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**LIVING RADICAL POLYMERIZATION OF  
TRIMETHYLSILYLSTYRENE**

by  
**B.W. McQUILLAN and S. PAGUIO**

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## LIVING RADICAL POLYMERIZATION OF TRIMETHYLSILYLSTYRENE

B.W. McQuillan and S. Paguio  
Inertial Fusion Division, General Atomics  
P.O. Box 85608  
San Diego, Ca 92186-5608  
(619) 455-2922

## ABSTRACT

We have demonstrated the synthesis of poly(4-trimethylsilylstyrene) by living polymerization techniques. The use of cuprous bromide, di-n-nonylbipyridine, and phenethylbromide to polymerize neat 4-trimethylsilylstyrene at 120°C results in a narrow molecular weight polymer. The method improves on the polymer specifications made by conventional free radical methods.

## I. INTRODUCTION

The ICF program at University of Rochester requires polystyrene films with silicon. In the past, they have used poly(trimethylsilylstyrene) [p(Si-S)] made by standard free radical polymerizations (AIBN or benzoyl peroxide). These methods are simple, but the polydispersity is 1.8-2.5 with polymer yields of <30%. We sought to obtain higher yields and more narrow polydispersity by using the ATRP (Atom Transfer Radical Polymerization) developed by Matyjaszewski and coworkers.<sup>1-3</sup> In particular for this work, we have followed the work of Matyjaszewski, Patten and Xia, who first made a homogeneous copper-bipy catalyst by adding alkyl chains to bipy (bipyridine).<sup>4</sup>

## II. EXPERIMENTAL

All reagents were obtained from Aldrich. Reactions were carried out under anhydrous and inert atmosphere conditions. 4-trimethylsilylstyrene was synthesized from the Grignard of 4-chlorostyrene in THF with trimethylsilylchloride, followed by vacuum distillation of the product (50%–70% yield) to separate it from a divinylbiphenyl side product.<sup>5</sup> (This side product can crosslink the polymer to an insoluble mess if not separated.) Di-n-nonylbipyridine was made following

Matyjaszewski's method for di-n-heptylbipyridine.<sup>4</sup> 4,4'-dimethyl-2,2'-bipyridine was reacted with butyl lithium in THF (-78°C) with di-isopropylamine, followed by addition of n-octylbromide. After washing with ammonium sulfate, the organic layer was separated and the solvent distilled. The crude product was reprecipitated from acetonitrile, to yield about 83% yield of di-4,4'-nonyl-2,2'-bipyridine. NMR confirmed the composition: (H NMR by NuMega Resonance Labs, San Diego, 500 MHz, CDCl<sub>3</sub>), δ(ppm): 8.54 (d, 1 H); 8.22(s, 1H); 7.12 (d, 1H); 2.68 (t, 2H); 1.68 (p, 2.12H); 1.32 (m) and 1.25 (s) sum to 12.6H; 0.87 (t, 3H).

The polymerization was performed with 128 g of trimethylsilylstyrene (0.727 mole), 0.100 cc phenethylbromide (0.733 mmole), 6.00 g di-4,4'-n-nonylbipyridine (14.7 mmole), 0.727 g CuBr (5.07 mmole) in a 500 cc flask with a water condenser under nitrogen flow. The ratio of trimethylsilylstyrene to phenethylbromide would ideally give chains of 992 monomer units, for a molecular weight  $M = 174.5 K$ , if the polymerization is taken to 100% yield. The trimethylsilylstyrene, CuBr, and di-4,4'-n-nonyl-2,2'-bipyridine are added to the flask with a stir bar and an N<sub>2</sub> sweep gas is passed through the system. The copper complex forms a deep blood red solution. The phenethylbromide is added via syringe, and the solution is stirred for an hour at room temperature. The 120°C oil bath is then raised around the flask, and the reaction proceeds for 92 hours. After 4 days, the solution is very viscous, but not solid, indicating the reaction has not gone to completion. The flask is cooled, and toluene is added. The toluene removes the monomer solvent, leaving a plug of polymer. Several additions of toluene are needed over several days to dissolve this plug of polymer. The toluene solution is then dripped into ethanol, to precipitate the polymer. Several cycles of toluene dissolution and ethanol

precipitation are required to obtain white polymer product, without the copper complex. (12 ppm residual copper remained in the final polymer.) We obtained 68.7 g of polymer (53.7% yield).

### III. RESULTS

Molecular weight analysis of this polymer by Viscotek on their Triple Detector gave  $M_W = 120,500$ ,  $M_N = 90,700$ , and a polydispersity = 1.33. For a living polymerization taken to 53.7% completion, one would expect  $M_N = 93,700$ , which is consistent with the  $M_N$  measured. The polydispersity is large, compared to the value for bulk styrene (1.07).<sup>4</sup> In the case of styrene, the  $M_N$  was only 5900, and the reaction was only run for 7 hours. For the higher molecular weights desired, the number of propagating chains is smaller, and the polymerization reaction rate is slower and can become similar to the thermal polymerization rate, thus broadening the polydispersity. However, the polydispersity of 1.33 is still much smaller than the 1.8–2.6 values obtained with a normal free radical polymerization of trimethylsilylstyrene.

Elemental analysis was performed by Desert Analytics. The calculated weight percentages for poly(trimethylsilylstyrene)  $C_{11}H_{16}Si$ : C, 74.97%; H, 9.09%; Si, 15.94%. Experimental values (average of duplicates): C, 75.35%; H, 8.87%; Si, 14.93%. The Si value is consistently lower than expected. Peak ratios of the proton NMR of the monomer which went into this batch also showed a lower Si content than expected (90% of monomer units had Si), which corresponds to 14.97 wt% Si. No Cl was found in this polymer, which rules out residual 4-chlorostyrene in the monomer. Thus, the polymer may have a small component of styrene, possibly caused by acid cleavage of the trimethylsilyl unit by HCl formed from slight excess of trimethylsilyl chloride being present upon hydrolysis and workup.

### IV. CONCLUSIONS

Living free radical polymerization to form poly(trimethylsilylstyrene) proceeds as anticipated, to give

a higher yield of narrow polydispersity polymer. The di-4,4'-n-nonyl-2,2'-bipyridine is an appropriate ligand for the copper catalyst.

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### REFERENCES

1. J-S. Wang and K. Matyjaszewski, "Controlled/'Living' Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition Metal Complexes," *J. Am. Chem. Soc.*, **117**, 5614, (1995).
2. J-S. Wang and K. Matyjaszewski, "'Living' /Controlled Radical Polymerization. Transition-Metal-Catalysed Atom Transfer Radical Polymerization in the Presence of a Conventional Radical Initiator," *Macromolecules*, **28**, 7572, (1995).
3. J-S. Wang and K. Matyjaszewski, "Controlled/'Living' Radical Polymerization. Halogen Atom Transfer Radical Polymerization Promoted by a Cu(I)/Cu(II) Redox Process," *Macromolecules*, **28**, 7901, (1995).
4. K. Matyjaszewski, T.E. Patten and J. Xia, "Controlled/'Living' Radical Polymerization. Kinetics of the Homogeneous Atom Transfer Radical Polymerization of Styrene," *J. Am. Chem. Soc.* **119**, 674, (1997).
5. A.E. Senear, J. Wirth, and R.G. Neville, "Synthesis of Monomeric Silanes," *J. Org. Chem.*, **25**, 807, (1960).