

SYNTHESIS OF A NEW ORGANIC AEROGEL

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ABSTRACT

A new organic aerogel made from (*N*-hydroxymethyl)-acrylamide (NA) and resorcinol is reported. The acidic solution of NA and resorcinol was irradiated by γ -rays with 1200—1800 Gy dose, then was heated to 60°C for at least 16hr to form a transparent sol-gel. The translucent aerogel can be obtained from the sol-gel with CO₂ as supercritical fluid. Synthetic conditions (e.g. acidity of the solution, ratio of NA to resorcinol) are discussed.

INTRODUCTION

Aerogels are those materials which have continuous pores, and a solid matrix composed of interconnected colloid-like particles or polymeric chains with diameter 10nm^[1,2]. This structure is responsible for the unusual acoustic, mechanical, optical, and thermal properties of these materials^[3,4]. Most of aerogels are inorganic, e.g. silica aerogels, few of them are organic, e.g. resorcinol-formaldehyde and melamine-formaldehyde^[5,6]. Usually, the reaction of condensation of organic monomers (e.g. resorcinol and formaldehyde) is the most common synthetic route for the formation of organic aerogels^[7]. In this paper, the synthesis of a new organic aerogel which was formed from condensation of poly (*N*-hydroxymethyl)-acrylamide and resorcinol is reported.

(*N*-hydroxymethyl)-acrylamide (NA) is a water soluble monomer, and can be easily polymerized by radical initiator to form a water soluble polymer. In addition, it can be condensed with a loss of molecule of water when reacted with phenolic monomers in acidic solution at proper temperature. Therefore, NA is a trifunctional monomer, having a double-bond (C=C) and an electrophilic group (—CH₂OH in acidic solution). Resorcinol is used as crosslinking agent, which is also trifunctional, activated at the 2, 4 and 6 of the ring positions.

We selected room temperature as the polymerization temperature to avoid heating induced reactions so that the course of overall reaction can be controlled. NA is easily condensed with resorcinol in acidic solution at 50°C. When the temperature of the solution is controlled below 30°C the rate of condensation reaction becomes very low. Therefore, polymerization of NA by γ -ray radiation at room temperature is the best manner for our requirements that a transparent polymer solution can be formed from mixed solution of NA and resorcinol.

The new organic aerogel was made with the following processes: at first the solution containing NA and resorcinol was irradiated by ^{60}Co γ -ray, which initiates the polymerization of NA; then in the presence of an acidic catalyst and at a proper temperature the poly-NA was reacted with resorcinol to form a polymeric gel. This gel was then treated with acetone for the removal of water from it and supercritical extraction with carbon dioxide was performed. The resulting foam with a density range of 0.25–0.5 g/ml was translucent, faint red in color.

The effects of γ -ray dose, cure temperature, cure time, catalyst level (pH), the ratio of NA to resorcinol on the polymerization of NA, and the condensation between poly-NA and resorcinol were examined in this paper. The characterization of resulting products-poly-NA-R aerogels by using BET, SEM, TEM were reported.

EXPERIMENTAL

NA was an industrial product, and was recrystallized in acetone solution; resorcinol (98% purity) was obtained from Shanghai Chemical Reagent Co.; sulfuric acid is analytical pure (98% purity). All solutions used in the experiments were prepared with distilled water. A typical gel formulation contained a total of 5 or 10 wt% reactants.

After mixing 2–5 mole NA with 1 mole resorcinol the resulting solution was deaerated with N_2 (99% purity) for about 10 min, then the solution was adjusted by adding some 50 vol % sulfuric acid. The solution was irradiated by ^{60}Co γ -ray to a dose of 1200–1800 Gy at room temperature. Usually, the dose rate for radiation was 0.667 Gy/s; the time for the radiation is about 70min. Then, the slurry was placed in an oven at 60°C for 16–30h. In general, the solution would turn into gel after irradiation, but the extended cure permitted the gel to be strong enough to avoid shrinking intensely as supercritical drying.

After the completion of cure, the gel was soaked in distilled water for one day to remove the remaining acid. The gel was rinsed with a 50:50 mixture of acetone and water, followed by a 75:25 mixture, and finally 100% acetone. Multiple exchanges

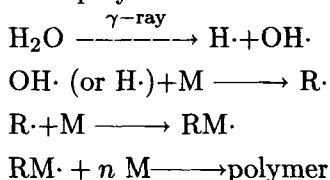
with fresh acetone were used to remove residual water from the gels. The acetone filled gels were dried in a jacketed pressure vessel by using liquid carbon dioxide as supercritical fluid. Details of this procedure have been described by Pekala^[3]. The aerogel removed from the pressure vessel were translucent in appearance. All samples were stored in desiccators to prevent from cracking.

The specimens for TEM were prepared by first fracturing the sol-gel with a razor after the sol-gel submerged in solid paraffin wax toluene solution, then washing the ultrathin specimens with acetone several times, finally, fumigating them with 2% osmic anhydride solution over 24hr at room temperature. Because the specimens were ultrathin, they were not easily cracked when acetone was vaporized, so it is unnecessary to remove acetone in them under supercritical condition. The specimens were imaged in H-800 TEM with voltage of 10KV. The specimens for SEM were prepared by fracturing the aerogels with tweezers at room temperature, then vacuum deposition of gold on the surface. The specimens were observed in X-05 SEM.

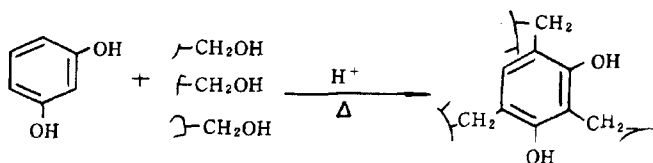
RESULTS AND DISCUSSION

In the presence of water, the polymerization of the condensation product of NA and resorcinol does not yield transparent polymer solution or sol-gel, because the product is water insoluble. In order to form a transparent sol-gel, the polymerization of NA must be carried out prior to the condensation between NA and resorcinol. Under γ -ray radiation, NA is polymerized at room temperature, whereas the reaction of condensation does not occur and a transparent polymer solution is obtained. The polymer solution is then turned into gel at 60°C and a transparent sol-gel is formed. Since resorcinol is trifunctional, it can react with three $-\text{CH}_2\text{OH}$ groups of the polymers under acidic condition at that temperature. The process of the gel formation can be illustrated by the following two steps.

(1) Formation of poly-NA



(2) Condensation between poly-NA and resorcinol:



Experimental results revealed that the minimum dose of γ -ray with which all NA is polymerized in the solution is related to the concentration of NA. As the solutions contain 5 wt% and 10 wt% NA, the lowest dosage is 1000 Gy and 1200 Gy respectively. However, if the dose exceeds 1800 Gy, the bubbles formed during the polymerization process will stay inside the gel after the solution becomes sol-gel. In the dose range of 1200–1800 Gy no difference of the density of the aerogels had been found. Most of the slurries were irradiated with 1300–1540 Gy.

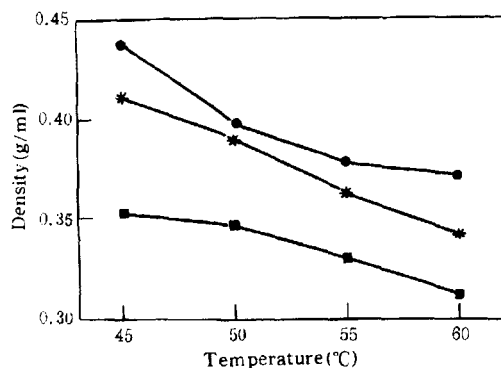


Fig. 1. The influence of cure temperature on the density of the aerogels. Solid content of the solution is 10%, the acid solution is 0.15 mol/L H_2SO_4 . Mole ratio of NA/Resorcinol $\oplus$ 4:1; * 3:1; $\blacksquare$ 2:1

The rate of condensation between poly-NA and resorcinol is related to the catalyst level and cure temperature. The rate increases with the increase of acid concentration at the same temperature. Table 1 revealed that aerogel density decreases with increase of acid concentration of the solution. This fact can be attributed to the influence of different condensation rate. Fig. 1 displays that when the cure temperature of sol-gel is increased the density of the final aerogels is decreased slightly in the same acidity. At 45°C the acidity of the solutions affects the aerogel density more than that at 60°C. These results illustrate that the rate of crosslinking affects the network structure of the gel. We consider that hydrophilicity of the polymeric chains is decreased as crosslinking of the polymer is increased, which causes the attraction between crosslinked chains until the integral network of the gel is formed thus preventing from further attracting. If the rate of crosslinking is high, the time used for the formation of integral network will be reduced and the attraction of free crosslinked chains will be weakened too. In the condition of high acidic solution, the specific surface area of the aerogel is high due to more integral network of it.

In order to get integral networks, the necessary cure time for the formation of an

enough strong sol-gel should be differed with the change of the cure temperature and the solution acidity. At 60°C and $[\text{H}_2\text{SO}_4]=0.15$ mol/L it is necessary to keep cure time for at least 16h. However, no obvious change of gel density could be found when the cure time was more than 16h. In this work, the cure time is kept for about 20h for most slurries. A cure temperature higher than 60°C is not appropriate because the sol-gel will be cracked easily.

Table 1 The influence of catalyst- H_2SO_4 on the density and specific surface area of the aerogel

Acidity (M)	Density (mg/ml)*	Specific surface area (m^2/g)*
0.037	413 (30)**	148 (48)
0.074	404 (30)	217 (48)
0.110	378 (24)	242 (24)
0.147	387 (24)	354 (24)
0.180	376 (24)	313 (24)

* The data were gotten from different samples in the acid solution

** The time (h) used for gel to be cured

Solution contains 10% solid, NA:R=4:1, cure temperature: 60°C

absorption dose: 1515—1610 Gy

Table 2 Variation of composition ratios, density and specific surface area of the aerogel

Ratios NA:R (mole)	Density (mg/ml)	Specific surface area (m^2/g)
5:1	416	193
4.5:1	395	239
4:1	368	330
3.5:1	354	345
3:1	338	353
2.5:1	291	395
2:1	306	529

Solutions contain 5% solid, catalyst: 0.147M H_2SO_4 , absorption dose: 1540 Gy, cure temperature: 60°C, cure time: 20h

It was found that the aerogel density is decreased as the ratio of NA to resorcinol decreases. This is due to high crosslinking of aerogel network as the relative concentration of resorcinol is increased. Nevertheless, as the ratio is less than 2.0 every resorcinol molecule does not have the opportunity to react with two or more $\text{—CH}_2\text{OH}$ groups of the polymer and crosslinking will no longer be effective. In addition, resorcinol has a tendency of inhibiting the polymerization of NA. Therefore, the molecular weight of poly-NA is lower than that of the ratios above 2.0. We found that the final aerogel becomes opaque as the ratio is lowered to 2.0, especially in the condition of high acidic solution and the mechanical strength of the aerogel is low. Due to low mechanical strength of the aerogels with the ratios below 2.0, their density has not been measured.

The pictures of TEM revealed that the aerogel had a porous structure. Perhaps the structure was coiled polymeric chains crosslinked by resorcinol. The intense shrinking of sol-gel after curing can be illustrated by the structure. Although the picture of SEM reveals that the microstructure of aerogel is destroyed by vacuum deposition of gold, we presume that the foams have an open-cell and network structure from the fact that aerogels have high specific surface area. In Fig. 2 the substructure of the aerogel at its polymeric chain level is not observable, and the pore size is difficult to estimate from these pictures. Therefore, its microstructure needs further investigation.

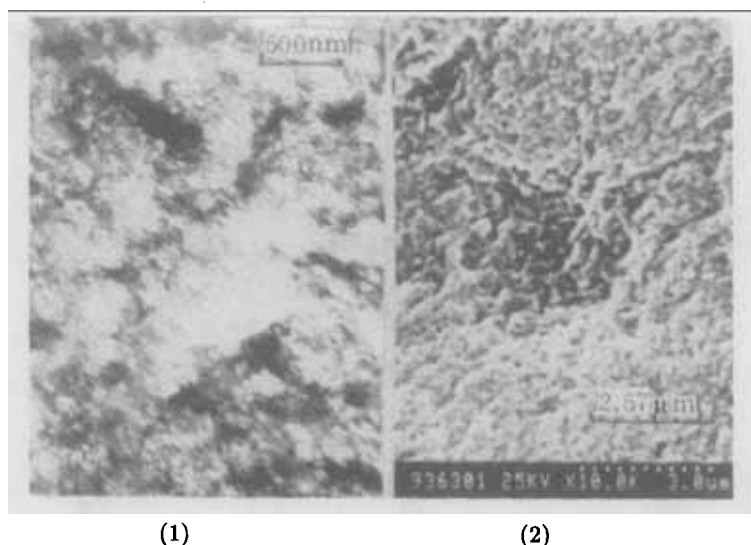


Fig. 2. (1) Transmission electron micrograph of an NA-R aerogel, (2) Scanning electron micrograph of an NA-R aerogel

CONCLUSION

It is possible that an aerogel is prepared from (N-hydroxymethyl)-acrylamide and resorcinol. In acidic aqueous solution, NA was polymerized by γ -ray radiation with ^{60}Co -source, the resulting polymer was condensed with resorcinol leading to the formation of the transparent sol-gel. Properties of the final aerogel depend upon the absorption dose for polymerization, acidity in the solution, cure temperature, and ratio of NA to resorcinol. The results of BET, TEM, and SEM revealed the foams having low density, high surface area, and ultrafine structure.

Keywords:

Aerogel; (N-hydroxymethyl)-acrylamide; Resorcinol; Radiation.

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