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HEXA-ARMED STAR-SHAPED POLY(VINYL ETHER) VIA CONTROLLED CATIONIC POLYMERIZATION WITH A NEW HEXA-FUNCTIONAL INITIATOR

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NOTE

HEXA-ARMED STAR-SHAPED POLY(VINYL ETHER) VIA CONTROLLED CATIONIC POLYMERIZATION WITH A NEW HEXA-FUNCTIONAL INITIATOR

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ABSTRACT

Reaction of hexa(methoxymethyl) melamine (HMMM) with trimethylsilyl iodide (TMSI) at -45°C , leads to quantitative formation of hexa(iodomethyl) melamine (HIMM), which, upon addition of ZnI_2 , acts as a hexa-functional initiator for the cationic polymerization of isobutyl vinyl ether (IBVE). Under the appropriate polymerization conditions, star-shaped, hexa-armed “living” polymers are obtained.

INTRODUCTION

In a previous paper [1], we reported the application of hexa(chloromethyl) melamine (HCMM) as a new multifunctional initiator to synthesize star-shaped polymers via controlled cationic polymerization of vinyl ethers. In that case, the synthesis of HCMM involved a rather tedious purification procedure. In the present communication, we report on another multi-functional initiator, hexa(iodomethyl) melamine (HIMM), that is prepared *in situ* by reaction of hexa(methoxymethyl) melamine (HMMM) with trimethylsilyl iodide (TMSI). The monomer was isobutyl vinyl ether (IBVE).

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EXPERIMENTAL

Reagents and Materials

Dichloromethane, toluene, and diethyl ether were dried over CaH_2 , purified by distillation, and before use, the solvents were distilled again. IBVE (b.p. = 83°C) was distilled over CaH_2 first, then distilled again just before use. Triethylamine (b.p. = 89°C) was distilled over calcium hydride just before use. ZnI_2 (99.99+ % of purity, from Aldrich) was dried under vacuum for 24 hours before use. TMSI (97%) and anhydrous benzyl alcohol (Aldrich) were used as received. Hexa(methoxymethyl) melamine (HMMM) (Cymel 303[®], from American Cyanamide) was used without further purification.

Synthesis of Hexa(Iodomethyl) Melamine (HIMM)

HIMM was prepared by a reaction of HMMM with TMSI. To obtain its ^1H -NMR spectrum, 50 mg of dried HMMM was dissolved in deuterated chloroform in an NMR tube at -45°C . Then, 115 μl of TMSI (6 molar equiv. relative to HMMM) was added into the solution. After 30 minutes at -45°C , the ^1H -NMR spectrum of the reaction solution was recorded at -45°C .

Polymerization Procedure of IBVE with HIMM/ ZnI_2 Initiator

A typical polymerization procedure is as follows: In a dry reactor of 200 ml, 0.05 g of HMMM was placed and dried at room temperature under vacuum for 4 hours. Then, a dry solvent mixture consisting of 80 ml of toluene and 20 ml of dichloromethane was injected under argon. After cooling the reactor to -45°C , 115 μl of TMSI was added into the solution and 30 minutes later, 1.77 g of IBVE was introduced into the system. Then, 95 mg of ZnI_2 dissolved in 1.5 ml of diethyl ether was injected into the system to initiate the polymerization. After 1 hour, the polymerization was terminated with 1 ml of benzyl alcohol/triethylamine (vol. ratio of 1:1). After most of the solvent was evaporated on a rotatory evaporator, 100 ml of dichloromethane was added to re-dissolve the product. Then, the solution was washed with 10% aqueous solution of sodium thiosulfate and water. Finally, the solvent was evaporated and the product was dried under vacuum until constant weight. 1.70 g of viscous polymer was obtained.

Analytical Methods

^1H -NMR spectra were recorded on a Bruker AC500 FT with CH_4Si as standard. Gel-permeation chromatography (GPC) was performed on a 60 cm Polymer Laboratories Column, 1000 \AA porosity, eluent chloroform with a refraction index (RI) or UV detector, and calibrated with polystyrene standards.

RESULTS AND DISCUSSION

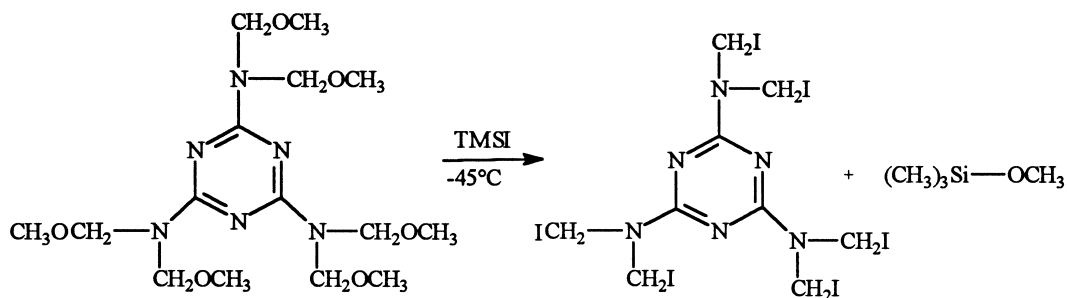
Synthesis of Hexa(Iodomethyl) Melamine (HIMM)

Trimethylsilyl iodide (TMSI) is widely used in organic synthesis to produce iodo-compounds [2]. In this study, it was investigated whether TMSI can react with hexa(methylmethoxy) melamine (HMMM) to form hexa-iodomethyl melamine (HIMM) (see Scheme 1). The formation of HIMM was proved by comparing the $^1\text{H-NMR}$ spectrum of HMMM with that of the resulting solution after the reaction. As shown in Figure 1, the singlet at 5.1 ppm, corresponding to the methylene groups in HMMM, has completely disappeared in the end-product and is replaced by a singlet at 5.6 ppm. The peak from the methoxy group in HMMM at 3.3 ppm shifted slightly down field to a singlet at 3.4 ppm, which is attributed to protons of the methoxy group in trimethyl methoxy silane. This data is evidence of the successful formation of HIMM.

Unlike HCMM, it was not possible to separate HIMM from the reaction solution, but it was investigated whether it would be possible to use it *in situ* as reported for other iodide initiators [3].

Polymerization of IBVE Initiated with HIMM

The polymerizations were performed at -40°C with ZnI_2 as an activator. When polymerizations were carried out in dichloromethane, as with the HCMM/ ZnCl_2 initiating system, the polymer showed a bimodal GPC peak. This could be due to the high reactivity of iodide chain-end to undergo chain transfer reaction or other side reactions, which are difficult to control in polar solvent [4-5]. As the result of many optimization efforts to find a suitable solvent, a mixture of dichloromethane (20% in volume) and toluene (80% in volume) was finally adopted. In this solvent, polymers displaying unimodal GPC curves could be produced (Figure 2 shows two examples of GPC analysis). The polymerizations were stopped after 1 hour by the addition of a mixture of benzyl alcohol and triethylamine, which is expected to produce the corresponding benzyl acetal at each



Scheme 1.

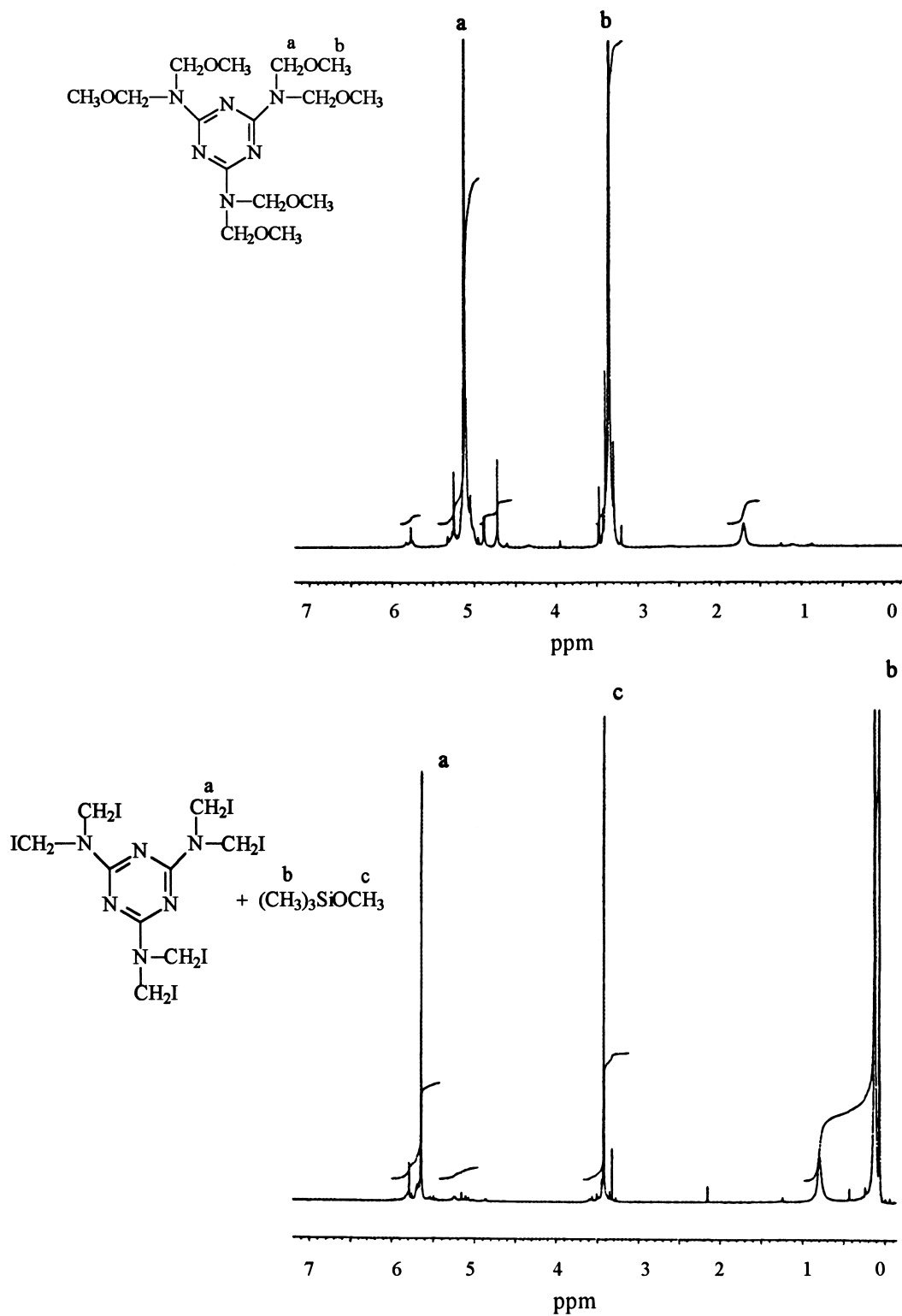


Figure 1. ¹H-NMR spectra of HMMM (up) and resultants (down) from reaction of HMMM and TMSI at -45°C, measured in CDCl₃ at -45°C.

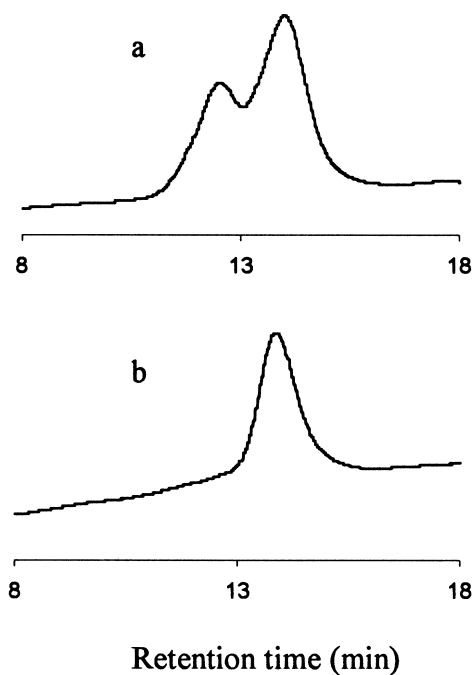


Figure 2. GPC curves of star poly(IBVE) obtained from polymerizations in different solvents. a) in dichloromethane; b) in mixture of toluene/dichloromethane with vol. ratio of 80/20.

chain end that was still active at the moment of the termination. The $^1\text{H-NMR}$ spectrum of the polymer shows a typical spectrum of polyIBVE end-capped with benzyloxy groups (Figure 3). Typical results for the HIMM/ ZnI_2 initiated polymerization under different monomer/initiator ratios are summarized in Table 1.

If it assumed that each HIMM molecule has formed one (star-shaped) polymer molecule, the calculated molecular weight of the end product should be given by $([\text{M}]/[\text{In}]) \cdot 100 + 846$ (in this formula, 100 is the molecular weight of IBVE and 846 is the sum of six benzyloxy end groups and one hexamethylene melamine central group). These calculated values are given in the second column of Table 1. The third column displays the ratio of benzyl end groups to IBVE units ($I_{\text{IBVE}}/I_{\text{benzyl}}$) in the polymers as measured by $^1\text{H-NMR}$. This ratio leads to the corresponding average DP's of the arms, based on which the M_n of arms can be calculated. The M_n of the star polymer, assuming 6 arms, is given by: $6 \cdot [I_{\text{IBVE}}/I_{\text{benzyl}}(\text{NMR}) \cdot 100] + 846$ (MW of melamine core and 6 benzyloxy end groups). These values are displayed in column 4. Columns 5 and 6 display the experimental GPC results.

It can be seen that the calculated values of M_n are in reasonable agreement with the values obtained from end-group analysis, assuming six armed structures. In all polymerizations, the molecular weight distributions are 1.2 or lower. The difference in molecular weight measured by GPC and those obtained from $^1\text{H-NMR}$

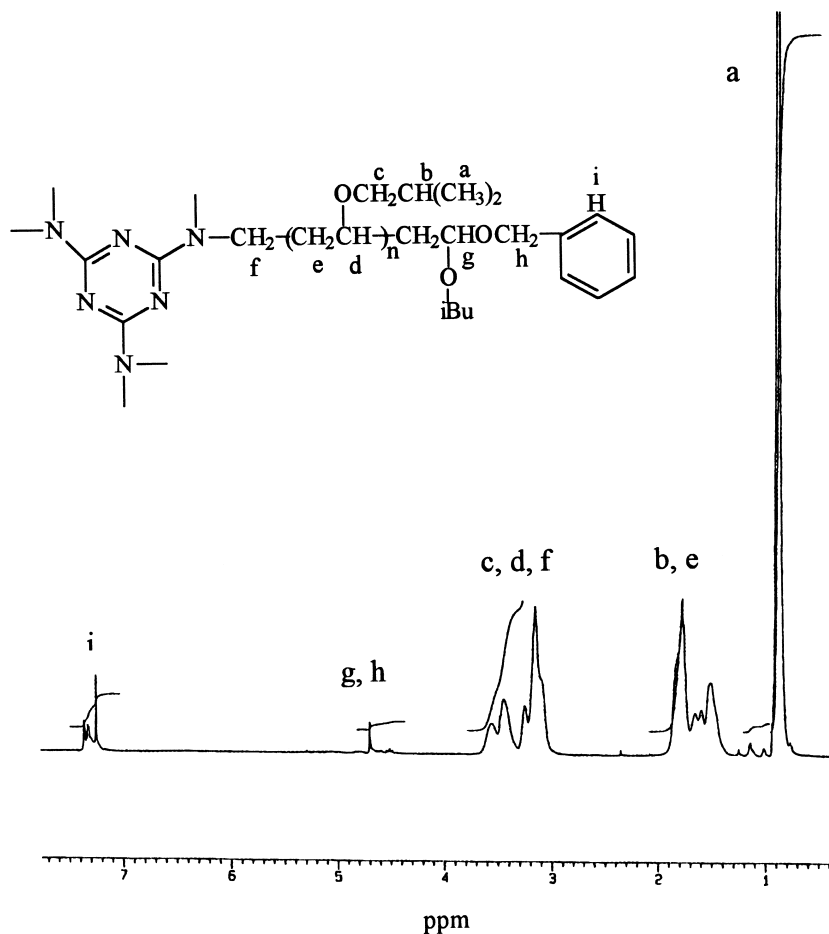


Figure 3. ^1H -NMR spectrum of a star poly(IBVE) end-capped with benzyloxy groups, measured in CDCl_3 .

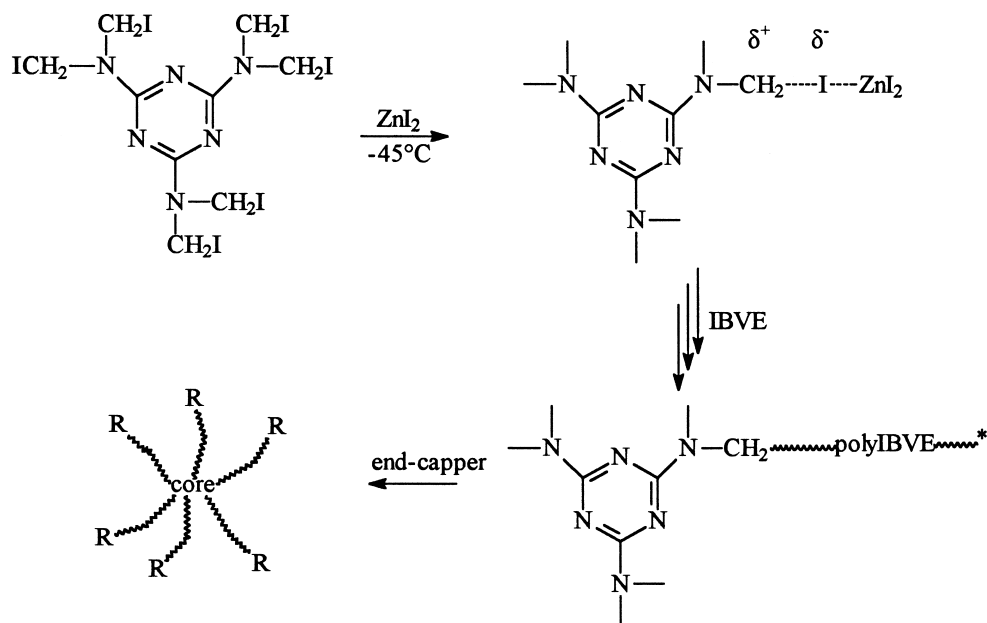
Table 1. Characterization of Hexa-armed Star Poly(IBVE)*

[M]/[I]	Mn(calcd.) ^a	$I_{\text{IBVE}}/I_{\text{benzyl}}(^1\text{H-NMR})$	Mn(NMR) ^b	Mn(GPC)	Mw/Mn
68	7650	10.2	6920	4530	1.17
132	14046	18.7	12860	7890	1.18
150	15846	22.3	14020	10580	1.20

*Obtained in toluene/dichloromethane (80/20 in volume) with HIMM/ ZnI_2 at -45°C , and end-capped with benzyloxy group (with polymer yield of 95%).

^a $[M]/[I]*100+846$ (Mw of hexa(benzyloxymethyl) melamine), assuming 100% of yield.

^b $I_{\text{IBVE}}/I_{\text{benzyl}}(\text{NMR})*100*6+846$ (MW of melamine core and 6 benzyloxy end groups).



NMR can be ascribed to the longer retention time of star polymers in GPC column due to their smaller hydrodynamic volume in dilute solution compared to their linear counterparts [6].

Based on these data, it is proposed that the polymerization reaction proceeds as described in Scheme 2.

CONCLUSION

The reaction of HMMM with TMSI at -45°C leads to quantitative formation of HIMM, which, upon addition of ZnI_2 , acts as a hexa-functional initiator for the polymerization of IBVE. If the polymerization is carried out in toluene/dichloromethane (80/20) at -45°C , star-shaped, hexa-armed “living” polymers are formed. Functional end-capping of these polymers should open the possibility to prepare star-shaped multi-telechelic poly(vinyl ethers).

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