Studies of Porous Polymer Gels. III. Swelling Behavior of Porous Poly(Methacrylic Acid) Gels

HENRYK GALINA and BOŻENA N. KOLARZ, *Institute of Organic and Polymer Technology, Technical University of Wrocław, 50-370 Wrocław, Poland*

Synopsis

Further studies of porous suspension copolymers of methacrylic acid and divinylbenzene (DVB) are reported. The qualitative structure model of the copolymers proposed previously is used to interpret the ion-exchange properties, sorption of water and aqueous sodium chloride solution, swelling, and neutralization rate. It is proposed that the close to ideal NON-SOL methacrylic acid–divinylbenzene copolymers are composed of rigid microgels and lightly crosslinked poly-(methacrylic acid). The latter swollen in water gives the gel, which tends to occupy the accessible space in the copolymer bead together with macropores detectable in the dry state. For the copolymers studied, the DVB content, 5.0 and 9.1% by weight, affects the rigid portion dimension and the extent of swelling of the whole bead, while the expansion of linear chains is determined by the distance between microgels.

INTRODUCTION

The swelling behavior of poly(methacrylic acid) gels has been widely studied because of their similarity to the crosslinked polyelectrolytes of natural origin.[1,2] Ion-exchange and acid–base properties related to the swelling have also been studied for these products.[3–7] Gregor et al.,[3] Howe and Kitchener,[4] Fisher and Kunin,[5] and Mathieson and Shet[6] studied the properties of moderately crosslinked poly(methacrylic acid) gels in series of products obtained with various amounts of crosslinking agent and methacrylic acid used in their preparation. The swelling behavior of methacrylic acid and ethylene dimethacrylate copolymers obtained with an inert diluent has been studied by Mikes.[7]

In this work an attempt is presented to correlate the swelling behavior of porous poly(methacrylic acid) gels with the model of their structure proposed previously.[8]

EXPERIMENTAL

Poly(methacrylic acid) gel samples in the form of milky white beads of 0.5–1.2-mm diameter were essentially the same as previously described.[8]

Ion-Exchange Capacity

The ion-exchange capacity of the gels has been determined using a method similar to that described by Gustafson.[9] Weighed samples (1–1.5 g) of air-dried resins in H (acid) form and 100 ml 0.2N aqueous NaOH were placed in stoppered polyethylene bottles. Simultaneously, another sample of the resin was dried

0021-8995/79/0024-0901$01.00

at 60°C in vacuum over P_2O_5 to determine the dry weight of the gels. After equilibrium had been reached (about 2 weeks), the solution was transferred from the bottles into 200-ml standard flasks through a glass filter, and the gels collected on the filter were washed with dry ethanol. Unreacted NaOH in combined filtrates was then determined titrimetrically.

Water Sorption

Amounts of water sorbed by samples have been determined by the centrifugation of swollen gels placed in stoppered poly(methyl methacrylate) tubes equipped with a fine polyamide mesh for 6 min at 3000 rpm. After the centrifugation, the gels were transferred into several weighing bottles and predried at 60°C, followed by drying at the same temperature in vacuum over P_2O_5 until constant weight was reached. Corrections for a change of dry weight of resins, being partly neutralized with sodium hydroxide, and for solution remaining at bead surfaces after centrifugation were taken into account.[10]

Swelling

Specific volumes of swollen gels at 25°C have been determined pycnometrically using the method described by Gregor et al.[11] The swollen gels were centrifugated, weighed and quantitatively transferred into pycnometer. n-Heptane saturated with water was used as a pycnometer liquid.

Vapor Sorption

Gel samples of known weight and neutralization degree were placed in a hygrostate and kept at 25 ± 0.5°C over saturated aqueous $K_2Cr_2O_7$ solution until constant weight was reached. The activity of water was 0.98.[12]

Neutralization Rate

Samples of water-swollen beads were neutralized with a constant excess of $0.2N$ aqueous NaOH solution. Changes in the concentration of the solution were followed conductometrically.

RESULTS AND DISCUSSION

The ion-exchange capacities of the methacrylic acid (MA) and divinylbenzene (DVB) copolymer gels are listed in Table I.

The capacity values depend directly on the monomer mixture composition used in the preparation. The largest amount of MA used leads to a copolymer having the highest capacity (sample 1). Increasing DVB content (samples 7–13) while keeping the amount of MA constant gives a decrease in H–Na capacity of the copolymer. The copolymer samples 2–6 prepared from the monomer mixture of 85% MA, 5% DVB, and 10% aromatic monovinyl monomer exhibit the capacity of 10.11 ± 0.07 meq/g. The differences between the capacities of copolymers in each group are only slightly higher than the accuracy of the capacity determinations. This suggests that the capacity value does not depend on the diluent used in polymerization.

TABLE I
Ion-Exchange and Swelling Properties of MA–DVB Copolymers

Copolymer number[a]	Ion-exchange capacity (meq/g)	Water sorption	
		H-form (g/g)	Na-form (g/g)
1	10.5_7	1.06_0	2.42
2	10.1_8	1.01_1	2.03
3	10.0_4	1.09_7	—
4	10.1_4	1.12_8	—
5	10.1_2	1.21_4	2.82
6	10.0_6	1.29_0	3.00
7	9.6_9	0.64_7	1.21
8	9.7_7	0.69_2	—
9	9.6_4	0.71_2	—
10	9.6_9	0.79_4	1.64
11	9.8_5	0.83_0	1.67
12	9.6_5	0.85_5	2.35
13	9.7_2	1.04_0	2.53

[a] Compositions of monomer and diluent mixtures used in preparation and porosity of the resulting copolymers have been reported previously (Ref. 8).

The decrease in capacity with the increase of cross-linking is a well-known relationship for ion-exchangers.[13] The capacity value is related to the accessibility of carboxyl group within the crosslinked gel. In general, the accessibility of functional groups in a polymer network is not only a function of crosslinking degree or chemical structure, but also a function of the swelling behavior. For instance, one can prepare two copolymers of styrene and DVB differing in swelling and having the same chemical composition and then fully sulfonate them. A higher-swelling copolymer will have a higher ion-exchange capacity than that which swells less because of differences in accessibility to sulfonation of the aromatic nuclei.[14]

The results of capacity determination show, however, that the accessibility of carboxyl groups in poly(methacrylic acid) gels being studied is independent on swelling. The amount of carboxyl groups which do not react with NaOH remains constant in each group of MA–DVB copolymers. This finding supports the structure model for the copolymers outlined previously[8]; that such gels are composed of rigid portions surrounded by lightly crosslinked portions of polymer. Inaccessible groups are present in the microgel portions, and the amount remains constant for each copolymer in a given group regardless of the kind and the amount of diluent used in copolymerization. It appears that the independence of the inaccessibility of the crosslinked gel portions for reaction or diffusion should be a typical behavior for ideal NON-SOL gels.

Specific volumes of copolymers in H-Na forms when swollen in water are presented at the Fig. 1. A significant increase of swelling is observed for the neutralization degree, increasing from $\alpha = 0.2$ to 0.5. Further neutralization of samples 2, 5, and 6 gives bent curves. The increase of α up to about 0.5 gives the rapid increase of the ionized carboxylic group concentration, followed by the expansion of flexible chains due to the strong electrostatic repulsion between them.[2] Then for α higher than about 0.5, the increase of the electrostatic repulsion is lowered by the formation of —COO⁻Na⁺ pairs.[12,15]

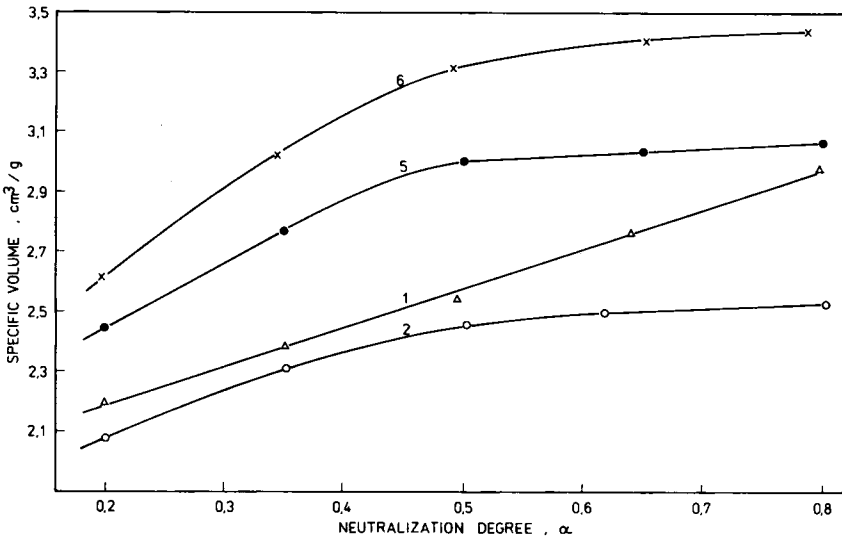Water-regain measurements are presented in Fig. 2. The amounts of water

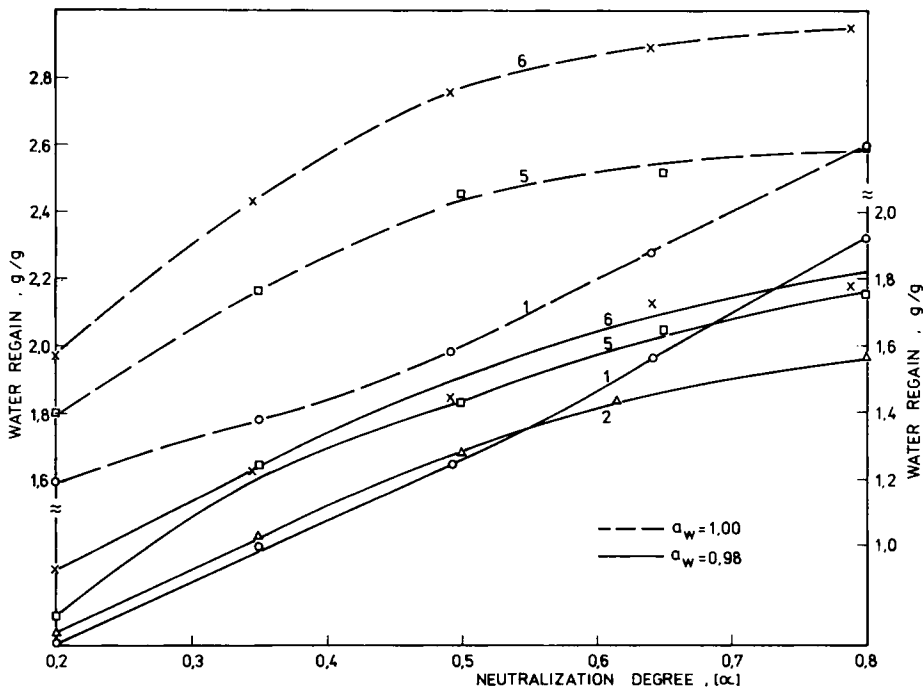Fig. 1. Specific volume of the swollen copolymers at different degrees of neutralization.

Fig. 2. Plots of the amount of water sorbed at specified water activity versus degree of neutralization.

$a_w = 1.00$ and water vapor $a_w = 0.98$ are related to the neutralization degree for each resin. The curves for both methods of measurements appear in the same order for the gel samples. This suggests that the differences in the centrifugally determined water sorptions for copolymers 2, 5, and 6 having the same chemical structure may not be explained only in the terms of a higher nongel porosity of

sample 6 over 5 and 6 and 5 over 2, as was found in the dry state.[8] In isopiestic measurements, water in gel (i.e., water-hydrating ions and so-called free water[16]) is detected.   Only a small amount of water may be sorbed as a result of a capillary effect in samples having very large pores.   If one assumes that the amount of water-hydrating ions remains constant in samples 2, 5, and 6 at a given neutralization degree, the isopiestically determined "free" water content in the samples increases according to the increase of their pore volumes in the dry state. On the other hand, the hydration of hydrophilic poly(methacrylic acid) chains is connected with their expansion freedom in the gel.[15]   Thus it is reliable that the expansion freedom is favored by increasing the pore volume in the dry copolymer.

In Figures 3–5 the specific volumes of the gel in equilibrium with aqueous NaCl solutions are shown.   The effect of NaCl solution concentration on the specific
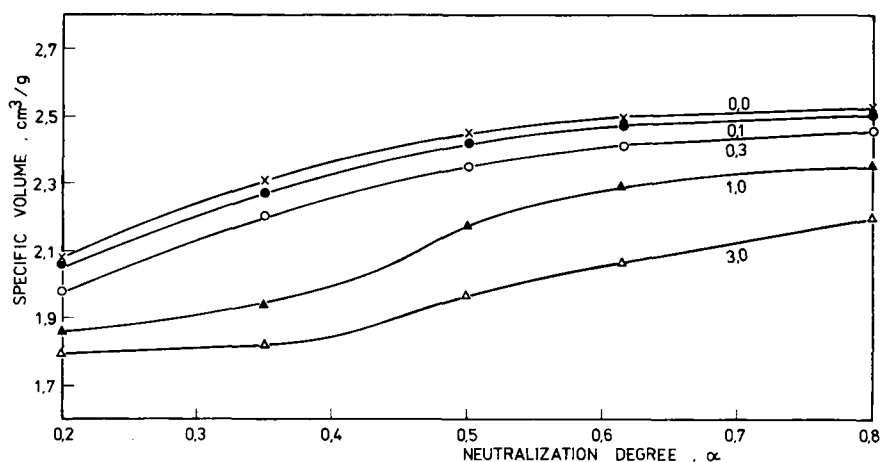

Fig. 3. Specific volume of the swollen copolymer 2 versus degree of neutralization at specified concentrations of external NaCl solutions.
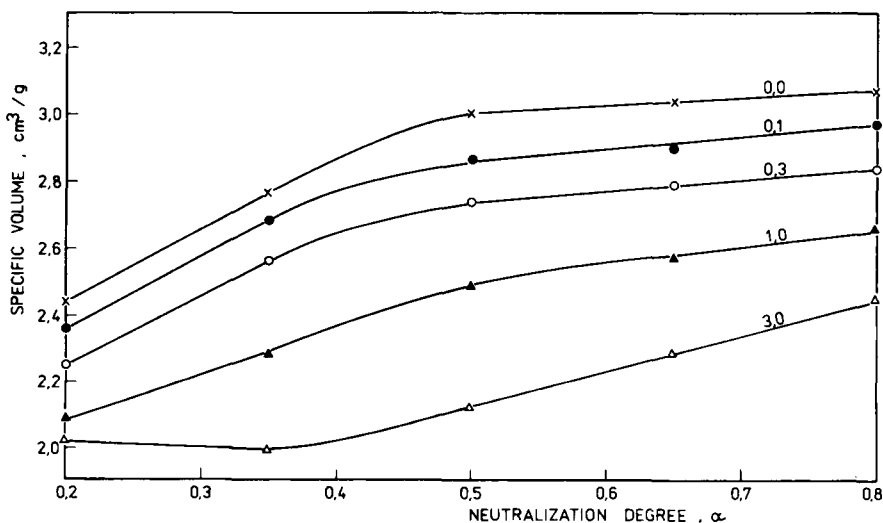

Fig. 4. Specific volume of the swollen copolymer 5 versus degree of neutralization at specified concentrations of external NaCl solutions.
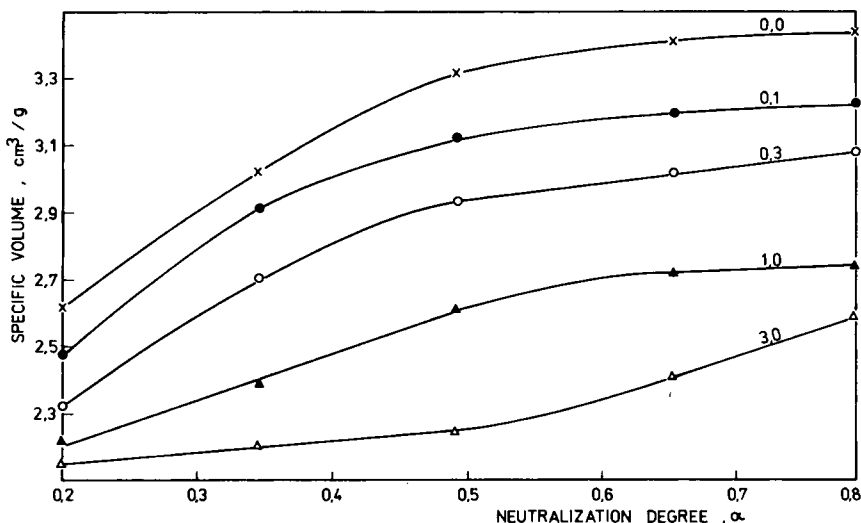
Fig. 5. Specific volume of the swollen copolymer 6 versus degree of neutralization at specified concentrations of external NaCl solutions.

volumes is small at low degrees of neutralization. For the neutralization degree of 0.35–0.70, the highest effect of the external electrolyte concentration on swelling is observed. For neutralization degrees higher than about 0.8, the swelling again does not depend strongly on NaCl concentration.

It follows from Figures 3–5 that the effect of NaCl concentration on the swelling is larger for copolymers having large pore volumes than for those with small pore volumes. This finding could also be explained on the basis of the qualitative structure model of MA-DVB copolymers accepted by us in terms of the higher expansion freedom of poly(methacrylic acid) chains in copolymers having large pore volumes in comparison with copolymers having small pore volumes in the dry state.

The conclusions presented above suggest that the macropores present in the dry poly(methacrylic acid) gels are in swollen state and occupied by the lightly crosslinked portions of the copolymer. Thus in the swollen state there are no "macropores," e.g., the portions of the swollen copolymer beads occupied by unperturbed water or an external solution.

Gustafson[9] found that in the crosslinked poly(methacrylic acid) which had 15 and 19% of voids per bead volume in the dry hydrogen and sodium form, respectively, after swelling, in 1 cm^3 of the gel 0.068 cm^3 of voids is detectable at neutralization degree of 0.5–1.0. The sodium indigosulfonate sorption method used by him, however, did not allow distinguishing between the dye solution in the voids or pores of grains and remaining at the bead surface after the centrifugation. The latter quantity always has a magnitude of several percent by volume,[10] so in fact Gustafson probably did not find the macroporosity of the swollen resin.

Glueckauf[17] has calculated that the extent to which electrostatic charges in a water-swollen ion-exchanger affect the environment is about $0.17 \mu m$. If one assumes that the electrostatic interaction has a controlling effect in the crosslinked polyelectrolytes, the distance between two neighboring chains in a "macropore" should be larger than $0.34 \mu m$. In dry poly(methacrylic acid) gels there

are macropores of such a diameter,[8] but the existence of such large nongel pores in the swollen bead seems to be impossible.

It does not mean, of course, that in water-swollen poly(methacrylic acid) gels there are no pores through which large molecules (e.g., antibiotics) may diffuse. The dimensions of those pores depend on the swelling ratio of the crosslinked polymer. The gel pores may be considered as portions of the gel occupied by the solvent solvating the polymer chains and, in the case of water-swollen poly-(methacrylic acid) gels, the portions occupied by the "free" water.

In Figure 6 the neutralization curves for samples 1, 2, 5, and 6 are presented. For the last three samples, the curves have nearly identical shape and are only shifted along the time coordinate. The rate of neutralization of poly(methacrylic acid) beads is a complex function of several parameters.[18,19] The rate-controlling factor, however, in this case is a diffusion coefficient of hydroxyl anions inside the gel.[18] Although the measurements made do not allow the exact determination of diffusion coefficients, it can be seen that their values increase in order $2 < 1 < 5 < 6$ at α values higher than 0.25.

CONCLUSIONS

Moderately crosslinked suspensions poly(methacrylic acid) gels are heterogeneous. They are composed of microgel portions having a high crosslinking density. The methacrylic acid units present in the microgels are partly inaccessible to neutralization. The fraction of the inaccessible units is the same in copolymers having the same chemical composition regardless of the swelling.
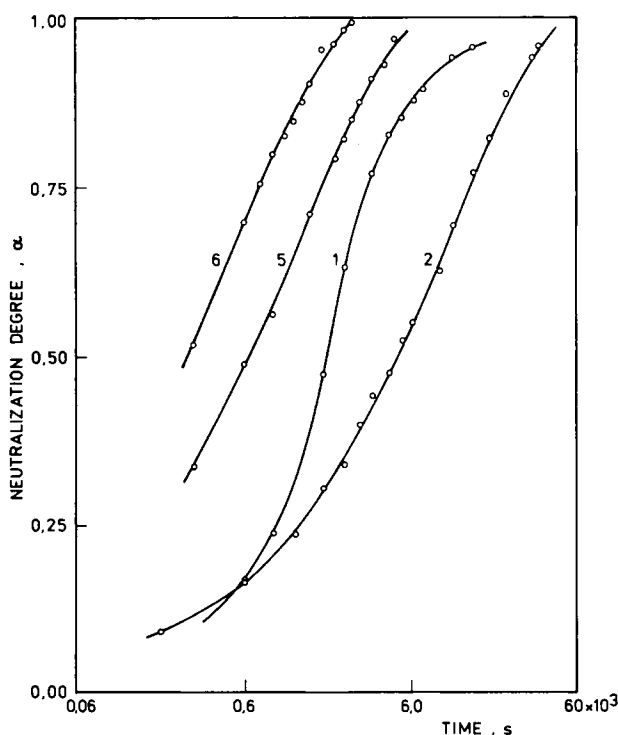

Fig. 6. Degree of neutralization of different MA-DVB copolymers versus time.

The rigid microgel regions are surrounded by crosslinked poly(methacrylic acid) containing comparatively long linear chains. A portion of this lightly crosslinked polymer can swell when immersed in water. The resulting gel tends to occupy the whole accessible space in the copolymer bead. The macropores detectable in the dry state vanish when the copolymer is placed into water.

The copolymers studied with the same composition contain essentially the same structural elements. An increase of DVB content gives an increase in the dimensions of the rigid domains, and the distances between them decrease. The copolymers obtained with a higher amount of DVB swell less than those obtained with a smaller amount of DVB. The effect of the DVB content on swelling is [in this approach] different from the effect of the crosslinking density in homogeneous networks. The amount of DVB in a copolymer determines the dimensions of rigid portions and thus the swelling of the whole copolymer grain. The expansion freedom of the linear chains in the copolymer of the type studied is determined by a distribution of those portions in space. The distribution of the microgels depends on the nature and amount of a NON-SOL diluent used in copolymerization.

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