



Influence of aliphatic acids on the phase transition of thermoresponsive hyperbranched polymer

Xu-Ran Mu^a, Jin-Ge Tong^a, Yi Liu^b, Xun-Yong Liu^b, Hua-Ji Liu^{a,*}, Yu Chen^{a,*}

^aDepartment of Chemistry, School of Sciences, Tianjin University, 300072 Tianjin, People's Republic of China

^bSchool of Chemistry and Materials Science, Ludong University, Yantai 264025, Shandong, People's Republic of China

ARTICLE INFO

Article history:

Received 9 November 2012

Received in revised form

24 January 2013

Accepted 3 March 2013

Available online 13 March 2013

Keywords:

Aliphatic acid
Hyperbranched
Phase transition

ABSTRACT

The influence of aliphatic acids on the phase transition temperature of thermoresponsive hyperbranched polyethylenimine possessing a large amount of isobutyramide and amine groups (HPEI-IBAm) was studied systematically. Nine saturated aliphatic acids including formic acid (C1), acetic acid (C2), n-pentanoic acid (n-C5), trimethylacetic acid (t-C5), hexanoic acid (C6), octanoic acid (C8), decanoic acid (C10), dodecanoic acid (C12) and hexadecanoic acid (C16) were used to measure their effects on the cloud point temperature (T_{cp}) of HPEI-IBAm in a mixture of H₂O/DMF ($v/v = 9:1$). For comparison, the effect of these aliphatic acids on the traditional thermoresponsive linear poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) and poly(N-isopropyl acrylamide) (PNIPAm) was also studied. The influence of aliphatic acids on different thermoresponsive polymers was different. The aliphatic acids with shorter carbon chains ($C \leq 8$) increased the T_{cp} of HPEI-IBAm, and those with long hydrocarbon chains ($C > 8$) depressed the T_{cp} . Moreover, the effect of aliphatic acids with $C \leq 5$ was similar, even though their configurations might be different. The specific ranking of aliphatic acids in raising the T_{cp} of HPEI-IBAm was as follows: C1 ~ C2 ~ n-C5 ~ t-C5 > C6 > C8 > C10 > C12 ~ C16. With respect of the linear PDMAEMA, all the aliphatic acids employed elevated its T_{cp} . The specific ranking of aliphatic acids in raising the T_{cp} of linear PDMAEMA was similar to that for dendritic HPEI-IBAm, but with a minor difference: C1 ~ C2 ~ n-C5 ~ t-C5 > C6 > C8 > C10 > C12 > C16. In the case of the linear PNIPAm, the aliphatic acids with $C \leq 6$ had almost no influence on the T_{cp} . Raising the carbon number to be 8 or higher leads to the obvious T_{cp} depression. The different effect of aliphatic acids on the phase transition of these thermoresponsive polymers was discussed, and it was mainly attributed to their structural and topological difference.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

During the past decade, polymers with stimuli-responsive properties, such as fast and reversible conformational or phase changes in response to variations in temperature and/or pH, have attracted much interest [1]. An appealing stimuli-responsive species is thermoresponsive polymer with a lower critical solution temperature (LCST) in aqueous solution, which show a large decrease in solubility in water above a specific temperature [2]. To date, the most studied thermoresponsive materials have been those with linear structure displaying LCST properties [3]. In other words, even though the thermoresponsive materials have some specific topology, such as hydrogels [4], star or grafted polymeric structures [5,6] and polymeric micelles [7,8], their LCST properties

are originated from their thermoresponsive linear polymer components, and are almost independent of their specific topology.

In 2004 Kono's group reported their pioneering work on the thermoresponsive dendrimers whose LCST could be tuned in a broad range by varying the molecular weight [9]. Following their pioneering work, more kinds of thermoresponsive dendritic polymers were reported [10–20]. Dendritic and linear polymers have significant difference in topology. Dendritic polymers usually have spheroid-like and compact structure, whereas linear polymers usually adopt the loose coil conformation [21,22]. Therefore, it was found that the thermoresponsive dendritic polymer as a new member of the family of thermoresponsive polymers exhibited the obvious difference in properties compared with the traditional thermoresponsive linear polymer [9–12].

Up to the present date, the effect of different additives, such as inorganic salts [23–31], surfactants [30–35] and organic compounds [36–40], on the LCST of thermoresponsive linear polymers has been well studied. As for the thermoresponsive dendritic

* Corresponding authors. Tel./fax: +86 22 27403475.

E-mail addresses: liuhuaji@tju.edu.cn (H.-J. Liu), chenyu@tju.edu.cn, chenyu.cy@gmail.com (Y. Chen).

polymers, the study of the additives' influence on their phase transition temperature is scarce [11–13,41]. Our group has systematically studied the effect of anionic and cationic ions on the thermoresponsive hyperbranched polymers with a large amount of amide and amine groups [11–13], where the phase transition temperature of the compact hyperbranched polymers exhibited higher sensitivity to ions than that of the traditional thermoresponsive linear polymers. Moreover, these thermoresponsive hyperbranched polymer systems were better than those thermoresponsive linear polymer systems [42] to mimic the interactions among ions and positively charged proteins [43–45]. Kono's group reported that the water-soluble Rose Bengal could interact with the thermoresponsive dendrimers employed by them, which led to the depression of the LCST [41]. However, in their work the comparison with the traditional thermoresponsive linear polymers was not performed.

Aliphatic acids are important bio-related compounds, while 'smart' materials are applicable in the field of biomedicine and biotechnology. Dendritic polymers usually had the ability of accommodating guests [41], thereby being used as smart drug-delivery vehicle. Aliphatic acid also exists in the body; therefore, it is worth studying how aliphatic acids influence the thermoresponsive properties of the polymers having the potential as the drug vehicle. Until now, only aliphatic acids in salt form have been studied with respect to their effect on the phase transition of the traditional thermoresponsive linear poly(*N*-isopropyl acrylamide) (PNIPAm) [31], and how aliphatic acids in acid form affect the properties of thermoresponsive polymers has never been done. In this contribution, we systematically studied the effect of aliphatic acids on the thermoresponsive hyperbranched polymers containing a large amount of amide and amine groups. Furthermore, the comparison with the traditional thermoresponsive linear polymers was also performed.

2. Experimental

2.1. Materials

Hyperbranched polyethylenimine (HPEI, Aldrich, $M_n = 10^4$ g/mol, $M_w/M_n = 2.5$), was dried under vacuum prior to use. Benzoylated cellulose tubing (MWCO 1000) was purchased from Sigma and used as received. Dimethylaminoethyl methacrylate (98%, DMAEMA) was purchased from Acros and distilled under vacuum before use. *N*-Isopropyl acrylamide (98%, NIPAm) was purchased from Acros and recrystallized from a 10/1 mixture of hexane and acetone before use. Triethyl amine (A.R., TEA) was dried over CaH₂ and distilled before use. Dimethylformamide (A.R., DMF), azobisisobutyronitrile (A.R., AIBN), acetic acid (99%, C2), *n*-pentanoic acid (99%, *n*-C5), *n*-hexanoic acid (99%, C6), dodecanoic acid (A.R., C12) and hexadecanoic acid (A.R., C16) were purchased from Tianjin University Kewei Chemical Company and used as received. Anhydrous formic acid (98.5%, C1) was purchased from Tianjin Guangfu Fine Chemical Research Institute and used as received. Trimethylacetic acid (99%, *t*-C5) was purchased from Beijing Hengyehongyuan Chemical Company and used as received. Isobutyric anhydride (98%), octanoic acid (98%, C8) and decanoic acid (99%, C10) were purchased from Alfa Aesar and used without further purification. De-ionized water was double-distilled before use. Linear poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) and linear poly(*N*-isopropyl acrylamide) (PNIPAM) were synthesized as described in the Supporting Information.

2.2. Characterization

¹H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. The chemical shifts are given in parts per million

(ppm). FTIR spectra were recorded on a Nicolet 5DXC FT-IR spectrometer. The measurement was done using KBr pellets covered with a dry thin film of the compound, and the scanning range was 4000–400 cm⁻¹. Light transmittance of the polymer solution was measured on a temperature-controlled Purkinje General (China) T6 UV/Vis Spectrophotometer at 660 nm, and the heating rate was 0.5 °C/2 min. The cloud-point temperature (T_{cp}) was taken from the intersection of the maximal slope tangent and the initial horizontal tangent in the resulting transmittance versus temperature curve. The temperature error is ±0.2 °C.

2.3. Synthesis of isobutyramide (IBAm) terminated HPEI (HPEI-IBAm)

The preparation of HPEI-IBAm is similar to that reported previously [12], but with a little modification. Under nitrogen atmosphere, isobutyric anhydride (27.45 g, 0.1735 mol) was added dropwise to the mixture of HPEI10K (12.77 g, 0.2169 mol of terminal groups) and triethyl amine (19.31 g, 0.1910 mol) in 50 mL of chloroform at room temperature with vigorous stirring. Subsequently, the reaction mixture was kept at room temperature for 24 h. Finally, the reaction temperature was raised to 72 °C for 2 h to finalize the reaction. The chloroform was removed under vacuum and the residue was dissolved in 50 mL of methanol. Five gram of potassium carbonate was added to the solution and the mixture was stirred at room temperature for 4 h. After centrifugation, the solution was concentrated to ca. 10 mL and then purified by dialysis against methanol using a benzoylated cellulose membrane (MWCO 1000 g/mol) for 2 days. Finally, the methanol solvent was removed under vacuum, and the product was dried in vacuum for 24 h. Degree of substitution of IBAm groups is 81%. ¹H NMR (CDCl₃): δ (ppm) = 1.08 ((CH₃)₂CHCON–); 2.20–3.90 ((CH₃)₂CHCON–, ethylene protons of HPEI polymeric backbone). $M_n(NMR) = 1.95 \times 10^4$ g/mol; The average numbers of IBAm groups and amino groups per polymer are 138 and 94, respectively.

2.4. Preparation of the solutions of polymers with aliphatic acids

The thermoresponsive polymer (50 mg) was mixed with different amount of aliphatic acid in 0.5 mL of DMF. This solution was stirred at room temperature for 24 h, and then 4.5 mL of double-distilled deionized water was introduced. The obtained solution was stirred for another half an hour before use.

3. Results and discussion

Hyperbranched polyethylenimine (HPEI) contains a large amount of primary, secondary and tertiary amine groups. Transformation of certain amount of primary and secondary amines into isobutyramide (IBAm) groups can result in HPEI-IBAm that shows LCST in water (Fig. 1) [11,12,17]. In this contribution, nine saturated aliphatic acids including formic acid (C1), acetic acid (C2), *n*-pentanoic acid (*n*-C5), trimethylacetic acid (*t*-C5), hexanoic acid (C6), octanoic acid (C8), decanoic acid (C10), dodecanoic acid (C12) and hexadecanoic acid (C16) were selected to study how aliphatic acids in acid form affected the thermoresponsive property of HPEI-IBAm.

HPEI-IBAm has a large amount of polar amide and amine groups and non-polar isopropyl units, therefore, mixing HPEI-IBAm with aliphatic acid should form a supramolecular complex through the acid–base neutralization [46]. Before the measurement of thermoresponsive property, whether a supramolecular complex between HPEI-IBAm and aliphatic acid could be formed was proved. C16 was chosen as the representative of aliphatic acid. C16 is soluble in DMF, but not in pure water, so HPEI-IBAm (0.51 mM) and

Download English Version:

<https://daneshyari.com/en/article/5181747>

Download Persian Version:

<https://daneshyari.com/article/5181747>

[Daneshyari.com](https://daneshyari.com)