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Synthesis and applications of quaternized highly branched polyacrylamide as a novel multi-site polymeric phase transfer catalyst

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Abstract In current study, quaternized highly branched polyacrylamide (HBAA) was synthesized and used as an efficient multi-site polymeric phase transfer catalyst in nucleophilic substitution reactions and also in synthesis of α , β -unsaturated nitriles from reaction of acetonitrile and carbonyl compounds. The quaternized HBAA was synthesized via two steps. First, HBAA was synthesized via self-condensing vinyl polymerization of acrylamide at appropriate molar ratio of monomer to diperiodatocuprate(III). In the second step, 3-acrylamidopropyl trimethylammonium iodide was polymerized on peripheral area of the HBAA in the presence of diperiodatocuprate(III) solution again. The thermal behavior of HBAA and that of the quaternized HBAA were studied by DSC and TGA analysis. This phase transfer catalyst was easily recovered after reaction and reused several times without any loss of activity.

Keywords Highly branched polymers \cdot Self-condensing vinyl polymerization \cdot Phase transfer catalyst \cdot α , β -Unsaturated nitrile

Introduction

Hyperbranched and highly branched polymers are a special type of dendrimers and have common similarity such as high degree of branching and high functional group density on the surface [1, 2]. In recent years, highly branched polymers have received much attention owing to their

H. Mahdavi (⊠) · M. Amirsadeghi School of Chemistry, College of Science, University of Tehran, P.O. Box 14155-6455, Tehran, Iran e-mail: hmahdavi@khayam.ut.ac.ir scientific and industrial important applications such as viscosity modifiers, drug delivery systems, efficient support of catalysts and scaffolds [3–6].

Generally, there are three main strategies for synthesis of highly branched polymers involving: (1) Step-growth polycondensation of AB_X and/or $A_2 + B_3$ monomers, (2) Self-condensing vinyl polymerization (SCVP) of AB^* monomers, and (3) Multi-branching ring-opening polymerization of latent AB_X monomers [7–9].

Self-condensing vinyl polymerization of AB^{*} monomers was proposed by Frechet in 1995 [10]. "A" denotes a vinyl group and "B^{*"} represents a functional group that can initiate group A into propagating site A^{*}. The feature of this approach is that the vinyl group A can undergo selfpolymerization, and hence, this method is called SCVP. According to this idea, Matyjaszewski [11] prepared hyperbranched polystyrene through one-pot atom transfer radical polymerization using *p*-(chloromethyl) styrene.

This approach has also been applied in the other living polymerizations, i.e., cationic [12, 13], ATRP [14], nitroxide mediated radical polymerization [15], GTP [16], and ring-opening polymerization [17].

Xi in 1999 [18] reported a smart method for preparation of highly branched polyacrylamide (HBAA), which was carried out in the presence of basic solution of potassium diperiodatocuprate. This method was a subclass of SCVP in which double bond of acrylamide is as A moiety and its nitrogen radicals that is generated via oxidation of amide group by potassium diperiodatocuprate play role of B^* moiety. The benefit of this method is that acrylamide used solely and no previous preparation of AB^* monomer was needed.

Among variety of phase transfer catalysts (PTC), quaternary ammonium and phosphonium salts have more application because of their appropriate activity and also low cost. Recently, many studies have been reported on attempts to develop multi-site phase transfer catalysts (MPTCs) containing more than one catalytic active site in a molecule [19–23]. This type of MPTCs offers the potential of providing greater PTC activity and accelerating the particular synthetic transformation even under mild conditions.

One important salient feature for employing MPTC for any chemical reaction is that the concentration of MPTCs required to conduct the reaction are relatively low compared to soluble single-site PTCs.

Herein, we report the synthesis and applications of quaternized HBAA as an efficient and novel multi-site polymeric phase transfer catalyst.

Experimental

Materials

Acrylamide was purchased from Merck and recrystallized from methanol. *N*,*N*-dimethylaminopropyl acrylamide (DMAPAA) and potassium periodate were purchased from Aldrich. Other reagents were purchased from Merck and used as received without further purifications. In order to obtain reaction yields, gas chromatography was used and recorded on a shimadzu GC14-A.

H-NMR spectra

IR spectra were run on a perkin-Elmer-IR-157.G spectrophotometer. TGA spectra were obtained by TGA-Q-50-V6.3 build 189. DSC measurements were made on a TA DSC Q100 V9.0 (New Castle, DE, USA) equipped with thermal analysis data acquisition software. The rate of heating was 5 °C/min.

Synthesis of potassium diperiodatocuprate solution

The potassium diperiodatocuprate solution was prepared according to reported procedure [24]. Typical procedure was as the following: $CuSO_4$ ·5H₂O (3.54 g, 14 mmol), KIO₄ (6.82 g, 30 mmol), K₂S₂O₈ (2.20 g, 8 mmol) and KOH (9.00 g, 160 mmol) were added to 200 ml of deionized water (DW). The mixture was refluxed for 40 min. After cooling to room temperature, the mixture was filtered through sintered glass and the filtrate was diluted to 250 ml with DW. The concentration of copper (III) in aqueous solution was determined by iodometric titration and also gravimetrically by the thiocyanate method. The final concentration of Cu (III) was titrated as 0.056 mol/L and the concentration of KOH as 0.55 mol/L.

Synthesis of 3-acrylamidopropyl trimethylammonium iodide

In a 100 ml flask, *N,N*-DMAPAA (1.56 g, 0.01 mol) was dissolved in dichloromethane (20 ml) and kept in an ice bath. An excess amount of iodomethane (5 ml, 0.08 mol) dissolved in dichloromethane (10 ml) was added drop wise to the flack content. The mixture was stirred for 2 h at 0 °C and then 4 h at ambient temperature. After that, the dichloromethane was evaporated and the viscose brown liquid of 3-acrylamidopropyl trimethylammonium iodide was obtained in 92 % yield (2.75 g). The FT-IR spectra of 3-acrylamidopropyl trimethylammonium iodide showed peaks at 2,930, 1,665, 1,613, 1,560, 1,480, 1,430, 1,373, 1,256, 1,054 and 990 cm⁻¹.

Synthesis of highly branched acrylamide

Highly branched acrylamide (HBPAA) was synthesized according to Xi procedure with some modification [18]. Typical procedure: 2.0 g acrylamide (28 mmol) and 100 ml potassium diperiodatocuprate solution (0.056 mol) were added to a 250 ml flask. The polymerization was carried out for 48 h at 40 °C under nitrogen atmosphere. Then, the reaction component was filtered and pH of the polymer solution was adjusted to 6–7 by addition of HCl solution (10 %), and that precipitated byproduct was filtered and poured into methanol. The resulting polymer was filtered and washed with methanol (three times) and then dried under vacuum at 50 °C for 2 days (yield 90 %).

Synthesis of quaternized highly branched polyacrylamide

50 ml potassium diperiodatocuprate solution and 0.5 g HBAA were added to a 150 ml flask equipped with nitrogen inlet and outlet, and were stirred under nitrogen atmosphere at 40 °C. Thereafter, an aqueous solution of 3-acrylamidopropyl trimethylammonium iodide (1.0 g in 5 ml of DW) was added to the reaction mixture through drooping funnel in 30 min. The polymerization was carried out at 40 °C for 48 h. In the next step, the pH of reaction mixture was adjusted to 7 by adding HCl. The precipitate was filtered, and the filtrate was concentrated and then poured to methanol. The precipitated polymer was filtered and washed with methanol and dried under vacuum at 60 °C. The yield of reaction was 62 %. The amount of iodide ion present in the quaternized HBAA was determined by Volhard's method and found to be 2.4 mmol/g.

Application of quaternized highly branched polyacrylamide as the phase transfer catalyst in biphasic reactions

Nucleophilic substitution on benzyl chloride

Typical procedure: 0.01 mol of nucleophilic salt (M^+X^-) was added to a 25 ml flask contained 10 ml distillated water. 0.12 ml benzyl chloride (1 mmol) dissolved in 3 ml toluene was added to flask and stirred at room temperature. 0.01 g of quaternized HBAA was added to reaction vessel and reaction was carried out at 70 °C. After appropriate time, a sample of reaction was taken from organic layer and after drying by sodium sulfate, the yield of reaction was determined by GC.

Condensation of acetonitrile with ketones

Typical procedure: 0.5 g of powdered KOH, 10 ml dry acetonitrile and 0.02 g quaternized HBAA were added to a 25 ml flask and stirred at room temperature. Thereafter, 1 mmol of ketone was added to the reaction mixture and refluxed at 83 °C for appropriate time. After that, a sample of reaction was taken from organic layer and the yield of reaction was determined by GC.

Selected spectral data

Cyclohexenylacetonitrile: bp 50 °C (0.5 torr) [lit [31]: bp 82–84 °C (3–4 torr)]; ¹H-NMR (CCl₄): δ 1.25–2.0 (m, 4 H), 1.25–2.0 (m, 2 H), 2.0–2.8 (m, 4 H), 3.3 (s, 1H); IR (neat) 2,252 (w) cm⁻¹.; 2,2-Diphenylacrylonitrile: Colorless oil: bp 128–131 °C (0.2 torr) [lit. mp 47–48 °C; bp 160–200 °C (1.5 torr) ¹H-MR (CCl₄) δ 5.69 (s, 1 H), 7.4 (d, 10 H); IR (neat) 2,218 (s) cm⁻¹.; *(E)*- and (*Z*)-2-Methyl-2-phenylacrylonitrile pale yellow oil [*E*/*Z* ca. 4.0 (NMR)]: bp 78 °C (0.2 torr) [lit. bp 120–129 °C (2 torr)]; ¹H-NMR (CCl₄) *E* isomer, δ 2.5 (d, 3 H), 5.7 (m, 1 H), 7.55 (s, 5 H); ¹H-NMR (CCl₄) *Z* isomer, δ 2.3 (d, 3 H), 5.45 (m, 1 H), 7.55 (s, 5 H); IR(neat) 2,221 (s) cm⁻¹.; 2-(9H-fluoren-9-ylidene)acetonitrile: yellow solid, mp 109–110 °C (lit. 30 mp 109–111 °C). ¹H-NMR(CCl₄) δ 5.98 (s, 1 H), 7.2–7.7, 8.2–8.35 (m, 8 H); IR (CCl₄) 2,205 (s) cm⁻¹.

Recycling of catalyst

In order to recover the catalyst at the end of reaction, the organic phase was separated and concentrated under reduced pressure. Then, the concentrated mixture was added to methanol (100 ml) as a non-solvent. The precipitated polymer was filtrated and washed three times by methanol (20 ml) and dried under vacuum at 50 °C.

Results and discussion

Diperiodatocuprate (III) is an efficient radical initiator that can generate radical on substance containing mono or disubstituted amine, amide or hydroxyl group [25–28]. The mechanism of initiation involves an one-electron transfer oxidation process. For example, the amide group can be converted to an amidyl radical in the presence of Cu(III). In this reaction, one electron of the nitrogen atom is taken by Cu(III) to form a cation radical. Then, the cation radical loses a proton in alkaline medium and produce amidyl radical, which is capable to initiate a radical polymerization (Scheme 1).

Xi et al. [18] demonstrated that HBAA could be synthesized via SCVP method using appropriate molar ratio of monomer to diperiodatocuprate(III) solution. They showed that by increasing amount of Cu(III), degree of branching increased and structure of polymer became more similar to highly branched polymers. Since only acrylamide monomer was used in this method for the synthesis of HBAA, the obtained highly branched polymer had a numerous amide groups on its surface.

In this research after preparation and purification of HBAA via mentioned procedure, it was resolved again and reacted with fresh solution of Cu(III) in the presence of 3-acrylamidopropyl trimethylammonium iodide as the functional monomer. It is envisaged in this approach that some of peripheral amide groups of HBAA react with Cu(III) complexes and generate corresponding radical species which are then able to initiate radical polymerization with appropriate monomer. Therefore, it is reasonable to expect that the final functional system have HBAA in its core and grafted poly (3-acrylamidopropyl trimethylammonium iodide) on its peripheral section (Scheme 2).

The resulting quaternized copolymer was characterized at first by IR spectroscopy. The IR spectrum showed peaks



Scheme 1 The mechanism of intiation process



Core-shell type quaternized polyacrylamide

Scheme 2 The synthesis steps of quaternized highly branched polyacrylamide

at 3,400 cm⁻¹ (N–H amide), 1,655 cm⁻¹ (C = O amide), 1,544 cm⁻¹ and 1,408 cm⁻¹. The capacity of quaternized copolymer was quantitatively estimated by Volhard [29] method and was found to be 2.4 mmol/g.

H-NMR spectra of quaternized HBAA in D_2O shows methylene group at 2.17 ppm (1.66), methyn groups at

3.29 ppm (0.68), methylene groups attached to quaternary nitrogen at 3.07 ppm (3.41) and methyen groups attached to nitrogen at 3.1 ppm (1.36).

To study the thermal behavior of samples, DSC measurements were carried out. Figure 1 represents the DSC thermograms of HBPAA and quaternized HBPAA. The thermal glass transition peak and the onset thermal glass transition of the two samples were 8.52, 13.66 and 11.02, 14.01 °C, respectively. By increasing the quaternary ammonium sites, change in the characteristic temperatures in DSC was clearly observed in Fig. 1b in comparison to Fig. 1a. Obviously, increasing Tg for quaternary ammonium sites.

The thermal degradation behavior of samples was measured. The thermo-gravimetric (TG) curves of HBPAA and quaternized HBPAA were plotted in Fig. 2. As observed, two samples exhibited one-step degradations but with different residual weight percent. The onset decomposition temperature (T_{on}), the temperature at 20 % weight loss (T_{20}), final decomposition temperature (T_f) and final weight loss percent (% WL_f) of the samples are listed in Table 1. The difference of T_{on} of the two samples was related to higher water content of quaternized HBPAA



Fig. 1 DSC curves of a HBPAA and b quaternized HBPAA



Fig. 2 TG curves of a HBPAA and b quaternized HBPAA

Table 1TG results of samples

Sample	$T_{\rm on}$ (°C)	$T_{20}(^{\rm o}{\rm C})$	$T_{\rm f}(^{\rm o}{\rm C})$	WL _f (%)
НВРАА	124	355	590	57.88
Quaternized HBPAA	90	405	590	49.47
CI			Nu	



Scheme 3 Substitution reaction of benzyl chloride

because of its quaternary ammonium salts. In addition, all the three other parameters obviously showed that quaternized HBPAA have higher thermal stability than HBPAA because of its additional salt structure.

Applications of quaternized HBPAA in biphasic reaction

At first, the activity of the quaternized HBPAA as a phase transfer catalyst was studied for the substitution reactions of benzyl chloride with a variety of nucleophiles (Scheme 3; Table 2).

These substitutions satisfactorily proceeded in excellent yields without detectable side reactions in the presence of quaternized HBPAA as a phase transfer catalyst at 70 °C. As reported before in the literature for other catalyst, in these nucleophilic reactions, there was no reaction proceeding or taking place in very low yield in the absence of the quaternized HBPAA [30]. Furthermore, in comparison to numerous reported results about same nucleophilic reaction in the presence of phase transfer catalyst [31], the quaternized HBPAA has higher reactivity. A reasonable description of this higher reactivity is that the quaternized HBPAA has multiple quaternary catalytic site because of it highly branched structure.

In continuation of applications, the quaternized HBPAA was used in a standard condensation reaction. For instance, the synthesis of α , β -unsaturated nitriles from reaction of acetonitrile and carbonyl compounds was selected as model reaction [32]. The condensation reaction of acetonitrile with various carbonyl compounds were carried out in the presence of the quaternized HBPAA as a phase transfer catalyst at 70 °C (Table 3). In this reaction, cynamoethide ion was generated via deprotonation of acetonitrile by KOH in the presence of the PTC. Then, cynamoethide ion was added to carbonyl group of ketones, and β -hydroxynitrile intermediate prepared that

 Table 2
 Substitution reactions of benzyl chloride with a variety of nucleophiles



Reaction condition: benzyl chloride 1 mmol in 1 ml toluene, Nu 0.01 mol in 5 ml H₂O, HBAA-APTMAI 0.02 g, T = 70 °C

spontaneously dehydrated to afford the α , β -unsaturated nitrile under reaction condition (Scheme 4).

Finally, in all of these applications workup of the reaction was easy and the polymer was removed from the reaction mixture via simple precipitation by adding to methanol and/or filtration. Interestingly, it was also observed that this recycled quaternized HBPAA after several times recycling (at least five times) could be used without any loss in their efficiency in the mentioned reactions.



Scheme 4 Phase transfer catalysis mechanism in synthesis of α , β -unsaturated nitriles

- Table 3 Synthesis of
- α , β -unsaturated nitriles

Entry	Substrate	Time (min)	Product	Yield (%)	Reported Yield(%)[32]
1		60	CN CN	95	72
2		45	CN CN	90	60
3	CHa	50	CN CH ₃	80	15
4	°	20	CN	100	76

Reaction condition: KOH (0.5 g), dry acetonitrile (10 ml), HBAA-PTMAI (0.02 g), ketone (5 mmol)

Conclusion

In conclusion, we have demonstrated a very effective method for the synthesis of quaternized HBAA. The quaternized HBAA was synthesized via two steps. First, HBAA was synthesized via SCVP of acrylamide using appropriate molar ratio of monomer to diperiodatocuprate(III). In the second step, 3- acrylamidopropyl trimethylammonium iodide was polymerized on peripheral area of the HBAA in the presence of diperiodatocuprate(III) solution again. This multi-site polymeric phase transfer catalyst was used effectively in nucleophilic substitution reactions and also in the synthesis of α , β unsaturated nitriles from reaction of acetonitrile and carbonyl compounds. This phase transfer catalyst was easily recovered and reused several times without any loss of activity.

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