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NMP of Chloromethylsytrene with Minimized PDI: The Role of the Initiator/Nitroxide System and the Meta Isomer

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S Supporting Information

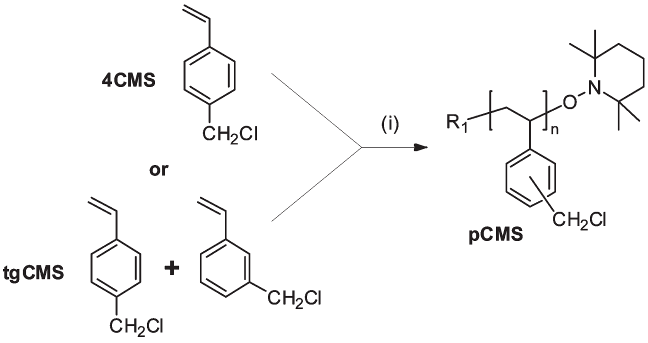
Poly(chloromethylstyrene) (pCMS), a functionalized styrenic polymer, has been widely applied as a material. Representative examples include its use in membranes,[1] absorbents,[2] and nonlinear optics.[3] Conventional radical polymerization of chloromethylstyrene (CMS) is known to produce highly branched polymers due to the propensity of the chloromethyl group to participate in transfer reactions. Atom transfer radical polymerization (ATRP) conditions have been used to purposely produce highly branched pCMS.[4,5]

Kazmaeir et al.[6] have shown that CMS polymerized under nitroxide-mediated polymerization (NMP) conditions (using a combination of benzoyl peroxide (BPO) and 2,2,6,6-tetramethyl-piperidinyl-1-oxy (TEMPO)) produces linear pCMS with polydispersity indexes (PDIs) in the range 1.3−1.4 at monomer conversions of up to 80%. Others have employed a unimolecular initiating approach using a TEMPO-capped alkoxyamine to produce linear pCMS.[7,8]

Like others, we are interested in pCMS as a precursor to functional materials as the chloromethyl group easily undergoes postpolymerization transformations.[9] For example, a diblock copolymer of poly(*p*-phenylenevinylene) (PPV) and styrene-*co*-CMS was synthesized by end-functionalization of a premade PPV block with a TIPNO-based unimer and subsequent treatment with styrene and chloromethylstyrene. This block copolymer served as a chemical precursor whereby the CMS functionality subsequently reacted with C_{60} to make the final desired product.[9d] In our case we are interested in minimizing the polydispersity index (PDI) of the precursor polymer to the greatest extent possible. In this Note we wish to highlight our recent observations which indicate the main variables allowing for the minimization of the PDI of pCMS is the initiation system used and the fraction of *meta*-CMS isomer present during the polymerization process.[10]

We initially polymerized 4-chloromethylstyrene (4CMS) in the bulk using a bimolecular system of BPO and TEMPO (Scheme 1).[11] We did add a small amount of 1,2,4-trichlorobenzene to serve as an internal standard for GC determination of monomer conversion. We have found GC is a rapid and efficient way to monitor conversion for this polymerization process. Depending on the speed of the polymerization, conversion can even be monitored in real time. Samples were taken hourly for GPC and GC analysis until the polymerization was too viscous to stir. Results of this experiment are outlined as run 1 in Table 1 and illustrated in Figure 1. GPC analysis shows M_n increased in a mostly linear fashion as a functional of conversion to ∼18 000 Da over the course of the polymerization (M_w of 29 400 Da for a PDI of 1.64). We did not achieve as low a PDI as did Kazmaier et al.,[6] but we will nonetheless consider this polymerization as a baseline for the remaining discussion. We then undertook a series of experiments to study the effect on PDI of the resulting pCMS with respect to the nature of the initiator, the ratio of initiator to nitroxide, the temperature of the process, and the grade of the monomer. With respect to the grade of monomer, we used both 4CMS and technical grade chloromethylstyrene (tgCMS).[10]

Scheme 1. Formation of Poly(chloromethylstyrene) (pCMS) from Either 4-Chloromethylstyrene (4CMS) or Technical Grade Chloromethylstyrene (tgCMS)[a]



[a] End group R_1 varies depending on polymerization method. Conditions: (i) see Table 1.

In the first instance we investigated the use of a unimolecular initiator 2-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl benzoate, more commonly referred to as benzoylstyrene TEMPO (BST),[12] for the polymerization of 4CMS. In this case, due to the nature of BST, the ratio between initiating/propagating radicals and TEMPO nitroxides is 1:1 at the beginning of the process. All other parameters are identical to run 1, and the results are again summarized in Table 1 and Figure 1. Run 2 showed a M_n and PDI consistently lower than for run 1 and a

Received: January 12, 2011
Revised: March 30, 2011
Published: April 14, 2011

Table 1. Polymerization of CMS under Various Conditions

run no.	monomer	initiating system	TEMPO:initiator ratio	reaction temp (°C)	reaction time (h)	conversion at time (%)	M_w (amu)	PDI at time
1	4CMS	BPO + TEMPO	1	125	4	35	29 400	1.6
2	4CMS	BST	1	125	2	56	18 200	1.5
3	4CMS	BST + TEMPO	1.2	125	5	59	20 700	1.5
4	4CMS	BST + TEMPO	1.2	115	5	45	19 000	1.7
5	4CMS	BPO + TEMPO	1.2	125	3	60	35 100	1.8
6	4CMS	AZO + TEMPO	1.2	125	3	43	37 600	1.9
7	tgCMS[a]	BST + TEMPO	1.2	125	4	74	14 700	1.2
8	50% tgCMS, 50% 4CMS[b]	BST + TEMPO	1.2	125	2	63	15 200	1.3
9	25% tgCMS, 75% 4CMS[c]	BST + TEMPO	1.2	125	2	63	18 300	1.4

[a] A molar ratio of 60:40 of *meta*-CMS and *para*-CMS, respectively, was determined by GC analysis prior to polymerization. [b] A molar ratio of 45:55 of *meta*-CMS and *para*-CMS, respectively, was determined by GC analysis prior to polymerization. [c] A molar ratio of 30:70 of *meta*-CMS and *para*-CMS, respectively, was determined by GC analysis prior to polymerization.

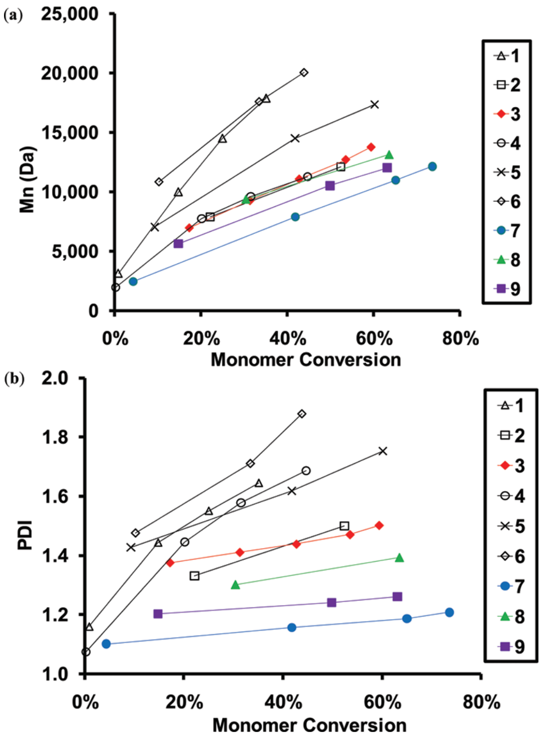


Figure 1. (a) Plot of M_n as a function of conversion and (b) PDI as a function of conversion for CMS polymerization. Runs 3, 7, 8, and 9 are highlighted in color for clarity.

more rapid conversion of monomer to polymer (56% conversion in only 2 h). Run 3 used the same temperature, initiating system (BST), and initiator concentration as run 2 but included 20 mol % excess of TEMPO with respect to BST.[13] This polymerization followed nearly the same progression of molecular weight as a function of monomer conversion while the PDI remained approximately the same but more consistent throughout the process compared to run 2. However, in this case 59% conversion took 5 h to achieve. Thus, the increased amount of TEMPO slowed the rate of the polymerization. For run 4 the reaction temperature was lowered to 115 °C from 125 °C. When comparing run 4 to run 3, the evolution of M_n as a function of conversion was identical while conversely the PDI increased rapidly with time. This result is counterintuitive, and a more in-depth study would be required to understand the lack of control with lower temperature. For run 5, we went back to the BPO/TEMPO bimolecular initiator system used for run 1 but adjusted the amount of TEMPO to be the same as runs 3 and 4 (20 mol % excess). The result was that the evolution of M_n as a function of conversion was lower than seen during run 1. This would be expected due to the retardation of the rate of polymerization from the excess TEMPO present. The PDI remained relatively high during the process and similar to run 1. In run 6 we used an alternative but conventional initiator system, 2,2′-azobis(2,4-dimethylvaleronitrile) (Figure S1), which has a 10 h half-life of 51 °C. We assumed a 100% efficiency of generation of radicals from the azo-initiator, and TEMPO was again present in a 20 mol % excess. This process did not exhibit the control seen in run 3 and in fact produced the largest molecular weight and the least controlled polymer in this series (see Table 1 and Figure 1).

On the basis of these observations, we could draw some intermediate conclusions. By comparison of runs 1−6, the best process—the one to exhibit the best control over PDI while achieving conversions >50%—is run 3, which used BST as the initiating system, 20 mol % excess TEMPO, and a temperature of 125 °C.

Thereafter, we used tgCMS in place of 4CMS under the identified best conditions. Using GC analysis, we independently determined that tgCMS contains 60% of the meta isomer 3CMS and 40% of the para isomer 4CMS (Scheme 1). During run 7, M_n evolved slower compared with all other runs achieving an M_n of 14 700 Da in 4 h at 74% conversion. Most notable was that the PDI stayed <1.2 over the course of the process, including at high conversions. Figure 2 illustrates the GPC traces of run 7 over time. At higher molecular weights there is very little tailing in the GPC trace, indicating minimal termination. The ratio between 4CMS and 3CMS changed by only 2.5% over the course of the process (70% total monomer conversion) with the 4CMS reacting marginally faster (Figure S1) as indicated by GC analysis against the internal standard. On the basis of these observations, we can conclude that the presence of 3CMS in the process resulted in a more controlled polymerization as indicated by the constant PDI with time, and given the GC results this is not a result of preferential polymerization. It is also not a result of impurities or other chemical species present in tgCMS since we purified the monomer by distillation prior to use. We could therefore

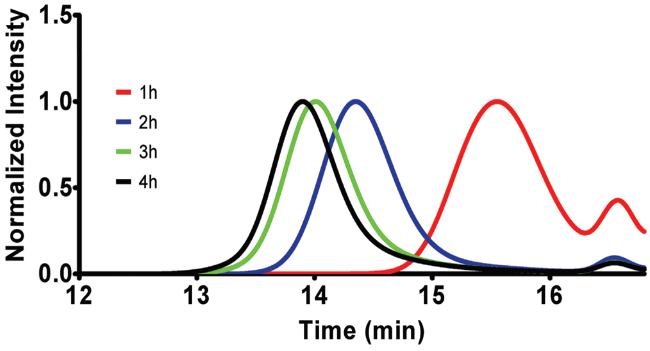


Figure 2. GPC traces of polymerization of tgCMS (run 7) over time (as indicated).

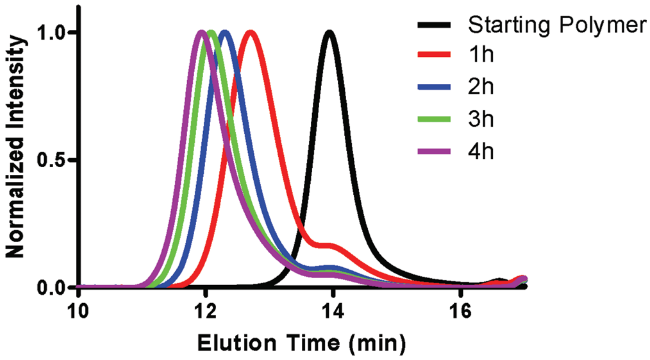


Figure 3. GPC traces of chain extension polymer with styrene of pCMS produced from run 7 over time (as indicated).

hypothesize that the low and constant PDI could be due to a difference in transfer rates of the chloromethyl group—the meta isomer having a lower rate.

To test this hypothesis, we simply mixed tgCMS with 4CMS and polymerized (runs 8 and 9). Run 8 used a 50/50 mass/mass mixture of tgCMS and 4CMS while run 9 used a 25/75 mass/mass mixture, resulting in the initial amount of 3CMS decreasing from 60% in run 7 to 45% and 30% in runs 8 and 9, respectively. During each run the ratio between 3CMS and 4CMS in the process did change by more than 3% (by GC analysis). In each case, M_n and PDI increased at a faster rate versus total monomer conversion compared to run 7 (tgCMS alone) but slower than run 6 (4CMS alone)—thus, the polymerization of mixtures of 4CMS and tgCMS fall directly in between the polymerization of each individual monomer. These results then confirmed our hypothesis that the para isomer, 4CMS, is more prone to transfer reactions than the meta isomer, 3CMS, since dilution of 4CMS lowered the PDI for a given conversion. As further confirmation of the lack of transfer reaction, ^{1}H NMR spectra were acquired of each of the final polymers which confirmed that the linear pCMS was obtained in each case (runs 4 and 7 in Figures S3 and S4, respectively) as there are known differences in the resolution of the resonances of the aromatic protons depending on degree of branching.[7] As a final confirmation we chain extended the polymer produced in run 7 (polymer from only tgCMS) with styrene. GPC traces shown in Figure 3 indicate the polymer is in end-capped with TEMPO and living in nature with ∼<15% of unreacted/terminated polymer present after 4 h.

In conclusion, we initially showed the use of BST and 20 mol % excess TEMPO produced pCMS from 4CMS with a minimized PDI. Using these conditions, we have shown that tgCMS produces pCMS with a further minimized PDI at conversions exceeding 70%. We have attributed the low PDI produced from tgCMS to a differential rate of transfer between the para and meta isomers: the meta isomer, 3CMS, having a lower rate. This may be due to steric or electronic factors of either the monomer or polymer and could be the basis for further study.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Complete experimental details and supplementary figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We thank The Natural Sciences and Engineering Research Council (NSERC) of Canada for funding of this project through the Discovery Grant Program (TB). We also thank Professor Michael Georges, The University of Toronto at Mississauga, for his advice and friendship.

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(10) CMS is available in two different grades: the para isomer sold as "4-chloromethylstyrene" or a technical grade which has a 2:3 ratio of the para and meta isomers sold simply as "chloromethylstyrene", which we will refer to hereafter as 4CMS and tgCMS, respectively. See also Scheme 1.

(11) In all polymerizations, the monomer(s) were purified by vacuum distillation immediately before use. Prior to all polymerizations the contents of the reaction vessel were sparged with nitrogen to removed dissolved oxygen, and during polymerization a constant positive pressure blanket of nitrogen was maintained. Samples were taken hourly for GPC and GC analysis until the polymerization was too viscous to stir. Additional experimental details are given in the Supporting Information.

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(13) A recent study from Georges et al. has shown that for the polymerization of styrene under NMP conditions a rate enhancement is possible through the use of elevated temperatures while maintaining good control over the polymerization due to the use of an excess of TEMPO. The excess nitroxide is claimed to allow for a higher temperature to be employed while maintaining the equilibrium between TEMPO-capped alkoxyamine and active propagating radicals at a point whereby termination processes are minimized. See: Dollin, M.; Szkurhan, A. R.; Georges, M. K. *J. Polym. Sci., Part A* **2007**, *45*, 5487–5493.