

UDC 541.64

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Synthesis and characterization of hydrophilic copolymers

Abstract

Two composition ratios of poly[N-isopropylacrylamide (NIPAAm)-co-2-hydroxy ethyl acrylate (2-HEA)] were prepared in ethanol/water mixtures (v/v, 1/1) using ammonium persulfate (APS) as initiator. The hydrophilic copolymers were characterized by DSC, TGA, GPC and SEM. The results showed that molecular weight, T_g, thermal stability increase with increase of NIPAAm in the copolymers. The increase of molecular weight is interpreted in terms of increasing the formation of primary radicals in high ratio of NIPAAm in the copolymer. SEM showed that the polymer became more hydrophilic with increasing the ratio of NIPAAm in the copolymer.

Keywords: poly[N-isopropylacrylamide (NIPAAm)-co-2-hydroxy ethyl acrylate (2-HEA)], hydrophilic copolymers.

Introduction

Poly(N-isopropylacrylamide) (PNIPAm) is a well-known polymer of which the aqueous solution undergoes phase separation on heating beyond 32°C induced by a reversible hydration-de hydration transition [1, 2], which is an attractive range for biomedical applications, particularly drug delivery [3–7]. Copolymers containing PNIPAAm with hydrophilic-hydrophobic segments can exhibit the similar phase transition properties in a large range of temperature [8]. The copolymers with acrylic acid units show a pH sensitive property as well as a thermosensitive one [9]. PNIPAAm-based gels also exhibit thermo-reversible swelling properties [10].

Many scientists believe that the hydrogen bonding effect and hydrophobic forces are the most important reasons in PNIPAAm phase transition process. Therefore, with a change in the ratio of hydrophilic and hydrophobic groups in the polymer, one can adjust the low critical solution temperature (LCST) of the system to match the desired critical region. Furthermore, different media affected the swelling behavior and the LCST of the hydrogel (11).

Understanding the effect of hydrophilic-hydrophobic balance on LCST phenomenon has been an active research area and some correlations have been identified so far. For example, it has been shown that the chemical structure and the concentration of hydrophilic and hydrophobic groups in thermoreversible gels can be used to fine-tune the volume phase transition temperature [12-13]. Similarly, it has been shown that hydrophilic comonomers increase the volume transition temperature, while hydrophobic comonomers decrease the volume transition temperature of thermoreversible gels [14-15].

A series of temperature-sensitive copolymeric gels was prepared by the redox polymerization of AAm, HEMA and NIPAAm. Hydrogels were obtained by changing the NIPAAm/AAm and NIPAAm/HEMA initial mole ratio and the total monomer concentration. The hydrogels thus prepared were characterized in terms of swelling-deswelling degree and swell-deswelling kinetics [16].

This article describes the preparation of hydrophilic copolymers from N-isopropylacrylamide (NIPAAm) and 2-hydroxyethylacrylate (2-HEA). Characterization of the copolymers was studied via DSC, TGA, GPC and SEM.

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Materials and Methods

Materials

N-Isopropylacrylamide (NIPAM) was purchased from TCI (Tokyo, Japan) and purified by recrystallization from n-hexane. 2-hydroxyethyl acrylate (2-HEA) and Ammonium peroxodisulfate (APS) were purchased from Sigma (USA). Ethanol was purchased from Altey, Kazakhstan.

Synthesis and Characterization of Copolymers

Hydrophilic copolymer of NIPAAm with 2-HEA with various ratios of hydrophilic chains (M1 = 70:30, M2 = 90:10 respectively) were synthesized by solution polymerization using APS as an initiator and ethanol/water (v/v: 1/1) as a solvent at 60 °C. The copolymers synthesized were reprecipitated several times from ethanol to diethyl ether and dried in vacuum desiccators at 30 °C until a constant weight was achieved. The polymer was prepared in the presence or absence of sodium hydroxide solution.

Instrumentation

Thermogravimetric analyzer (TGA) was recorded on TGA/SDTA851^e, METTLER TOLEDO. Glass transition temperature of samples were measured using differential scanning calorimetry (DSC), on a NETZSCH DSC200 PC, using aluminum crimped pans under N₂ flow at 20 mL min⁻¹. The measurements were carried out between -50 °C and 200 °C at a heating rate of 10 °C Min⁻¹. Molecular weights of the hydrophilic copolymers were obtained from gel permeation chromatography (Waters Co., USA) equipped with a series of 1 Styragel® columns (10⁴, 10⁵, 10⁶ Å pore sizes), HPLC pump (Waters 501), RI detector (Waters 410),

and integrator at 40 °C. Polystyrene standards and universal calibration were adapted to reduce measuring error. Sampling of the copolymers was carried out five times during the chain extension step to investigate the effects of molecular weights. Tetrahydrofuran was used as an eluent at 1.0 mL min⁻¹ flow rate and 1.0x10³ Pa pump pressure. The microstructure of the hydrophilic copolymers was investigated by scanning electron microscopy (SEM) was recorded on Carl-Zeiss SMT, Oberkochen

Results and Discussion

Synthesis of NIPAAm-co-2-HEA copolymer

Copolymer of NIPAAm with 2-HEA was prepared by free radical copolymerization of the monomers in 70: 30 and 90: 10 ratios in presence of APS as initiator at 60 °C for 3 hr.

Gel Permeation Chromatography (GPC)

The molecular weights of the copolymers of NIPAAm with 2-HEA with different compositions were determined by GPC. The results of effect of the different ratios of the monomers on Mw of the copolymer are shown in Table 1. The data obtained showed that the molecular weight increased with increasing the ratio of NIPAAm from 70 to 90 % in the copolymer. As increase in the ratio of NIPAAm would facilitate the formation of primary radicals and leading to an increase in molecular weight [17-18]. It is noted that the small value of polydispersity indexes (Mw/Mn) (1.3) demonstrated that the copolymers had narrow molecular weight distribution. The unimodal and fairly narrow distribution of molecular weight indicates that the copolymer was successfully prepared [19].

Table 1 - Molecular characterization of copolymers

Polymer	Mn ^a	Mw ^b	PDI ^c	Peak	Tg ^d , °C	PDT _{max} ^e , °C
M1	23641	30423	1.3	Narrow	103.45	189 - 898
M2	32832	43437	1.3	Narrow	125.22	215 - 896

a Number average molecular weight.

b Weight average molecular weight.

c Polydispersity index (Mw/Mn).

d Determined from DSC curves.

E Determine from TGA.

Differential Scanning Calorimetry (DSC)

Glass transition temperature (T_g) which is an important property for a polymer was determined by Differential Scanning Calorimetry (DSC). A

heating program is used for the measurements (-50 to 200°C) with heating rate 20 K/min under N₂ atmosphere. Values of T_g obtained for the copolymers, as shown in the Table 2 and Figure 2. As it is known, the glass transition temperature

depends on number of factors which affect rotation of chain links, mobility, and chain-chain interaction. These factors include molecular structure, molar mass, degree of branching, nature of end groups, and interactions like hydrogen bonding within the polymer structure. The studied copolymers did not show any melting in the observed temperature regime. However, it can be

seen that the T_g of the copolymer moves toward the higher temperature as the ratio of NIPAAm in the copolymer increases. Furthermore, the T_g values are affected by the molecular weight of the copolymer as shown in Table 2. As expected, while the molecular weight of the copolymers is decreased, the glass transition temperature shifts downward, similar result [20].

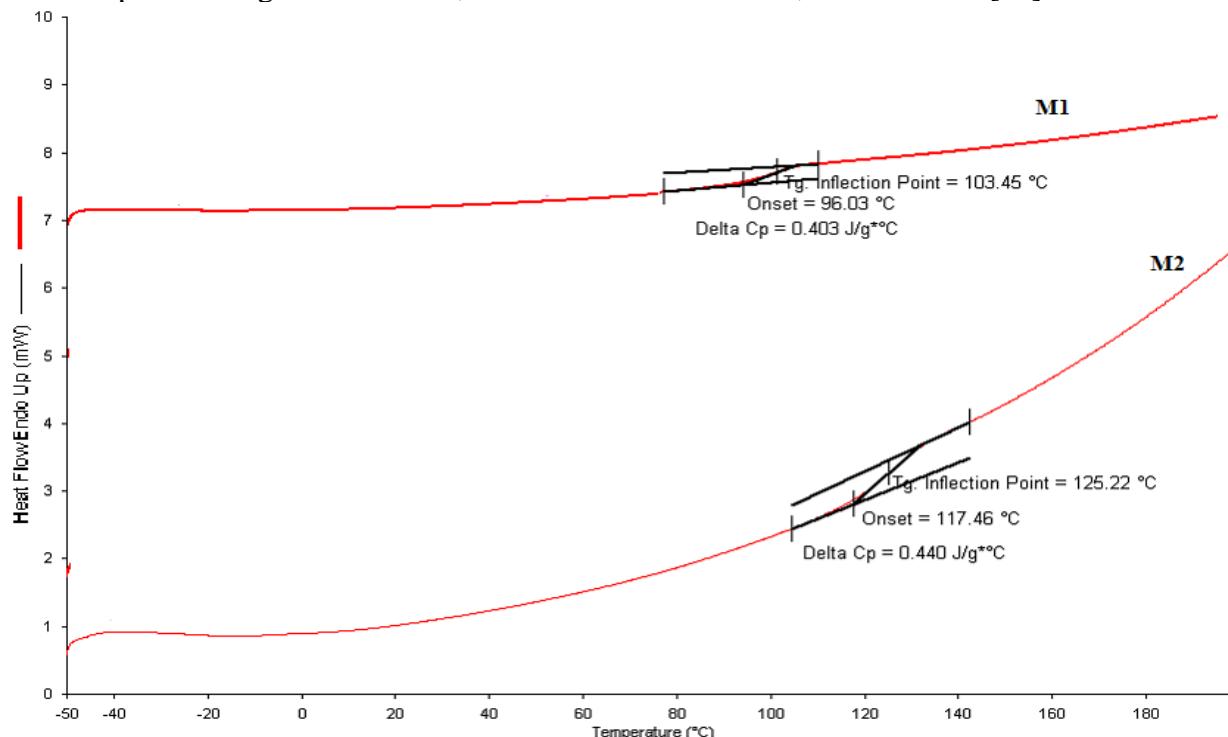


Figure 1 - DSC curves of NIPAAm-co-2-HEA

Thermogravimetric Analyses (TGA)

Thermal stability of copolymers (M1 & M2) was studied by thermal gravimetric analysis (TGA) in a temperature program 50-850 °C with heating rate 10 K/min⁻¹ and using N₂ gas as inert atmosphere. The typical TGA thermogram for M1 and M2 is given in Figure 3, illustrating the determination of the characteristic temperatures. The TGA thermograms show there were two decomposition stages. The weight loss of 14.3 wt.% between 30 and 189 °C for M1 and 10.2 wt.% between 30 and 215 °C for M2 are attributed to the desorption of physically adsorbed water and organic molecules such as residual and impurities from solvents and moisture. TGA showed that copolymers have relatively good thermal stability up to 189 °C then the degradation starts till maximum at about 300 °C. Of course the temperature for maximum degradation depends on the polymer structure whether the polymer is linear or hyperbranched

[21-22]. It was noticed that M2 polymer higher thermal stability than M1 polymer. The second weight loss was 81.1 wt.% for M1 and 86.1 wt.% for M2. This weight loss could be attributed to the exothermic decomposition of the N group and decomposition of other parts of 2-HEA. The rate of degradation in the second step is slightly faster than that in the other stages and is considered as rate determining step. The maximum polymer degradation temperature (PDT_{max}) corresponds to the temperature at which the maximum rate of weight loss occurred and appeared in the range 189 - 898°C for the prepared M1 and 215 - 896 °C for M2. The PDT_{max} increases as the ratio of NIPAAm within copolymer structure increases.

Scanning Electron Microscopy (SEM)

The surface morphology of the polymers containing different of NIPAAm and 2-HEA was observed by scanning electron microscopy (SEM) and is shown in Figure 4. It is clear that the

surface morphologies of M1 with 30 % of 2-HEA are compact, smooth and dense, while the surface of M2 has a pronounced porous structure which is also noticeable to a lesser ratio of 2-HEA in the microstructure of copolymer. As increase the ratio of NIMP in the copolymer has induced a change in polymer structure, such that more water

molecules can diffuse into it and the polymer swells more. It is also notice that surface of M2 shows a much open surface which more water molecules can penetrate through the surface. Therefore more water absorption can be observed with M2 more than M1.

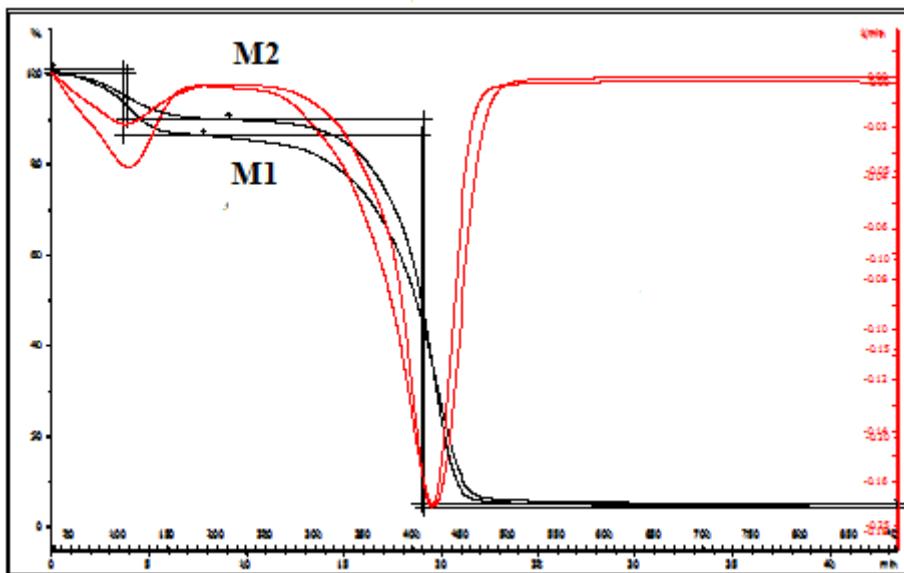


Figure 2 - TGA curves of NIPAAm-co-2-HEA.

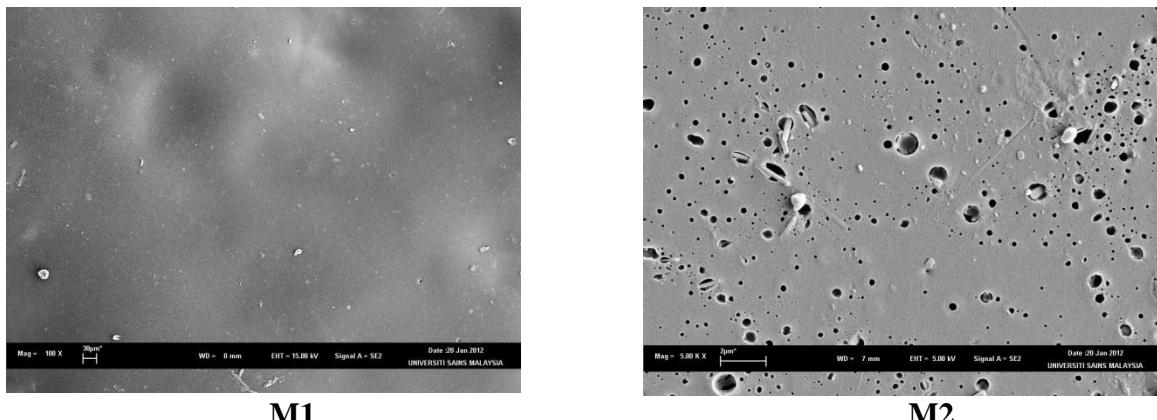


Figure 3 - SEM of the NIPAAm-co-2-HEA.

Conclusions

Copolymerization of NIPAAm with 2-HEA has been carried out successfully in an aqueous homogeneous solution. T_g of the copolymer increases with increasing of the ratio of NIPAAm in the copolymer. Furthermore, it was found that T_g of the copolymer increases with increasing molecular weight of the copolymer. TGA showed that copolymers have good thermal stability, especially with increasing NIPAAm. The scanning electron microscopy of NIPAAm-co-2-HEA shows that an increase the ratio of

NIPAAm in the copolymer has induced a change in polymer structure.

Acknowledgements: We would like to express our great thanks to the Universiti Sains Malaysia for financial support (RU grant No.1001/PKIMIA/814111).

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Received 20 April 2012