

Preparation of polymeric porous materials by interparticle crosslinking

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Suspensions of poly(acrylic acid) particles with an average diameter of about 90 nm in benzene were prepared by dispersion polymerization. Using dioyl dichloride or diglycidyl ether as crosslinking agent the poly(acrylic acid) particles can be linked with each other, and a gel with three-dimensional network structure was formed. After removal of the solvent from the gel by freeze-drying a porous polymeric material can be obtained. Depending on the concentration of crosslinking agent and the polymer content of the suspension a porous material of poly(acrylic acid) with porosity as high as 0.95 and density as low as 0.07 g cm^{-3} is achieved. The process of gelation was studied by dynamic rheology, light scattering and calorimetric measurements. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Porous polymeric materials are used as sorbents, the stationary phase for gas chromatography, ion-exchange resins, membrane materials and carriers for catalysts as well as biologically active substances¹. Most porous polymeric materials are prepared by crosslinking copolymerization with an inert component (diluent) which may be extracted after polymerization, leaving holes in the structure^{1–4}. In this paper we report a new method to prepare a porous poly(acrylic acid) material.

Using the stabilized precipitation polymerization of acrylic acid in organic media it is possible to prepare poly(acrylic acid) dispersions with particles of about 100 nm^{5,6}. The poly(acrylic acid) dispersion can be crosslinked by using bi- or multifunctional crosslinking agents⁷.

EXPERIMENTAL

Preparation of polymer nanoparticles

Acrylic acid (20 g) (BASF, distilled under vacuum at 50°C) as monomer, 2.5 g distilled water and 3 g SE3030 (Th. Goldschmidt AG, polystyrene-*block*-polyethylene oxide copolymer) as stabilizer were added into 230 g benzene (Aldrich, for h.p.l.c.). After purging with nitrogen for 20 min at 50°C, 200 mg 2,2'-azobis(2,4-

dimethylvaleronitrile) (ADVN, Wako Pure Chemicals) were added to the reaction mass to start the polymerization. In about 30 min the reaction was completed and a suspension of poly(acrylic acid) particles in benzene was formed. The precipitation polymerization of acrylic acid was also run in 1,2,4-trimethylbenzene (Aldrich, 98%) as solvent. The particle size of the suspension formed was determined by dynamic light scattering (Malvern, 4600).

Crosslinking of the nanoparticle suspension

For crosslinking with a diglycidyl ether (butanediol diglycidyl ether (Aldrich, 95%) or hexanediol diglycidyl ether (Witco, 66%)) the concentration of the crosslinkers was varied from 0.08 mol l^{-1} to 0.80 mol l^{-1} , and the polymer content in the suspension was varied between 4 and 15 wt%. The reaction was studied in a temperature range from 70 to 110°C. For example, 1.4 g butanediol diglycidyl ether (Aldrich, 95%) was added to 20.0 g of a suspension of 7.0 wt% polymer content in 1,2,4-trimethylbenzene at room temperature. The crosslinker content in the resulting mixture was 6.2 wt% (0.29 mol l^{-1}), the poly(acrylic acid) content was 6.5 wt% (0.84 mol l^{-1}). Then the mixture was kept at 90°C without any stirring. After about 24 h the formed gel was cooled at room temperature.

To study the kinetics of the crosslinking process rheology measurements were carried out at 90°C with a frequency of 0.15 Hz and strain amplitude of 0.02 using a dynamic rheometer of BOHLIN Instruments, CS 10.

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D.s.c. measurements were run at constant temperature of 90°C using a differential scanning calorimeter (Perkin-Elmer, DSC 7). The sample was put in a pressure-resistant steel cell and the temperature was raised from room temperature to 90°C in 1 min.



Figure 1 SEM micrograph of the porous material: crosslinking agent (hexanedioyl dichloride) content: 1.48 wt%; polymer content in the suspension: 8.0 wt%; crosslinking temperature: 72.5°C

When hexanedioyl dichloride (Aldrich, 98%) or decanedioyl dichloride (Aldrich, 99%) were used as crosslinking agents, for example, 0.094 g hexanedioyl dichloride were added to 6.16 g suspension with a polymer content of 8.0 wt% at room temperature. Then the mixture was kept at 72.5°C for 20 min.

The formed polymer gel was dried by freeze drying, i.e. the gel was frozen using liquid nitrogen and dried under vacuum ($< 0.5 \times 10^{-3}$ mbar) for 24 h.

Analysis of the gel

For taking micrographs with a scanning electron microscope, Hitachi F-4000, the dried gel was coated with a layer of gold.

For determination of porosity, the dried gel was immersed in a non-swelling solvent such as toluene or benzene. After determining the absorbed mass (g/g) of solvent the porosity of the gel was calculated according to the method described in ref. 8. The density of poly(acrylic acid) was taken as 1.39 g cm^{-3} .

RESULTS AND DISCUSSION

After addition of dioyl dichloride into the suspension of poly(acrylic acid) in benzene (average particle diameter 93 nm) the suspension became turbid but the viscosity

Table 1 Porosity of crosslinked polymer at different crosslinking agent and polymer contents

Crosslinking agent	Crosslinking agent content (wt%)	Polymer content (wt%)	Solvent for absorption	Absorbed mass of solvent (g/g)	Porosity of polymer (%)
Hexanedioyl dichloride	11.30	8.0	Benzene	3.9	86.1
			Toluene	3.9	86.1
			n-Hexane	3.1	86.9
	7.15	8.0	Benzene	7.9	92.5
			Toluene	7.4	92.2
			n-Hexane	5.5	92.1
	1.48	8.0	Benzene	11.8	94.9
			Toluene	11.4	94.8
			n-Hexane	8.5	94.7
	3.10	4.0	Benzene	11.2	94.6
			Toluene	10.8	94.5
			n-Hexane	8.0	94.4
	1.48	4.0	Benzene	13.1	95.4
			Toluene	12.5	95.0
			n-Hexane	9.2	95.1
	0.90	4.0	Benzene	13.9	95.7
			Toluene	13.4	95.6
			n-Hexane	10.9	95.8
1.48	8.0	Benzene	11.8	94.9	
		Toluene	11.4	94.8	
		n-Hexane	8.5	94.7	
1.48	4.0	Benzene	13.1	95.4	
		Toluene	12.5	95.0	
		n-Hexane	9.2	95.1	
1.48	2.8	Benzene	13.6	95.5	
		Toluene	13.2	95.5	
		n-Hexane	10.1	95.5	
Decanedioyl dichloride	18.20	8.0	Benzene	2.9	82.2
			Toluene	2.8	82.0
			n-Hexane	2.2	82.0
	13.60	8.0	Benzene	4.1	86.6
			Toluene	3.9	86.3
			n-Hexane	3.1	86.7
	4.21	8.0	Benzene	7.1	91.8
			Toluene	7.0	91.8
			n-Hexane	4.9	91.1

was still low. However, on keeping the suspension at 72.5°C for several minutes (depending on the concentration of crosslinking agent and the polymer content of the suspension) the viscosity of the suspension increased suddenly and a pudding-like gel was formed. When hexanediol diglycidyl ether was used as crosslinking agent, then the temperature was kept at 90°C and it took a few hours until the viscosity increased strongly.

After removal of benzene from the gel by freeze-drying a porous polymer material was formed. *Figure 1* shows the typical structure of such a porous material. BET measurements with nitrogen show that the specific surface area of the prepared porous materials is about 20 m² g⁻¹.

Porosity of the poly(acrylic acid) gels

Influence of crosslinking agent concentration. The porosity of the porous materials depends on the concentration of the crosslinking agent, if freeze-drying was used for the removal of the solvent. The higher the concentration of the crosslinking agent, the more compact is the structure of the porous material. As can

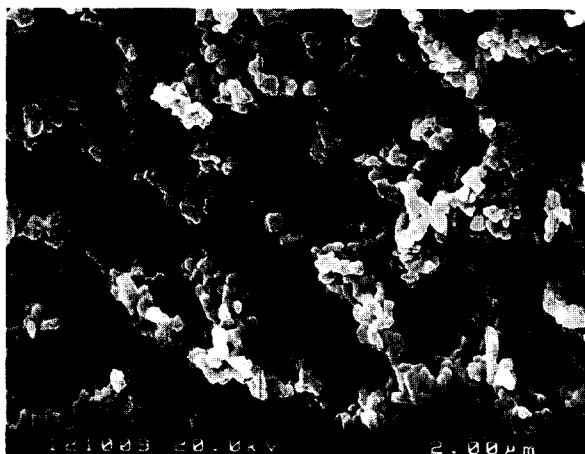


Figure 2 SEM micrograph of the porous material; crosslinking agent (hexanediol dichloride) content: 1.48 wt%; polymer content in the suspension: 4.1 wt%; crosslinking temperature: 72.5°C



Figure 3 SEM micrograph of a sample formed by vacuum drying at room temperature; hexanediol dichloride content: 1.48 wt%; polymer content in the suspension: 8.0 wt%

be seen in *Table 1*, porosity and absorbed masses increase with decreasing diol dichloride concentration at constant polymer content of the suspension. If the concentration of hexanediol dichloride is lower than 0.8 wt% referred to the mass of the suspension (corresponding to 3.9 mol% of the crosslinking agent referred to the acid groups in the polymer suspension), no gel will be formed after addition of crosslinking agent, when the polymer content of the suspension is 8.0 wt%. When using hexanediol diglycidyl ether as crosslinking agent this critical concentration is 6.0 mol% with polymer content of 8.0 wt%.

Influence of polymer content. The porosity of the materials depends also on the polymer content of the suspension, if freeze-drying was used. *Figure 2* shows the structure of a porous material formed by using the same crosslinking agent concentration as used in *Figure 1* (hexanediol dichloride, content: 1.48 wt%), but lower polymer content. At low polymer content the average pore diameter is larger than at high polymer content. The absorbed mass and the porosity increase slightly with decreasing polymer content of the suspension (*Table 1*).

Influence of the kind of drying on the structure of the porous materials. Using freeze-drying as a method to remove the solvent from the gel, the network structure of the gel is kept stable until all solvent is removed. By vacuum drying at room temperature, on the other hand, a volume shrinkage can occur and the original structure of the gel can be partially destroyed. Furthermore, because the process of volume shrinkage by vacuum drying at room temperature is not uniform, the structure of the porous materials is heterogeneous. As can be seen from *Figure 3*, a compact structure is formed after vacuum drying at room temperature.

No regular relationship exists between the porosity and crosslinking agent concentration when vacuum drying is used at room temperature. However, if the crosslinking agent concentration ranges from 2.70 to 10.16 wt% (referred to the mass of the suspension) the porosity varies from 78.6% to 86.4% and the density from 0.19 to 0.30 g cm⁻³ in a random way.

The process of gelation

Isothermal studies of the crosslinking process in a differential scanning calorimeter at 90 or 100°C show that the rate of reaction is maximum at the beginning of the measurement and decreases with increasing time. No discontinuity of the reaction rate can be observed.

Figure 4 shows the result of a dynamic rheology measurement using a sample with butanediol diglycidyl ether content of 6.2 wt% (0.29 mol l⁻¹), polymer content of 6.5 wt% and 1,2,4-trimethylbenzene as solvent at 90°C. After about 4.5 h, when the measured heat flow of the isothermal d.s.c. run of an identical sample is nearly zero, a strong increase of the complex viscosity, the loss modulus and the storage modulus can be observed. The total gelation process seems to last for several hours.

A dynamic light-scattering measurement during the crosslinking reaction of the mixture shows that the particle size increases from about 100 nm to more than 1 μm in the last hour before gelation occurs. The increase of the particle size may be caused by cluster formation

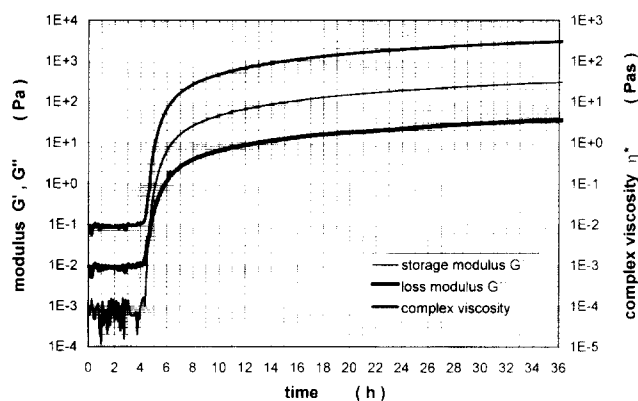


Figure 4 Complex viscosity η^* , storage modulus G' and loss modulus G'' (dynamic measurement; frequency: 0.15 Hz; strain amplitude: 0.02) as a function of time for the crosslinking reaction of butanediol diglycidyl ether with poly(acrylic acid) suspension at 90°C (polymer content: 6.5 wt%; crosslinking agent content: 6.2 wt% (0.29 mol l⁻¹))

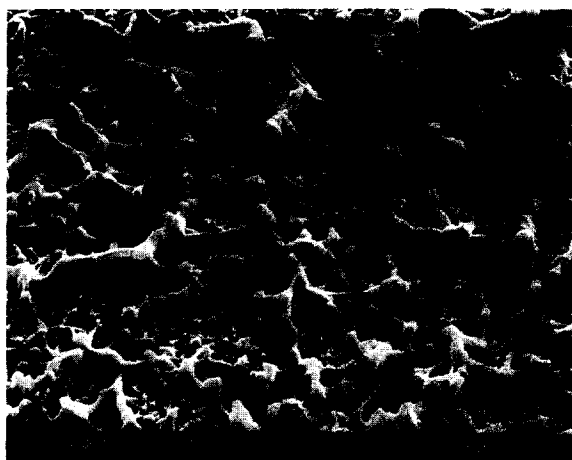


Figure 5 SEM micrograph of the fracture of poly(acrylic acid) and polystyrene: poly(acrylic acid) content: 10.0 wt%

through interparticle crosslinking. A cluster-like structure can be seen in the SEM micrographs (Figure 1). It seems that a strong increase of the complex viscosity does occur when a critical size of the clusters is reached.

Polymerization of styrene in the presence of poly(acrylic acid)

A piece of the poly(acrylic acid) gel containing trimethylbenzene was added to a large excess of styrene. The mass was swirled for 1 day in order to exchange the solvent against the styrene. Then the lump of gel was

heated to 80°C for about 3 days. The polymer formed was broken at room temperature. Figure 5 shows the surface of the fracture. As can be seen, a relatively uniform blend of polystyrene in the porous matrix of poly(acrylic acid) was formed.

Poly(acrylic acid) gel as catalyst supporting material

The following procedure was used to support the poly(acrylic acid) gel with a palladium catalyst: 0.3 g of the porous material crosslinked with diglycidyl ether was immersed in a solution of 0.014 g palladium(II) nitrate in 12 ml of water and stirred at room temperature for 2 h. The material was carefully dried under vacuum at 40°C and resuspended in 50 ml benzene. Next, 1 g sodium tetrahydridoborate was added to reduce Pd(II), and the mixture turned black after a few minutes. After stirring for another 2 days at room temperature the substance was dried as described above and excess sodium tetrahydridoborate was hydrolysed with 50 ml of water. Without stirring the swollen black particles settled within minutes. When this material was used for the reduction of nitrite with hydrogen in water, the activity was comparable to that of commercial palladium catalysts, for example palladium on γ -aluminium oxide (Pd content: 2 wt%) with particle diameter of about 63 μ m (Degussa).

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REFERENCES

- 1 Kolarz, B. N., Wojuczynska, M., Trochimczuk, A. and Luczynski, J. *Polymer* 1988, **29**, 1137
- 2 Seide, J. and Malinsky, J. *Adv. Polym.* 1967, **5**, 113
- 3 Sederel, W. L. and Dejong, G. J. *J. Appl. Polym. Sci.* 1973, **17**, 2835
- 4 Jacobelli, H., Bartholin, M. and Guyot, A. *Angew. Makromol. Chem.* 1979, **80**, 31
- 5 Fengler, S. *Ph.D. Thesis*, TU Berlin, 1995
- 6 Fengler, S. and Reichert, K.-H. *Angew. Makromol. Chem.* 1995, **225**, 139
- 7 Fock, J., Körner, G., Reichert, K.-H., Fengler, S. and Smolin, R. Patent Application EP94104818.3 Th. Goldschmidt AG, 1994
- 8 Dullien, F. A. L. 'Porous Media', Academic Press, New York, 1979, p. 77