



Polymer Communication

Synthesis and polymerization of maleimide-type new macromonomer with polystyrene having controlled chain length

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ARTICLE INFO

Article history:

Received 16 November 2010

Received in revised form

4 March 2011

Accepted 9 March 2011

Available online 16 March 2011

Keywords:

Maleimide

Macromonomer

Polymerization

ABSTRACT

A new reactive and functionalized polystyrene with a maleimide moiety at the one polymer end was synthesized with *N*-(4-(1-chloroethyl)phenyl)maleimide (CEPMI)/SnCl₄/tetra-butylammonium chloride (TBAC) initiating system. The polymer obtained with the CEPMI/SnCl₄/TBAC initiating system under the condition of [TBAC]/[SnCl₄] = 1 was to be maleimide-type macromonomer with polystyrene having controlled molecular weight of polystyrene (VI). VI could be polymerized with anionic and radical initiators to give new type graft polymer (poly[*N*-(4-ethylphenyl)maleimide]-*graft*-polystyrene) with controlled chain length with respect to side chains.

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1. Introduction

Graft copolymers with well-defined structure including “comb polymer” and “polymer brush” have been receiving much attention in recent decades as promising polymeric materials with multi-functions [1].

As for preparation of graft copolymers having well-defined or designed structure, synthesis and polymerization of correspondent macromonomer are one of the virtually most convenient methods, and a number of works [1,2] on the macromonomer have been developed since Milkovich and Chiang [3] demonstrated syntheses and applications of some macromonomers.

Maleimide derivatives are very attractive compounds in terms of chemical reactivity. They give rise to some interesting reactions such as Diels–Alder reaction with dienes [4] and the nucleophilic Michael-type addition of thiols or amines to the vinylene moiety [5]. In fact, the maleimide derivatives have been utilized as modifying reagents of proteins [6,7] and materials for immobilization of enzymes [8,9].

Meanwhile, the vinylene group of a maleimide moiety having 1,2-disubstituted ethylene structure can be polymerized with radical or anionic initiators to yield the polymer with a poly-(succinimide-3,4-diyl) (poly(2,5-dioxoazacyclopentane-3,4-diyl))

framework, which possesses high thermostability or heat-resisting property [10]. Poly(*N*-phenylmaleimide) and poly(*N*-ethylmaleimide) actually have very high decomposition temperatures at 375 and 330 °C, respectively [10]. Poly(*N*-phenylmaleimide) has been utilized for improving thermostability of thermoplastic polymers by copolymerization [11].

Being able to introduce a highly reactive maleimido group at the end of polymer with well-defined structure, it can be a maleimide-type macromonomer as a useful, reactive and functional polymer.

In this communication, synthesis of new type reactive and functional polymer with a maleimido group at the end of polystyrene having controlled molecular weight by using a new initiating system consisting of *N*-(4-(1-chloroethyl)phenyl)maleimide (CEPMI) with 1-chloroethylbenzene moiety, SnCl₄ and tetra-butyl ammonium chloride (TBAC) is described. The polymerization reactivity of the obtained polystyrene with maleimido group at the polymer end is also investigated as a maleimide-type new polystyrene macromonomer.

2. Experimental

CEPMI was used as a component of the new initiating system (CEPMI/SnCl₄/TBAC) for the cationic polymerization of styrene. The synthetic method of CEPMI, polymerization procedures of styrene with CEPMI/SnCl₄/TBAC initiating system, and other experimental methods are described in “Supplemental information” (Section S2) in detail.

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3. Results and discussion

3.1. Synthesis of CEPMI (I)

CEPMI was synthesized by the electrophilic addition reaction of hydrogen chloride to the vinyl group of *N*-(4-vinylphenyl)maleimide [12]. CEPMI was obtained in reasonably high yield (81.5%) as a yellow needle after recrystallization. The structure of the obtained CEPMI was confirmed by NMR (S2.2) and also an X-ray diffraction analysis (Refer to “Supplemental information” (S3.1)).

3.2. Synthesis of polystyrene having a maleimido group at the initial end (“maleimide-type polystyrene macromonomer”)

3.2.1. Polymerization of styrene with CEPMI/SnCl₄/TBAC initiating system

A novel reactive and functional polymer with a maleimido group at the end of polystyrene with well-defined structure was prepared by modifying the method developed by Higashimura et al. [13,14] using *N*-(4-(1-chloroethyl)phenyl)maleimide (CEPMI) instead of 4-(1-chloroethyl)benzene (CEB) as a component of the initiating system.

Table 1 shows results of synthesis of maleimide-type polystyrene macromonomer (VI in Scheme 1) having maleimido group at the initial end by the cationic polymerization of styrene with CEPMI/SnCl₄/TBAC initiating system.

When [SnCl₄]/[TBAC] ≥ 1 at 0 °C (Run 1–5 in Table 1), CEPMI/SnCl₄/TBAC initiating system is able to polymerize styrene to give polystyrene in good yield. Especially, when [SnCl₄]/[TBAC] = 1 (Run 4, 5 in Table 1), the obtained polystyrenes have unimodal and narrow (*M_w/M_n* = 1.15–1.16) molecular weight distributions and *M_n*'s estimated from SEC eluograms are in good agreement with those from signal intensities in ¹H NMR. A typical SEC eluogram is depicted in A of Fig. S4 in “Supplemental information” part.

In the case of [SnCl₄]/[TBAC] > 1, the molecular weight distributions of the polystyrenes show bimodal profiles though the polymers are produced in more than 70% yield at 0 °C (Run 1–3 in Table 1), and *M_n*'s estimated from SEC eluograms are, however, in rather low agreement with those from signal intensities in ¹H NMR.

On the other hand, when [SnCl₄]/[TBAC] < 1, this initiating system can not give rise to polymerization of styrene.

It was reported by Higashimura et al. [14] that the cationic living polymerization of styrene with the initiating system consisting of a compound with chlorobenzyl moiety such as CEB, SnCl₄ and TBAC proceeds through “nondissociated” propagating species (IV) to produce having narrow molecular weight distribution, while “dissociated” propagating one (V) operates non-living polymerization to give polymer with broad molecular weight distribution [14]. The fact that the feature of the polymerization of styrene with

CEPMI/SnCl₄/TBAC initiating system is highly sensitive to the ratio of [SnCl₄]/[TBAC] can be, therefore, explained in terms of the initiating ability of the species formed from the reaction between CEPMI (I) and SnCl₄ in the initiating step (Eq. (1) in Scheme 1) and the propagating ability of the species formed from the reaction between the chlorobenzyl moiety and SnCl₄ in the propagation step ((IV) and (V) in Scheme 1).

In the case of [TBAC] = [SnCl₄] for CEPMI/SnCl₄/TBAC initiating system, the polymerization can be initiated by the cationic species being in the equilibrium condition of II and III in Eq. (1) and be propagated predominantly through “nondissociated” species (IV) so that polystyrene with unimodal molecular weight distribution can be produced. On the other hand, when the ratio of [SnCl₄] to [TBAC] is larger than one for the polymerization of styrene with CEPMI/SnCl₄/TBAC initiating system (i.e. [SnCl₄]/[TBAC] > 1), the polymerization is initiated by the cationic species (being in the equilibrium condition of II and III) to be propagated through both “nondissociated” (IV) and “dissociated” (V) species so that the yielded polystyrene has bimodal molecular weight distribution. Furthermore, when [SnCl₄] being lower than [TBAC] (i.e. [SnCl₄]/[TBAC] < 1), no polymerization takes place probably because the concentration of the initiating species II or III generated from the reaction between CEPMI and SnCl₄ may be too low to initiate the polymerization due to less electron releasing ability of 4-maleimidophenyl group compared to phenyl group [15].

No polymerization occurred at low temperature (–15 °C) either, whereas the polymerization of styrene took place to yield polystyrene in good yield in the case of using CEB as a component of initiating system [14]. This may be also due to the difference of strength of initiating ability of the initiating species produced from the reaction of the chlorobenzyl moiety in CEB or CEPMI with SnCl₄.

3.2.2. Analysis of polymer with CEPMI/SnCl₄/TBAC initiating system

The structures of the polymers obtained were analyzed by NMR and IR. The spectral results revealed that the polymers prepared with CEPMI/SnCl₄/TBAC initiating system under the condition of [SnCl₄]/[TBAC] = 1 possessed polystyrene structure with a maleimide and a chlorobenzyl moiety at the respective polymer ends, which could be a maleimide-type polystyrene macromonomer (VI).

¹H and ¹³C NMR spectra (Fig. S2) and explanation of the spectra including assignments of signals are described in “Supplemental information” (S3.2.2).

Other polymers obtained with CEPMI/SnCl₄/TBAC initiating system showed almost the same ¹H NMR, ¹³C NMR, and IR spectra.

3.2.3. Living nature of the polymerization with CEPMI/SnCl₄/TBAC initiating system under the condition of [SnCl₄]/[TBAC] = 1

Fig. 1 shows conversion vs. *M_n* plots of the cationic polymerization with [CEPMI]/[SnCl₄]/[TBAC] = 1/2/2 initiating system. The

Table 1
Synthesis of polystyrene macromonomer having maleimido group at the initial end by cationic polymerization of styrene with CEPMI/SnCl₄/TBAC initiating system.^a

Run	[Styrene]/[CEPMI]/ [SnCl ₄]/[TBAC]	Time/h	Temp/°C	Yield/g	Styrene Conv/%	<i>M_n</i> × 10 ⁻³	<i>M_w/M_n</i>	Distribution
1	20/1/5/0	24	0	0.872	71.9	6.5 ^b (4.8 ^c)	4.7	Bimodal
2	20/1/5/2	24	0	0.897	74.9	4.3 ^b (3.1 ^c)	1.2	Bimodal
3	20/1/5/4	24	0	0.916	76.6	4.6 ^b (3.8 ^c)	1.2	Bimodal
4	50/1/5/5	24	0	1.214	87.6	3.7 ^b (3.3 ^c)	1.2	Unimodal
5	50/1/2/2	12	0	1.192	86.0	3.8 ^b (3.3 ^c)	1.2	Unimodal
6	50/1/4/5	24	0	0.000	0	–	–	–
7	50/1/5/5	24	–15	0.000	0	–	–	–

^a [CEPMI] = 0.025 mol/L.

^b Estimated from SEC eluograms.

^c Measured from signal intensities of ¹H NMR.

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