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A Facile Method Synthesizing Hydrogel Using Hybranched Polyether Amine (hPEA) as Coinitiator and Crosslinker

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Inhomogeneities are responsible for the poor mechanical properties of hydrogels. To achieve good performances, this study reports here the design and synthesis of hydrogels with negligible defects named as initiator-crosslinker (IC) hydrogel where hybranched polyether amine (hPEA) performs as both coinitiator and crosslinker. The initiation mechanism used in this system is classical but the crosslinking mechanism is different from the conventional hydrogels. A series of hydrogels with various mechanical properties are synthesized by varying the content ratio of coinitiator hPEA and initiator ammonium persulfate. Tensile tests demonstrated that IC hydrogels had excellent mechanical properties elongation at break up to 3000%. The toughness calculated from stress–strain curve highly depended on the content of hPEA and the largest one is about 4.02 MJ m^{-3} which is much higher than the conventional hydrogels (0.03 MJ m^{-3}). Rheological and swelling results also indicated the obtained hydrogels are indeed crosslinked by both chemical bond and physical interaction.

1. Introduction

Hydrogels are soft and wet materials in which aqueous solution exists as a solvent, could absorb a large amount of water and swell extensively, without dissolution or loss of structural integrity. Taking advantage of their high water content and structure stability, hydrogels have been widely applied in many fields, such as sensors, drug delivers, water treatment, and biological supports, etc.[1–4] Although new applications are being researched and developed, low mechanical strength of hydrogels resulting from micro-inhomogeneities retards the progress. The inhomogeneities of the hydrogels are usually categorized into spatial, topological, and connectivity inhomogeneities.[5–8] When hydrogels sustain stress, inhomogeneities cannot work cooperatively to dissipate energy effectively. Therefore, breakages usually start from the weakest links and fractures come up ultimately.

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Various types of hydrogels with distinctive network have been developed to strengthen hydrogels, including nanocomposite (NC) hydrogel,[9–14] double-network (DN) hydrogel,[15–20] topological hydrogel,[21–26] interpenetrating polymer network (IPN) hydrogel,[27–33] tetra-arms hydrogel,[34–38] etc. For instance, the incorporation of nanoparticles can significantly strengthen hydrogels and the preparation method is convenient and efficient, but the mechanical properties of NC hydrogel highly depend on the compatibility of polymer and nanoparticles. DN hydrogels, first reported by Gong et al.,[16] have attracted much attention in recent years, due to its strategy of enhancing the energy dissipation during crack propagation. However, DN hydrogels are permanently damaged after deformation and mechanical properties dramatically fall down when second load. In addition, methods used to prepare DN hydrogels are time-consuming and the multistep process is tedious leading to the inaccuracy of the molar ratio of two networks. Although these efforts have shown effective reinforcement toward hydrogels with different degrees, there is still an urgent facile method to synthesize hydrogels with an ideally homogeneous network structure which is expected to have outstanding mechanical properties under mild conditions.

To obtain an ideally homogeneous network, the crosslinks should be distributed uniformly. It means that gelation by traditional organic crosslinking agents or macromonomers and physical crosslinking are unsuitable. As we all know, random crosslinks usually originate from these crosslinking mechanisms. Recently, Liu et al.[39] prepared graphene oxide (GO) composite hydrogel with excellent mechanical properties using graphene peroxide (GPO) via the radiation-induced peroxidation of GO as initiator and crosslinker. It seems that the coupling termination employed in this work is a promising way to form homogeneous crosslinks. However, the γ-rays used in the preparation of GPO may limit its wide application. Carlsson et al.[40] pointed out *N, N*-dimethylacrylamide (DMA) could be used to prepare hydrogels due to its self-crosslinking process. Cipriano et al.[41] and Hu et al.[42] also used the same monomer DMA as a composition to synthesize hydrogel with different mechanical properties. It is worth noting that the initiator potassium persulfate/ammonium persulfate can react with tertiary amine under ambient conditions. But to the knowledge of the authors, there is no other monomers containing tertiary amine reported preparing hydrogel so far.

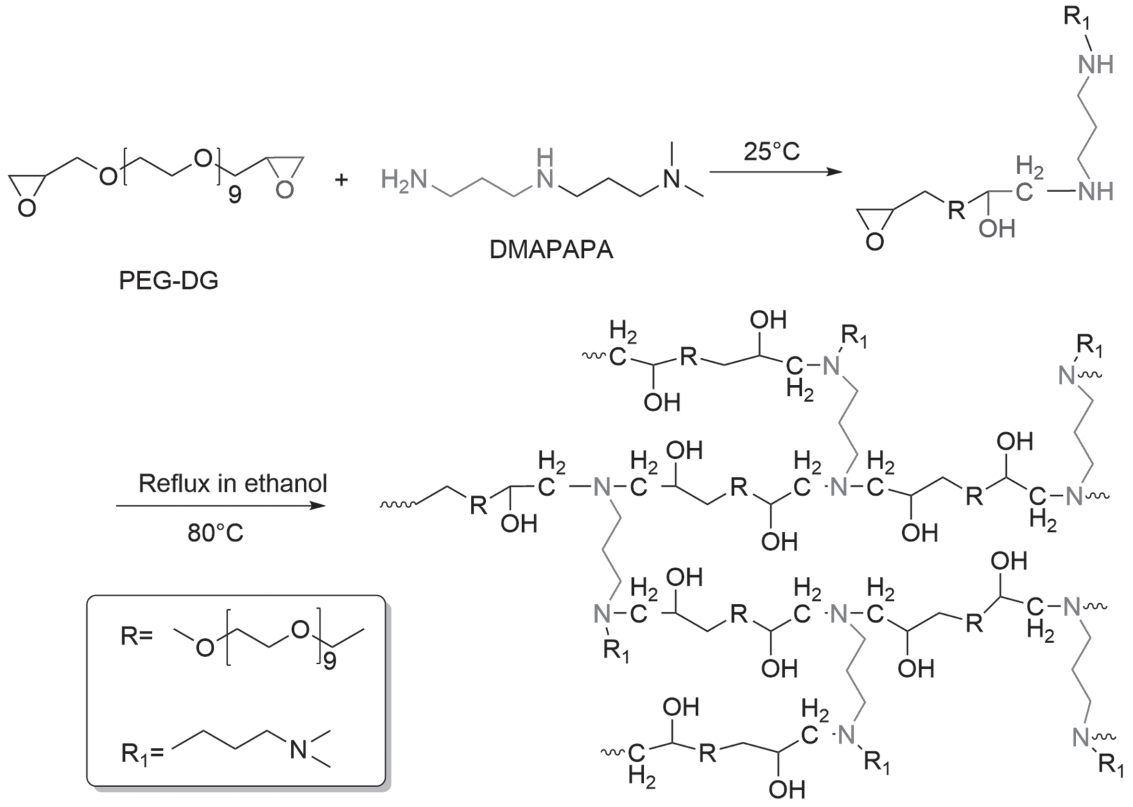
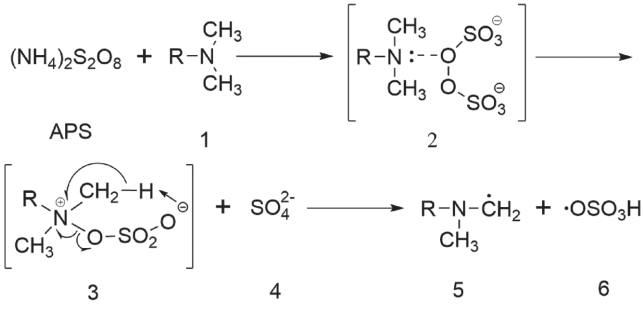


Figure 1. The synthetic mechanism of hPEA.

Inspired by these articles, a facile and universal method is proposed that initiating the monomer growing from a center and then crosslinks are formed by the coupling termination. In this way, hydrogels with homogeneous network resulted from the statistic equal distances between the two centers are possibly obtained. Compared with the GPO initiation mechanism, the redox system of peroxydisulfate and water soluble aliphatic amine is usually applied to initiate the polymerization of hydrogel via a contact charge transfer complex and a cyclic transition state which is still the most widely used initiator today.[43,44] By means of this redox initiation mechanism, a competent molecule which has some coinitiate sites as the growing center is required when applied to the preparation of hydrogels. Recently, our group has done some attempts to prepare hydrogel using linear polyether amine (PEA) on the basis of aforementioned method.[45,46] The obtained hydrogels showed good mechanical properties and convinced us the feasibility of the method. In addition, hybranched polyether amine (hPEA) also synthesized by our group have been studied detailed in our previous works.[47–52] In contrast to PEA, the hPEA exhibited 3D globular architecture, high functionality, and abundant coinitiate sites which is more suitable as coinitiator and crosslinker for hydrogel.

In this article, we focus on hPEA as coinitiator and crosslinker to prepare hydrogel which could be noted as initiator-crosslinker (IC) hydrogel. This is a facile and universal method with redox system as initiation mechanism to prepare hydrogels, the hydrogel network is anticipated uniform with negligible inhomogeneities.

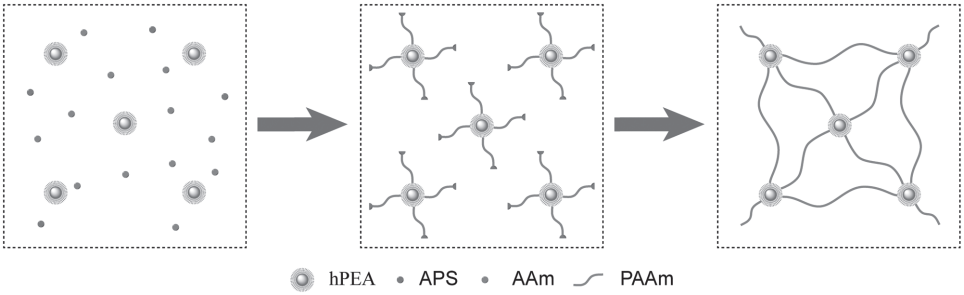


Scheme 1. The initiation mechanism of persulfate/tertiary amine redox system, hPEA was represented tertiary amine because of its structure complexity.

2. Experimental Section

2.1. Materials

Poly(ethylene glycol) diglycidyl ether (PEG-DG, M_n = 500 g mol^{-1}), *N,N*-dimethyldipropylenetriamin (DMAPAPA,99%) were purchased from Sigma-Aldrich, the monomer Acrylamide (AAm), and initiator ammonium peroxydisulfate (APS), as well as solvent ethanol were of analytical pure reagent (A.R.) grade supplied by Sinopharm Chemical. Deionized water was used for the preparation of the hydrogels and any further steps. All chemicals were used without any further purified.



Scheme 2. Schematic illustration of preparation of hydrogels. PAAm are first grafted from hPEA and then crosslinked by coupling termination to form a network.

2.2. Preparation of hPEA

hPEA was synthesized by the condensation polymerization between epoxy and amino groups in PEG-DG and DMAPAPA, respectively, according to the previous report.[53] The polymerization was conducted in a 100 mL two-necked flask equipped with a reflux condenser and a stirrer. PEG-DG and DMAPAPA were added into the flask, the molar ratio of two monomers was 1.5. Then ethanol was poured into the flask to dissolve the monomers. The total monomer concentration was kept at 0.5 g mL^{-1}. When the solution mixed uniformity, the reaction was first stirred for 24 h at room temperature and then refluxed at 80 °C for another 24 h. Finally, the reaction solution was poured into 10 times volume of *n*-hexane and washed with *n*-hexane three times to remove unreacted monomers and solvent. The raw product was dried in an oven at 60 °C until the weight was constant. Yield of hPEA was about 98%.

2.3. Preparation of hPEA-PAAm Hydrogels

9 g of AAm and calculated weight of hPEA were dissolved in deionized water, the content of water was kept as 70%. The aqueous was stirred vigorous and bubbled with pure nitrogen for 10 min in a flask. After specified APS aqueous was added, the pregel solution was first degassed for 1–2 min under reduced pressure by a vacuum pump and then transferred to glass molds made by placing a silicone (2 mm thickness) between two flat glass plates. The gelation was performed at ambient temperature for 48 h.

Table 1. The synthesis recipe of the IC hydrogel.

Sample[a)]	AAm [g]	APS content [wt%]	hPEA content [wt%]
$I_{0.05}$–$C_{0.04}$	9	0.05	0.04
$I_{0.05}$–$C_{0.12}$	9	0.05	0.12
$I_{0.05}$–$C_{0.20}$	9	0.05	0.20
$I_{0.05}$–$C_{0.28}$	9	0.05	0.28
$I_{0.05}$–$C_{0.36}$	9	0.05	0.36
$I_{0.10}$–$C_{0.40}$	9	0.10	0.40
$I_{0.15}$–$C_{0.60}$	9	0.15	0.60
$I_{0.25}$–$C_{1.00}$	9	0.25	1.00

[a)]For convenience, different composition of IC hydrogels were denoted as I_m–C_n, where *m* and *n* were the mass percentage of Initiator APS and coinitiator hPEA relative to Aam, respectively.

2.4. Tensile Testing

The mechanical properties of prepared hydrogels were determined with an Instron 4465 electronic universal testing machine (Instron Corporation, MA, USA) at a crosshead speed of 100 mm min^{-1}. Dumbbell-shaped specimens were cut according to GB/T528 (overall length: 50 mm; inner width: 4 mm). The tensile stress (σ_t) was calculated according to the formula: σ_t = load/S (S represented the cross-sectional area of specimens gauge part). The tensile strain (ε_t) was defined as the change in the length relative to the initial gauge length, and the breaking tensile strain (ε_b) is the strain at which the specimen breaks. At least five specimens per experimental point were tested in all mechanical measurements to obtain reliable values. Notably, to avoid the evaporation of water influencing the reliability of data during the tests, the hydrogels specimens were coated with a thin layer of silicon oil.

2.5. Rheological Property Measurements

Rheological tests were conducted by a TA ARES-G2 rheometer using parallel plates of diameter 20 mm at room temperature. The distance between the two parallel plates was set at 1 mm. The frequency sweep was performed over the frequency range of 0.1–100 rad s^{-1} at a fixed strain of 0.5%.

2.6. Scanning Electron Microscopy (SEM)

To characterize the structure of the obtained gels, SEM characterization was operated on Nova NanoSEM 450. The gel samples were immersed into liquid nitrogen to get brittle fracture surface, followed by freeze-dried and coated with a thin layer of gold in order to avoid charging effects.

3. Results and Discussion

First, hPEA was synthesized through nucleophilic addition/ring-opening reaction of epoxy and amine monomer which

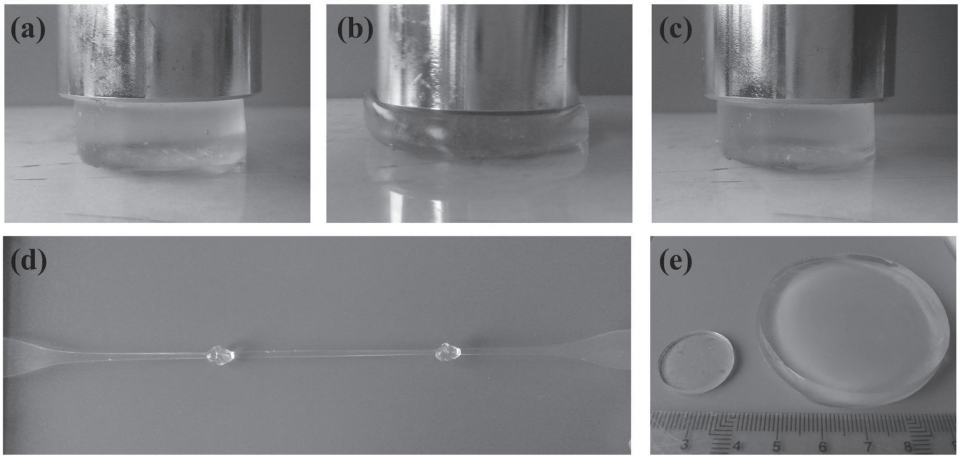


Figure 2. The mechanical properties of IC hydrogel: a) before compressed the hydrogel, b) compressed hydrogel, c) release the pressure. d) Knotted hydrogel along with elongation. e) Left one is prepared hydrogel plate, the right one is swollen state.

possessed characterization of "click-chemistry" (**Figure 1**). The process of synthesis was simple and "green" without small molecules produced. ^{1}H-NMR and GPC ($M_n = 4.3 \times 10^4$ g mol^{-1}) characterizations confirmed the successful synthesis of hPEA (Figures S1 and S2, Supporting Information).

The initiation mechanism of the redox system used in this work is shown in **Scheme 1**, the unbonded pair electron of nitrogen atom attacked the peroxide bond of APS to form the unstable intermediate **3** and a sulfate (SO_4^{2-}). The O^- in the intermediate **3** abstracted the proton from α-carbon atoms. As a result, two types of free radical **5** and **6** which were responsible for monomer polymerization were produced due to the decomposition of intermediate **3**.

In addition, APS itself was also decomposed quickly into peroxy radical like radical **6** if temperature is over 70 °C. In this regard, there were only two types of radical in the initiation system. One is radical **5** pendent on hPEA and the other is not. The radical **5** initiated the monomer acrylamide (AAm) to grow from hPEA as illustrated in **Scheme 2**. Ultimately, crosslinks were formed as a result of the coupling termination between two propagating radicals suspended in hPEA. Considering propagation rate was a constant in the polymerization, the length of the chain between two hPEA centers was statistical equal. Therefore, hydrogels with negligible defects were realized. The formulation of the component for the preparation of hydrogels was summarized in **Table 1**.

The as-prepared hydrogels had good mechanical performances. As shown in **Figure 2**a–c, when the object was compressed under multi-kg loads, it immediately sprang back to its original shape upon removal of the load. What is more, the gels were so strong and extensible that they could be tied into knots along with stretched dozens of times without any visible cracks or breaks (Figure 2d). After immersing in urea solution (5 mol L^{-1}) for 7 d, the hydrogel still kept its disk-like shape, absorbing tens of hundreds percentage weight of water compared to their dried state (Figure 2e).

To quantify the mechanical properties of obtained hydrogels, a series of hydrogels with different hPEA content and 0.05 wt% APS were prepared and tested. In **Figure 3**a, with the increase of hPEA content, the elongation at break first increased to a maximum about 3000%, and then decreased to about 1700%.

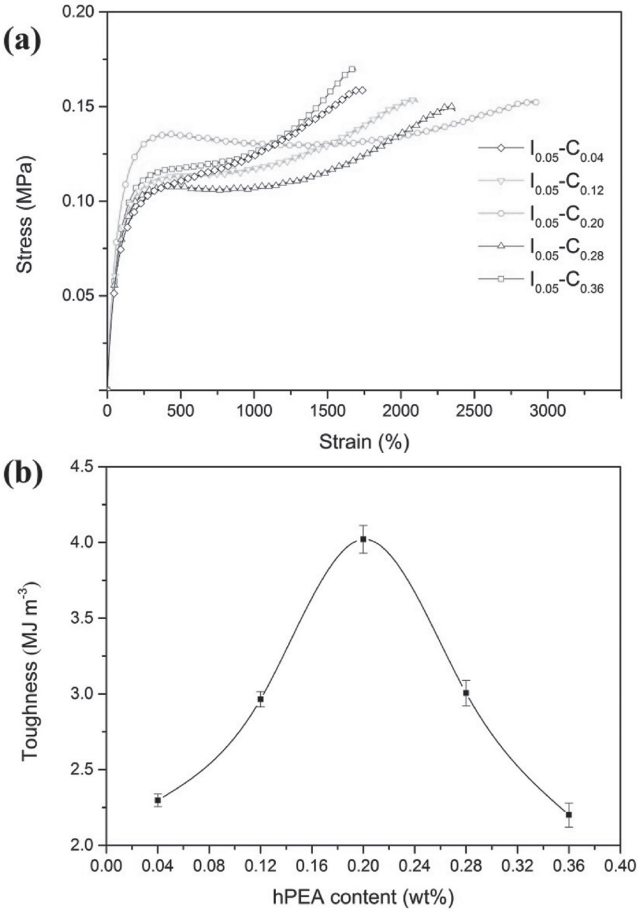


Figure 3. a) Stress–strain curves of IC hydrogels with different contents of hPEA. b) The toughness of IC hydrogels with different contents of hPEA. APS content is a constant 0.05 wt%. The error bars correspond to the standard deviation obtained from at least five samples.

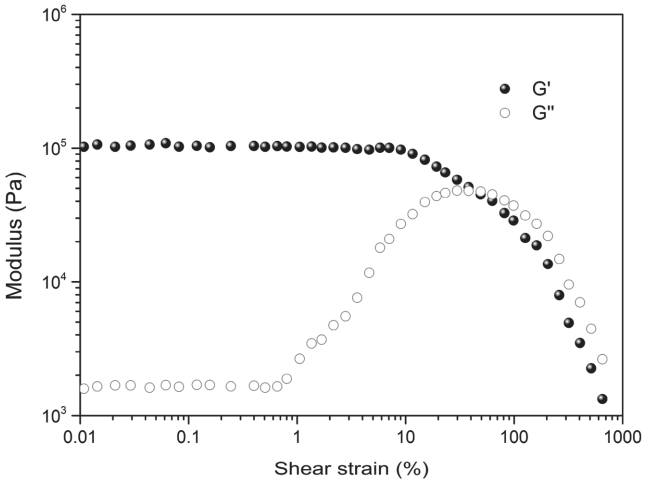


Figure 4. Typical amplitude sweeps (frequency 10 Hz) of $I_{0.05}$–$C_{0.20}$ hydrogel.

The relation between hPEA content and toughness was shown in Figure 3b. Notably, different hPEA content had significant influences on the toughness of the obtained hydrogels. With the hPEA content increasing, the toughness first increased to a maximum value about 4.02 MJ m^{-3} when hPEA was about 0.2 wt%, then gradually decreased to 2.2 MJ m^{-3} with 0.36 wt% hPEA. To illuminate this case, probable explanations were proposed as follows: (1) while hPEA content was below 0.2 wt%, physical entanglements as well as inter- and intramolecular hydrogen bonds between hPEA and PAAm mainly account for strengthening the hydrogel, because of radical **6** were more than radical **5** both of which were responsible for initiating the monomer to form a chain. This was confirmed when low hPEA content hydrogel was immersed in urea solution, most part of the gel was dissolved after 72 h and the residue could not disappear even after 7 d. In addition, with the increase of hPEA content, the residue also increased. (2) When hPEA content was about 0.2 wt%, the gel could remain their initial shape for a long time in urea solution. This phenomenon indicated that crosslink density reached up to a certain degree. Certainly, the free chains initiated by radical **6** also existed in gel, but under this condition, they were trapped by the network like Semi-IPN network and could not be released even with the help of urea. Rheology experiments which were discussed later affirmed the existence of free chains. (3) With more hPEA was added, the network became heterogeneous due to the dispersity of trigger position get bigger if no corresponding APS was added.

Oscillatory shear rheological measurements were conducted. Strain amplitude sweeps (frequency 10 Hz) indicated that the gel exhibited a clear plateau of storage (G′) and loss (G″) modulus (**Figure 4**). The plateau is usually referred to as the linear viscoelastic (LVE) region. In addition, the high value of G′/G″ is indicative of the crosslinked polymer networks. The end of the LVE region represents the shear strain that the gel can sustain until the range of inelastic deformation comes up.[54]

To verify the material synthesized was indeed a gel and not a viscoelastic polymer solution, we turned to frequency sweeps (strain amplitude 0.5%). In **Figure 5**, a series of samples synthesized by various content of hPEA and APS were tested.

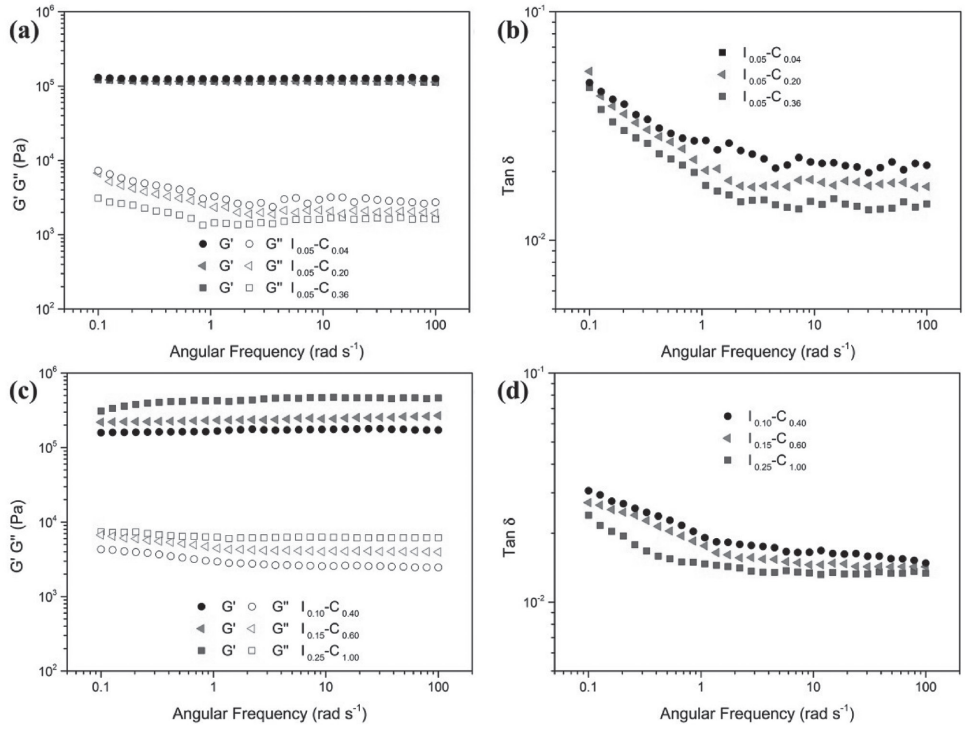


Figure 5. a,c) Rheological behavior storage modulus G′ and loss modulus G″ as a function of angular frequency with different contents of APS and hPEA; b,d) corresponding loss tangent tan δ calculated from the test results.

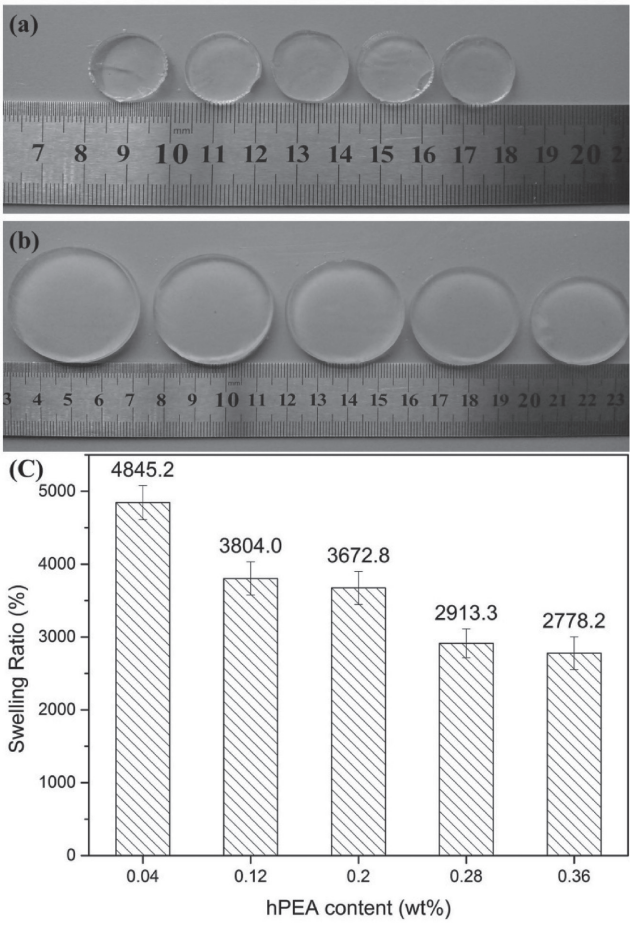


Figure 6. Swelling test of the prepared hydrogel: a) before immerse water; b) the swollen state of the hydrogel; c) the relation between swelling ratio and hPEA content.

The storage modulus (G′) of all samples was always an order of magnitude higher than the loss modulus (G″) over the tested range from 0.1 to 100 rad s^{-1}. In addition, G′ was nearly independent of angular frequency. Generally, these two features in dynamic rheology indicated the as-prepared gels were crosslinked and gel-like. Loss tangent tanδ = G″/G′, which was a standard measure of the extent of viscous dissipation, was also calculated and plotted as a function of angular frequency.

In Figure 5a,b, when APS content was kept as a constant 0.05%, G″ decreased while hPEA content increased from 0.04% to 0.36%. Tanδ also had a similar tendency. This might illustrate what we had discussed above, the free chains trapped in the network reduced and the network was improved gradually. Furtherly, $I_{0.10}$–$C_{0.40}$, $I_{0.15}$–$C_{0.60}$, $I_{0.25}$–$C_{1.00}$ three gels were also tested under same condition. Different from $I_{0.05}$–$C_{0.04}$, $I_{0.05}$–$C_{0.20}$, $I_{0.05}$–$C_{0.36}$, the ratio of hPEA content and APS content was kept as a constant 4, considering the toughness reached its maximum (Figure 3b). In Figure 5c,d, G′ and G″ increased simultaneously with the increasing of both hPEA and APS content, but tanδ decreased. This could be ascribed to the crosslink density of network improved although the free chains also got more because of more APS were added into the system.

The prepared hydrogel with different hPEA contents were cut into disk like plate (**Figure 6**a) and then immersed in water at 40 °C for 5d (Figure 6b). Although a large amount of water was absorbed into the plates, they kept original rounded shape. The xerogel mass (m_1) was calculated and the swollen hydrogel mass (m_2) was recorded. Swelling ratio (Q) could be acquired according to Equation (1)

$$Q = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)$$

The relation between the swelling ratio and hPEA content was revealed directly as shown in Figure 6c. With increasing

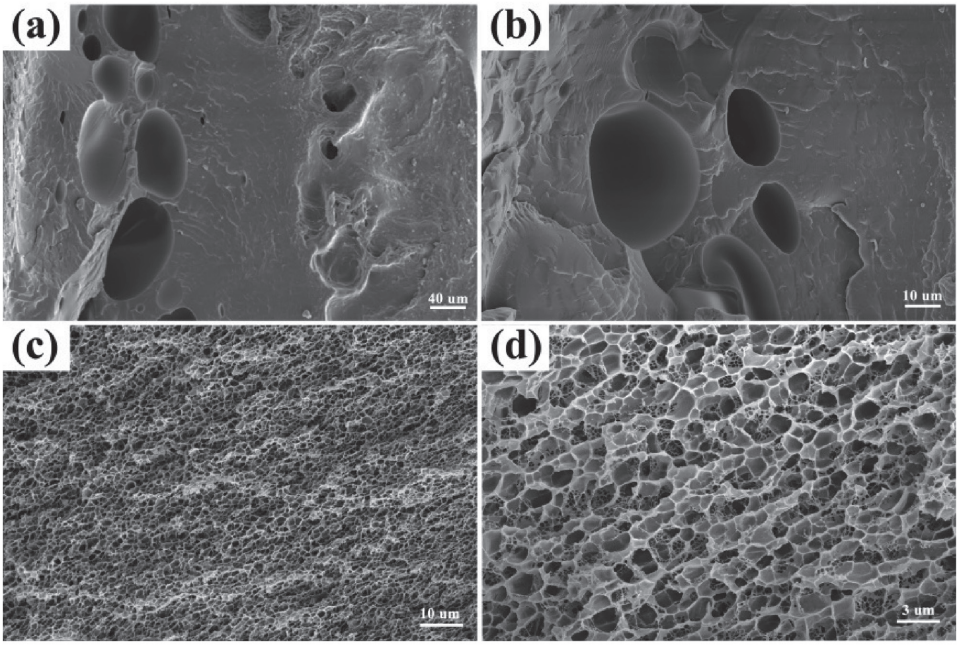


Figure 7. Representative SEM images of a,b) conventional hydrogels and c,d) $I_{0.05}$–$C_{0.20}$ hydrogels in different scales.

hPEA content from 0.04 to 0.36 wt%, swelling ratio decreased obviously. This experiment demonstrated crosslink density was in agreement with hPEA content when APS content was 0.05 wt%. This fact was also in accordance with the conclusions of stress–strain and rheology experiments.

SEM images of obtained IC hydrogels and conventional hydrogels are shown in **Figure 7**. Obviously, the pore size distribution of IC is more uniform than conventional hydrogels. We believe this difference reflects the distribution of crosslinks in the two types of networks. It could be concluded that the inhomogeneities of IC were less than conventional hydrogels due to the advantages of the designed mechanism in this work.

4. Conclusion

In summary, we prepared hydrogels with negligible defects and good mechanical properties by a classical initiated mechanism where hPEA performed as coinitiator and crosslinker. Crosslinking mechanism in the gelation process is a result of coupling termination of two chain radicals suspended on the crosslinker hPEA which is essential different from the existing hydrogel, such as the introduction of macromolecular crosslinking agent, DN hydrogel, NC hydrogel, topological hydrogel, etc. This hydrogel could be named as IC hydrogel. A series of experiments and characterizations demonstrated the toughness of IC hydrogel is about 4.02 MJ m^{-3} much higher than conventional hydrogel about 0.03 MJ m^{-3}. The huge enhancement is ascribed to the addition of hPEA making crosslinked network more uniform. In addition, the ratio of hPEA and APS is pivotal to the formation of negligible defects, 4 is optimal in this article. The preparation method used in this work is facile and the initiation mechanism is universal. Moreover, the crosslinking mechanism may provide a new way to synthesize hydrogel.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

coinitiator, crosslinker, hydrogel, hyperbranched polymer

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