

Synthesis of Star like Random Copolymers from Resorcinarene-based Alkoxyamine Initiator *via* Nitroxide Mediated Free Radical Polymerization

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Introduction

Nitroxide-mediated free-radical polymerization (NMP) has emerged in the past decade as a powerful tool of macromolecular engineering. Nitroxides are kinetically persistent free radicals that are easily oxidized or reduced and act as reversible traps for other free radical species. This special ability enabled them to be utilized for a wide range of applications^{1,2}. Star shaped polymers have also received significant attention due to their desirable properties that arise from a highly branched structure³. There are many strategies to synthesize star polymers with tunable properties and fascinating architectures and among them nitroxide derivatives of TEMPO or other commercially available free radicals are demonstrated as efficient initiators with control over the chain growth.⁵

In this paper we describe the synthesis of an octafunctional resorcinarene based TEMPO derivative NMP initiator and its ability to yield random star copolymers of styrene and methyl methacrylate. The effect of the initiator conformations towards its activity and the conditions that permit the formation of well-defined star block copolymers is also investigated in detail.

Experimental

Materials and Methods. The NMR spectra were measured with a 300 MHz Varian Gemini NMR spectrometer. Elemental analysis was carried out on a Vario-EL element analyzer. The IR spectrum was measured on a Shimadzu IR prestige-21 spectrometer. All manipulations were carried out under purified nitrogen using standard Schlenk techniques and glove box. All the chemicals used were purchased from Aldrich chemicals Ltd. and were purified prior to use. The monomers and solvents were purified according to the standard procedures and were stored under nitrogen. Resorcinarene were synthesized according to the previously reported procedure.⁶

Synthesis of octa-2-bromopropionylresorcinarene(1). In a 100 mL three necked flask, resorcinarene (1.2g) was dissolved in 30 mL dry THF, followed by triethylamine (5.8mL). The solution was cooled to 0 °C, and a solution of 2-bromopropionyl bromide (4.3mL) in THF was added drop wise to the vigorous stirred solution over 30 minutes and continued stirring at room temperature for 2 days. The white precipitate of triethyl ammonium bromide formed was removed by filtration and the product solution was concentrated by solvent evaporation. It was then redissolved in diethyl ether and washed with aq. K₂CO₃ solution. Finally the ether layer was washed with water, dried, evaporated to isolate the crude product. It was then purified by column chromatography. The light yellow solid was obtained upon evaporation and evacuation. The product was characterized by NMR IR and element analysis.

Synthesis of octafunctional NMP initiator(2). In a 100 mL Schenk flask, compound 1 (1.1g) was taken and dissolved in 30 mL CH₂Cl₂. To this solution CuBr (0.54g) and 2,2'-bipyridine (1.8g) was added and stirred well until the complex is formed. Further, TEMPO free radical was added and stirred vigorously for 2 days at room temperature. Then the mixture was filtered, washed with aq. CuSO₄ solution and the organic phase was dried over sodium sulphite. The crude product was isolated as an yellow oil and was purified by column chromatography to yield an yellow solid. The product obtained was confirmed by NMR and IR spectroscopy.

Synthesis of copolymer. A mixture of styrene, methyl methacrylate and the obtained initiator (2) was transferred in a Schlenk flask and degassed 3 times with dry nitrogen and then immersed in an oil bath thermostated at 120 °C. It was allowed to polymerize for 3 hours and the remaining unreacted monomers were removed under vacuum. The polymer was precipitated, filtered dried and characterized. The molecular weight and PDI of the polymers were determined using NMR and GPC respectively.

Results and discussion

The multi arm NMP initiator with a resorcinarene core was synthesized by coupling with the resorcinarene derivative with TEMPO free radical using a CuBr/BiPy catalyzed reaction. The conformation of the initiator was investigated in order to find out the differences between the initiating groups and was analyzed by 2D ROESY NMR. The molecular structure of the initiator and its possible two dimensional energy minimized conformation is depicted in figure 1. The initiating sites are oriented in an unhindered fashion providing equal possibility to initiate polymerization simultaneously. This results in the formation of star polymers with equal chain lengths.

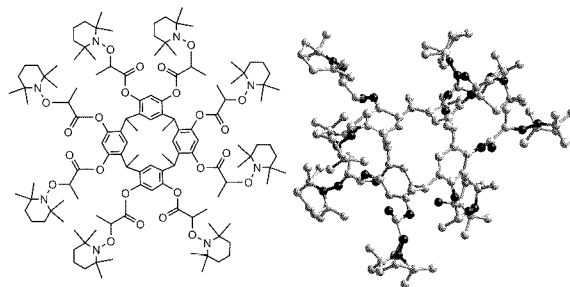


Figure 1. Molecular structure and orientation of Initiator.

Random copolymerization of styrene with methyl methacrylate were conducted with various monomer feed ratios. The polymerizations were performed in the bulk under an inert atmosphere at temperature 120 °C. The evolution of molecular weight with monomer conversion was evaluated and obtained a linear relation ship. The characterization results of the polymers are tabulated in table 1.

Table 1. Polymerization results

Entry No.	% Styrene	Molecular weight ^a	PDI ^b
1	80	14300	1.34
2	70	13670	1.28
3	60	12300	1.43
4	50	12115	1.57
5	40	11420	1.66

^a measured by NMR, ^b measured by GPC

The molecular weight of the polymers was calculated from the NMR spectrum and the molecular weight distribution was obtained from GPC. It's clear from the table that observed molecular weights are in excellent agreement with theoretical value with moderately low poly dispersity index.

Conclusions

An octafunctional alkoxyamine derivative was synthesized with a resorcinarene core for the controlled polymerization of styrene and methyl methacrylate. Well-defined random copolymers were obtained with controlled molecular weight and low PDI depending on the monomer feed.

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