Polymer Bulletin 9, 5-10 (1983)

Polymer Bulletin

Polymerization of Acrylic Acid Initiated with Poly-γ-Mercaptopropylsiloxane

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Summary

A water soluble polyacrylic acid has been obtained by polymerization of acrylic acid initiated with silica-supported poly-γ-mercaptopropylsiloxane in the presence of water and carbon tetrachloride. A super absorbent sodium polyacrylate (water absorbing capacity 300 g/g) has been prepared by copolymerization of acrylic acid with a small amount of p-divinylbenzene with the same initiator in a mixture of aqueous sodium hydroxide solution, carbon tetrachloride, n-hexane and Tween 80.

Introduction

It is well known that acrylic acid can be polymerized in the presence of benzoyl peroxide, azobisisobutylonitrile, sodium persulfate, ammonium persulfate and so on. However, bulk polymerization has not been adopted because the reaction occurs too violently. In the polymerization in aqueous solution, the monomer concentration cannot be over 25% for obtaining the water soluble polymer (ARAKI, 1971).

Recently we have found that silica-supported poly-γ-mercaptopropylsiloxane(abbreviated as $\textcircled{\scriptsize Si}$ -SH) can initiate the polymerozation of acrylic acid to give water soluble polymer even when the monomer concentration in aqueous solution was over 60%.

The so-called super absorbent polymer which absorbs several hundred times as much water as its own weight was at first obtained by the method of hydrolyzing starch-acrylonitrile graft polymer (GUGLIEMELLI,1969). Later, different

0170-0839/83/0009/0005/$01.20

kinds of super absorbent polymers have been developed. They have been prepared mostly by slight crosslinking of the water soluble polymers such as polyacrylamide (DOW CHEM.,1966), polyethylen oxide (UNION CARBIDE,1973), sodium polyacrylate (KAO SOAP, 1978), polyvinyl alcohol (INDUSTRIAL RESEACH INSTITUTE, 1975).

Here we have found that a super absorbent of sodium polyacrylate could be prepared by the copolymerization of acrylic acid with a small amount of p-divinylbenzene initiated with the above system of us.

Experimental

Preparation of $\textcircled{Si}$-SH

To a mixture of 400 ml of toluene and 20 g of silica gel (surface area 370 m^2/g) 20 g of γ-mercaptopropyltriethoxysilane was introduced, then 30 ml of ethanol solution containing 6 ml of water and 0.6 ml of 10% hydrochloric acid were added slowly, and the mixture was heated to reflux. During reflux, the white opaque mixture became colorless and transparent. After refluxing for 4 hr, the product was allowed to cool, filtered, dried in vacuo, and extracted with toluene to yield 32.2 g white powder. The sulphur content was 9.28 wt.% (determined by elemental analysis).

Preparation of water soluble polymer

Polymerization of acrylic acid was carried out in a flask equipped with a reflux condenser and a magnetic stirrer under a nitrogen atmosphere. In a typical experiment, acrylic acid (1 ml), $\textcircled{Si}$-SH (0.015 g), water (1 ml) and carbon tetrachloride (0.5 ml) were charged into the flask, which was placed in a water bath maintained at 75°C for 6 hr. After cooling, an excess amount of acetone and ethyl acetate mixture (1:1 by volume) was poured into the product to precipitate the polymer. The polymer obtained was warmed in a vacuum evaporator to remove the solvents.

Preparation of super absorbent polymer

Apparatus and procedure were similar to those of the above experiment. In a typical experiment, acrylic acid

(1 ml), (Si) -SH (0.015 g), water (1 ml), carbon tetrachloride (0.5 ml), p-divinylbenzene (0.42 mol %), n-hexane (4 ml) and Tween 80 (0.075 g) were charged into a flask and it was placed in a water bath maintained at 62°C for 6 hr. The polymer obtained was warmed in a vacuum evaporator to remove the solvente, and the product was ground to a fine powder.

Measurment of the water absorbing capacity

0.1 g of the powder (20-40 mesh) was mixed with 50 ml water in a flask to allow swelling for 30 min, the solution was filtered through a Nylon screen for 15 min. The water absorbing capacity was obtained by dividing the weight increased by 0.1 g.

Results and Discussion

Table 1 shows the effect of the amounts of water and carbon tetrachloride on acrylic acid polymerization initiated by (Si)-SH. It can be seen that the polymerization was remarkably accelerated in the presence of water and carbon tetrachloride. In fact, 100 % of conversion could be obtained if proper amounts of water and carbon tetrachloride were present. On the other hand, polymerization did not occur if either of them was absent. The polymer obtained was soluble in water when the concentration of acrylic acid was in the range of 20-67 %. As mentioned above, it is difficult to obtain the water soluble polymer by other initiators when the concentration of acrylic acid is over 25 % (ARAKI, 1971).

From the fact that the reaction did not proceed in the absence of carbon tetrachloride, and that the reaction proceeded even in the presence of a large quantity of water, the reaction is probably a radical polymerization. The existence of free radical in the reaction mixture was confirmed by ESR. The mechanism of initiation was thus assumed to be as follows:

$$\begin{aligned} &-\mathrm{SH} \longrightarrow -\mathrm{S}\bullet + \mathrm{H}\bullet \\ &-\mathrm{S}\bullet + \mathrm{CCl_4} \longrightarrow -\mathrm{SCl} + \bullet\mathrm{CCl_3} \\ &\bullet\mathrm{CCl_3} + \mathrm{AA} \longrightarrow \mathrm{AA}\bullet \end{aligned}$$

TABLE 1

Effect of the Amounts of Water and Carbon Tetrachloride on Acrylic Acid Polymerization by $\textcircled{Si}$ -SH

H_2O ml	Conc. of AA in water soln., %	CCl_4 ml	Conversion %
0	100	0.5	0
0.5	67	0.5	100
1.0	50	0.5	100
2.0	33	0.5	95
3.0	25	0.5	70
4.0	20	0.5	62
1.0	50	0	1
1.0	50	0.3	100
1.0	50	1.0	100
1.0	50	2.0	100
1.0	50	3.0	87

acrylic acid (AA), 1 ml : $\textcircled{Si}$ -SH (S, 9.28 wt.%), 0.015 g : 75°C, 6 hr

The influence of the amounts of $\textcircled{Si}$-SH on acrylic acid polymerization is shown in Table 2. A very small amount (-SH/AA molar ratio = 10^{-5}) of $\textcircled{Si}$ -SH could initiate the polymerization. For comparison, a low molecular weight mercaptan such as propylmercaptan was used as initiator instead of $\textcircled{Si}$-SH for polymerization of acrylic acid, but polymerization did not occur.

Table 3 shows the relationship between the content of crosslinking agent (p-divinylbenzene) and the water absorbing capacity of sodium polyacrylate. It can be seen that 0.32-0.42 mol % of p-divinylbenzene is optimum for obtaining high absorbing capacity (437-477 g/g).

Table 4 shows the effect of the degree of neutralization on the water absorbing capacity. It can be concluded that

TABLE 2

Influence of the Amounts of (Si) -SH on Acrylic Acid Polymerization

(Si)-SH g	-SH/AA molar ratio	Conversion %
0	0	1.7
0*	0	2.4
0.01	$2.8x10^{-5}$	90
0.02	$5.5x10^{-5}$	100
0.04	$1.1x10^{-4}$	100
0.10	$2.8x10^{-4}$	100

acrylic acid (AA), 1 ml ; H_2O, 1 ml ; CCl_4 , 0.5 ml ; (Si) -SH, S 9.28 wt. % ; 0* , 0.015 g silica gel (no-SH group) ; 75°C, 6 hr

TABLE 3

Relationship between the Content of Crosslinking Agent and the Water Absorbing Capacity of Sodium Polyacrylate

p-Divinylbenzene mol %	Absorbing capacity g/g
0.21	223
0.32	437
0.42	477
0.53	307
0.63	43

acrylic acid, 1 ml ; (Si)-SH (S, 9.28 wt %), 0.015 g ; aqueous 8.58 N NaOH soln., 1 ml ; n-hexane, 4 ml ; CCl_4 , 0.5 ml ; Tween 80 , 0.075 g ; 62°C , 6 hr

the absorbing capacity was also affected greatly by the degree of neutalization. It was shown early that the polymerization velocity of acrylic acid was greatly affected by the pH, and if the polymerization was too violent the crosslinked polymer was produced (ARAKI , 1971). So the crosslinking density of polymer may be affected by the degree of neutralization.

TABLE 4

Effect of the Degree of Neutralization on the Water Absorbing Capacity of Sodium Polyacrylate

Aqueous NaOH Soln. ml	Degree of neutralization,%	Absorbing capacity g/g
0.90	52.8	43
1.00	58.7	465
1.04	61.1	455
1.08	63.4	459
1.10	64.6	477
1.12	65.7	226
1.16	68.1	151
1.20	70.4	85
1.25	73.4	79
1.30	76.3	10

acrylic acid, 1 ml ; $\textcircled{\scriptsize Si}$-SH (S, 9.28 wt %), 0.015 g ; aqueous NaOH Soln., 8.58 N ; n-hexane, 4 ml ; CCl_4, 0.5 ml; p-divinylbenzene, 0.42 mol % ; Tween 80 , 0.075 g ; $62^{o}C$, 6 hr

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Received August 27, accepted October 27, 1982 *S*