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Facile preparation of PNIPAM gel with improved deswelling kinetics by using 1-dodecanethiol as chain transfer agent

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Abstract A poly(*N*-isopropylacrylamide) (PNIPAM) gel was synthesized by using 1-dodecanethiol (DDT) as chain transfer agent. This PNIPAM gel exhibits higher swelling ratio at low temperature and much faster deswelling rate than conventional gel, which could be attributed to the presence of dangling chains in the gel mainly caused by DDT.

Keywords Chain transfer · Hyperbranched · Graft · Hydrogels

Introduction

P(*N*-isopropylacrylamide) (PNIPAM) gels show interesting phase behavior in aqueous solution. Phase transition happens as the temperature is increased above its lower critical solution temperature (LCST) around 32 °C [1]. Due to the unique properties, PNIPAM gel has been utilized in many fields. But conventional PNIPAM gels are limited by their slow swelling and deswelling rates [2], and some successful strategies have been worked out to enhance the response rates.

One approach was to synthesize PNIPAM gels [3–5] with comb-type grafted chains. And the formation of a porous structure has been shown to effectively enhance the deswelling rate of PNIPAM gels [6–8]. Some other strategies were used to improve the response rate, such as composite gels with microgels or nanoparticles [9], using mixed solvent [10], utilizing micelle-forming ability of surfactant [11] and adding RAFT reagent [12]. These reports have successfully obtained PNIPAM gels with fast shrinking rate. The goal of this study was to supply a simple and new method to prepare gels with fast deswelling kinetics by using thiol as chain transfer reagent during the polymerization reaction.

Experimental

Materials

1-dodecanethiol (DDT, >90%) was diluted by 1,4-dioxane to 1% (*v*/*v*), *N*-isopropylacrylamide (NIPAM, from Acros, 99%), 2,2′-azobis(isobutryonitrile) (AIBN), *N*,*N*-methylenebisacylamide(BIS), 1,4-dioxane and all other reagents were used as received.

Preparation of PNIPAM gel adding DDT (designated as DDT gel)

To synthesize DDT gel, a mixture of DDT solution (1.3 ml), NIPAM (0.4 g), BIS (13.3 mg), AIBN (8 mg) and 1,4-dioxane (2 g) were put into a glass tube, degassed and sealed under nitrogen. The polymerization was conducted at 60 °C. To remove unreacted monomer and linear polymers, the obtained gel was immersed in 1,4-dioxane for several days at room temperature, and 1,4-dioxane was replaced every day. Then it was immersed in deionized water to remove the solvent. The dry gel was obtained by thorough drying under vacuum at 50 °C for 24 h. For comparison, conventional gel (designated as CG) was synthesized with NIPAM (0.4 g), BIS (13.3 mg) and AIBN (8 mg) at 60 °C.

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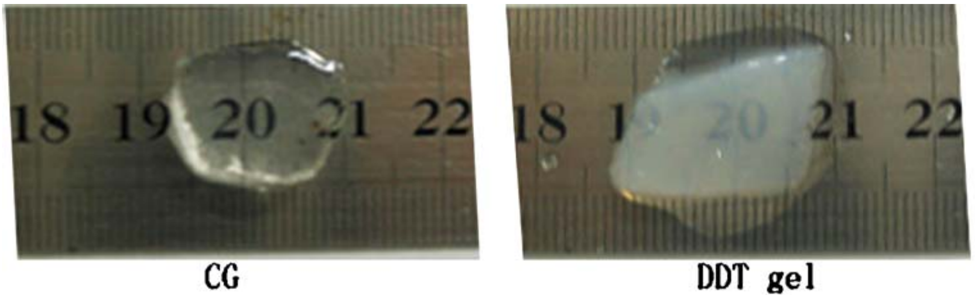
Fig. 1 Photo pictures (recorded by Canon PowerShot G1) of CG and DDT gels after immersed in water at room temperature for 10 h



Measurement of gelation time

Gelation time is defined as the time to reach the point where the solution can’t flow in the container and it was determined macroscopically by a tilting method (tilting the container and observing whether the sample moves or not) [13].

Swelling equilibria for the gels

The swelling ratio (W_{H2O}/Wp) is defined as the weight of absorbed water (W_{H2O}) per weight of dried gel (Wp). Equilibrium swelling weights for the gels in water at various temperatures were measured gravimetrically after wiping excess water from the gel surface using filter paper. The gels were cut into disks (15 mm in diameter and 3 mm in thickness) and equilibrated at higher temperature (50 °C). After determining the gel mass, the temperature was lowered, and the gels were equilibrated to reach swollen conditions at this temperature. This process was repeated until the temperature reached 20 °C.

Swelling and deswelling kinetics of the gels

Swelling and deswelling kinetics are defined as temporal weight changes for the gels. For the kinetics studies, disk-shaped PNIPAM gels were first equilibrated in deionized water at predetermined temperatures (20 °C). And the gels were weighted at each given time. After confirming no further changes in swelling ratios over time, the gels were quickly transferred into water at 40 °C. At specific time points, these gels were removed from the water and weighed. The weight data were converted to the normalized swelling which indicated the volume changes of gels between equilibrium swollen (100%) and equilibrium shrunken (0%) states, which was calculated from the ratio of the wet weight of the gel at time t (Wt) to the equilibrium swollen weight (Wt) of the gel.

Results and discussion

The gels are transparent and clear in 1,4-dioxane. But the appearance is different between CG and DDT gel after the gels were immersed in water after a period of time. CG was transparent and clear but DDT gel appeared turbid after immersed in deionized water (see Fig. 1). It is known that the turbidity of a gel is a direct result of light scattered from the spatial inhomogeneities of its refractive index [14]. This might indicate somewhat inhomogeneous structure for DDT gel compared with CG.

The structural homogeneity or heterogeneity would affect the swelling property of the gels. The swelling property of the gels was investigated. Equilibrium swelling ratios for the gels in deionized water are shown in Fig. 2. At low temperature, DDT gel indicated a higher swelling ratio than CG. Figure 3 shows the swelling kinetics of the gels. As can be seen, it took over 10 hours to reach their equilibrium state for both of the gels. The similar swelling kinetics between two types of gels also suggested that DDT was not used as pore-forming agent during the cross-linking reaction. It is known that the introduction of pore-forming agent would lead to porous structure and accelerate swelling kinetics (reach equilibrium state in 10 h) [6–8]. Figure 4 shows the deswelling kinetics of the gels. CG shrank slowly and would take long time to reach its equilibrium state due to the skin layer formation during the deswelling process [2]. Compared with the CG, DDT gel showed fast shrinking kinetics. In previous reports, comb-type grafted PNIPAM gels were synthesized by using thiol

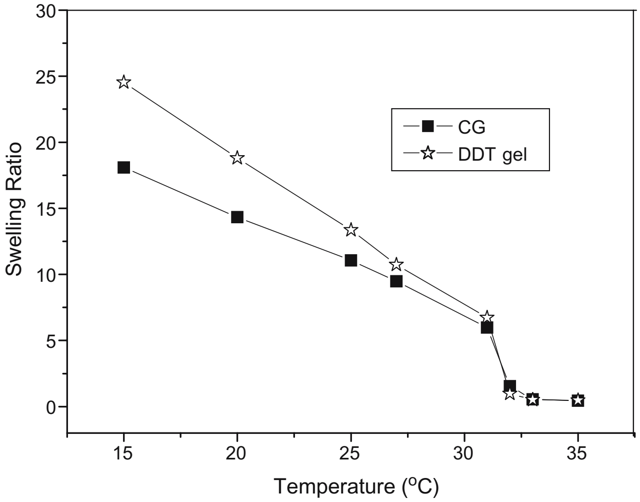


Fig. 2 Equilibrium swelling ratio for the gels as a function of temperature

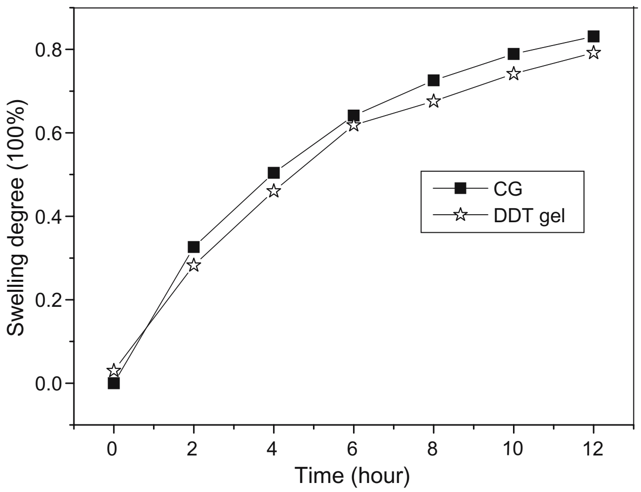


Fig. 3 Swelling kinetics of the gels at 15 °C from dried gel state

as a starting material through three steps [2–4], and PNIPAM gels with improved shrinking rate was prepared using RAFT reagent by living free radical polymerization mechanism [12]. Comparing with these methods, this report supplies a simple method to synthesize rapid responsive gels by conventional free radical polymerization.

We attempted to explain the different swelling behavior between DDT gel and CG disclosed above. DDT gel had the same feed composition and reaction conditions with CG except the presence of DDT. So the different swelling behavior between DDT gel and CG could be ascribed to the presence of DDT. There are two main effects brought by chain transfer agent. One is to introduce hydrophobic moiety into the gel. It was reported that the generated surface skin layer would be denser and thicker, and the diffusion rate of water is blocked greatly as the hydrophobic moiety in the network increased [15]. The other is retardation effect to the cross-linking reaction, which could be observed by the gelation time of two gels (about 1 h for CG and about 5 h for DDT gel). It has reported that the hyperbranched structure could be obtained by limiting the rate of chain growth through degradation reaction [16], chain transfer reaction [17] or living polymerization mechanism [18, 19]. The reaction would produce branched or hyperbranched structure during the time before gelation according to these reports. Notably, the vinyl-type network polymers formed via highly branched prepolymer have abundant dangling chains as their characteristic feature because terminal parts of prepolymer chain would be dangling chains [20, 21]. So some of the branched chains will remain in the network structure and lead to DDT gel with a number of dangling chains when gelation occurs. But for CG system, the reaction is so quick and leads to the generation of microgels even at relatively low conversions. At a critical conversion, these microgels will be tied up and form gel. The different progression of gelation between them could lead to different intrinsic structure of gels (see Fig. 5).

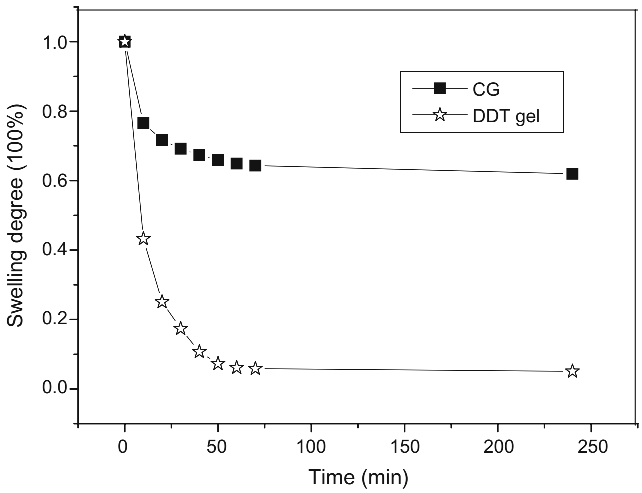


Fig. 4 Deswelling kinetics of the gels after T-jump from 15 to 40 °C

The large number of dangling chain could lead to phase separation of network because dangling chains are structurally separated from the backbone cross-linked network [2, 22–24], which could lead to the turbid appearance of DDT gel. And the accelerated shrinking kinetics of DDT gel could also be attributed to the presence of dangling chains. But the presence of dangling chains couldn't improve swelling kinetics of DDT gel compared with CG because the swelling kinetics of the grafted-type gel was governed by polymer network diffusion [3]. According to the reports before, the dangling chains in the network polymers could increase the swelling ratio of gel [2–4]. Hence, it was reasonable to believe that the turbid appearance and swelling behavior of DDT gel are evidences of the existence of abundant dangling chains.

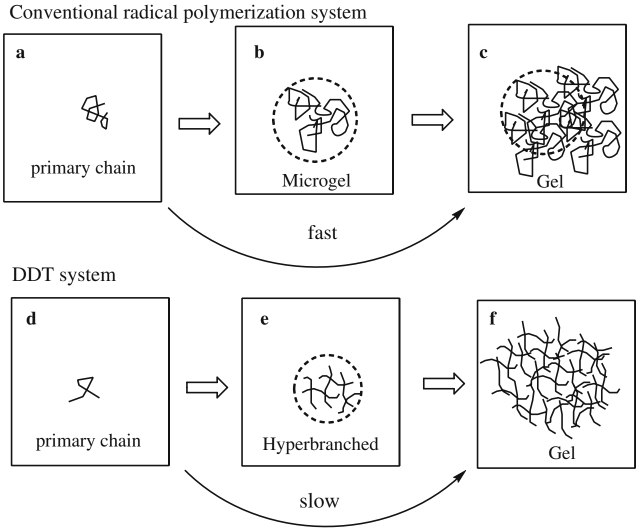


Fig. 5 Schematic presentations of the progression of gelation and different intrinsic structure of gels for (**a**–**c**) conventional radical polymerization system (**d**–**e**) DDT system

Conclusions

In this paper, PNIPAM gel is prepared using DDT as chain transfer reagent. It was found that the presence of DDT could lead to fast shrinking kinetics of the gel. It supplies a simple and new method to prepare rapid responsive gels, which is important for gels applications in some aspects.

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