of octa-functional alkoxyamine **II** at 130 °C due to formation of TEMPO radical by the homolysis of C-O bond.

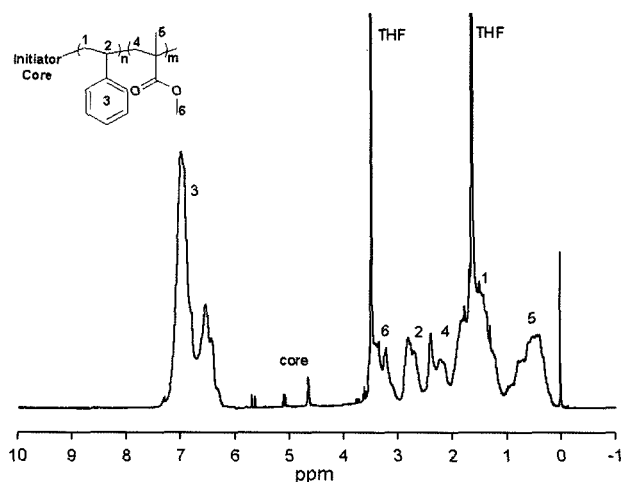


**Figure 4.** The first order kinetic plots of the copolymerization from di and octa functional alkoxyamine initiators. The evolution of  $\ln([M]_0/[M])$  as a function of time.

chain length. It was also observed that the PDI increases with decrease of styrene monomer in the feed.<sup>25</sup> The kinetics of polymerization was determined by evaluating monomer conversion at consecutive time intervals. The polymerization by the star initiator shows a linear behavior at the beginning but deviates with high monomer conversion. A first order kinetic plot of copolymerization initiated by both initiators at a monomer feed ratio 4 : 1 is shown in Figure 4.

Usually inter- and intramolecular couplings occur at high monomer conversion (< 60%) and hinder the easy formation of well-defined star polymers with high MW. These unwanted processes can be minimized by adding a trace amount of free radical to the reaction system. The free radicals protect the growing radicals, thus prevent termination reactions to certain extent. The obtained results showed that the efficiency of these initiators to form well-defined polymers is moderately high up to certain limit of conversion (60%) without any activity decline or active site deterioration. The GPC analysis usually underestimates the molecular weight ( $M_n$ ) of star polymers due to its small hydrodynamic radii compared to the linear analogues having same molecular composition. So the  $M_n$  of the star polymers obtained by NMR analysis was taken as the accurate value.<sup>12</sup> A typical NMR spectrum of the copolymer is depicted in Figure 5.

**Monomer Reactivity Ratio and Copolymer Composition.** The polymerization with difunctional initiator yielding linear polymer is observed to be kinetically linear without any side reactions even at 90% monomer conversion. Polymerizations were conducted with both initiators with same initial concentration (based on the number of initiating sites)



**Figure 5.**  $^1\text{H-NMR}$  spectrum of eight arm star poly(styrene-co-methyl methacrylate) ( $M_n = 51,100$  and  $I = 1.43$ ) synthesized using alkoxyamine **II**.

of the alkoxyamines and it was observed that the reactions occurred with same conversion rate resulting in polymers which differ by approximately 4 to 5 times of  $M_n$  value. This shows the efficiency of all initiating sites of the star shaped alkoxyamine to trigger the polymerization. The copolymer composition was obtained by  $^1\text{H-NMR}$  using the equation given below, where  $I_A$  is the intensity of aromatic protons and  $I_M$  is the intensity of methyl protons.

$$m_1 = \frac{(I_A/5)}{(I_A/5 + I_M/3)} \quad (2)$$

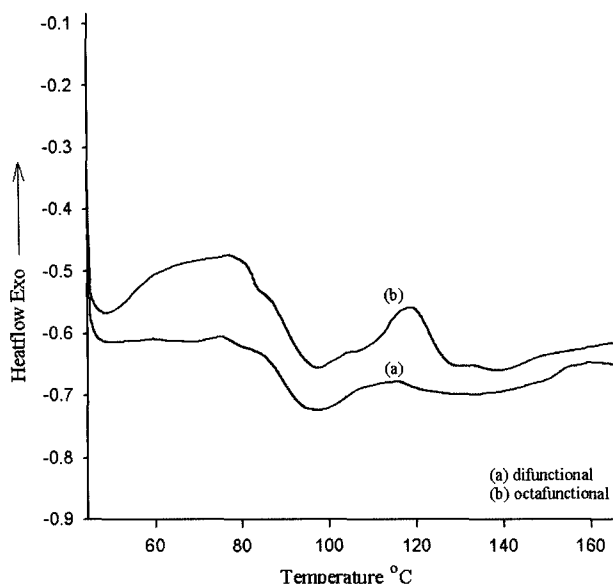
DSC analysis of the copolymers obtained at different feed ratios was also carried out and a slight increase in the glass transition temperature was observed with the increase of the PMMA content.<sup>26,27</sup> The  $T_g$  of PS and  $T_g$  of PMMA were observed around 100 and 122°C respectively. Representative DSC curves of a linear and star copolymer is shown in Figure 6. The presence of two different  $T_g$  reveals the block-random nature of these copolymers.

The copolymerization reactivity ratios were estimated by using Fineman-Ross method.<sup>21</sup> The calculations are based on the following equation. The feed ratio of styrene is represented by  $f_a$  and  $F_a$  is the compositional ratio of polystyrene in the copolymer.

$$r_b = -G + Hr_a \quad (3)$$

$$\text{where } G = \frac{f_a(1 - 2F_a)}{(1 - f_a)F_a} \text{ and } H = \frac{f_a^2(1 - F_a)}{F_a(1 - f_a)^2}$$

It was observed that  $r_a = 0.42$  ( $a = \text{styrene}$ ) and  $r_b = 0.33$  ( $b = \text{MMA}$ ) for initiator **I** and  $r_a = 0.45$  and  $r_b = 0.39$  for initiator **II**. The small value of  $r_a \times r_b$ , 0.14 for initiator **I** and 0.18 for initiator **II**, demonstrates that copolymers have alternating structure to some degree. In all cases the reactiv-



**Figure 6.** DSC heating profiles of copolymer synthesized by linear and octa-functional alkoxyamine initiators.

ity ratios of styrene and MMA depends on the rate constant between chain radicals and monomers. The structure of monomer or the stereo effect of initiator doesn't make any effect towards the copolymerization. The molecular weight of all polymers produced by using octa- and difunctional initiators is linearly proportional to about 75% of monomer conversion. The polydispersity of the polymers was observed to increase with decrease in styrene ratio, similar to the previous reports on linear polymers.<sup>25</sup>

## Conclusions

An octa-functional TEMPO based alkoxyamine having resorcinarene as the core molecule was synthesized to serve as octa-functional initiators for the controlled radical random copolymerization of styrene and MMA. The difunctional analogues of them were also synthesized and linear copolymers were prepared in order to compare the polymer characteristics. The purity, efficiency and conformation of these initiators were studied using NMR, ESR and molecular modeling. Well-defined star polymers were obtained with appreciable molecular weight and narrow size distribution. Polymerizations were carried out with various monomer feed ratio and conditions to yield well-defined polymers were optimized. The initiating efficiency of all sites of the octa-functional alkoxyamine was determined by experimental means and the copolymer reactivity ratio was also calculated.

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