Swelling of Porous Copolymers Based on Alkyl Methacrylate Esters in Water

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ABSTRACT: Porous copolymers based on alkyl methacrylate esters (AMA) were prepared in the presence of toluene as the inert diluent, and their swelling properties in water were investigated by measuring the water uptake of the copolymers with or without being pretreated with methanol. With ethylene glycol dimethacrylate (EGDM) being used as the crosslinking agent, the obtained AMA/EGDM copolymers, regardless of their inherent hydrophobic nature, were found to be able to swell in water directly. The swelling was negligible in the lower degree of crosslinking region. However, once it increased to a value beyond a certain EGDM percentage, the swelling transition occurred, and the water uptake, which was measured by direct contact of the copolymers with water for all three kinds of AMA/EGDM copolymers based on methyl MA (MMA), ethyl MA (EMA), and butyl MA (BMA), reached very high values. The direct swelling of highly crosslinked AMA/EGDM copolymers in water was very fast at the beginning of the swelling with the swelling rate order of MMA/EGDM > EMA/EGDM > BMA/EGDM, but thereafter it progressed very slowly with most swelling being achieved. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 250–258, 2000

Key words: porous copolymers; alkyl methacrylate esters; swelling in water; water uptake

INTRODUCTION

We recently showed that when a great amount of solvent with relatively high solvating power was used as an inert diluent, the obtained styrene-divinylbenzene (St-DVB) copolymers could swell in water in a wide range of degrees of crosslinking.[1] Because of the hydrophobicity of St-DVB copolymers, the swelling behavior of the copolymers in water cannot be investigated by measuring the swelling capacity directly in water. It is necessary to measure the swelling capacity by first immersing the copolymer in methanol and subsequently displacing methanol from the swollen copolymer by water. According to Davankov et al.,[2] the value of the swelling capacity of the hydrophobic polymer in water obtained in this way is independent of the particular solvent displaced; the measurement by this approach can therefore be considered as an appropriate establishment of the polymer–water equilibrium. They used the same method to study the water-swelling properties of hypercrosslinked polystyrene, which was prepared by crosslinking the polymer chains in solution or in a swollen state via a Friedel–Grafts reaction; thus, it had a structure completely different from that of porous St-DVB copolymers.[3,4]

The swelling experiments so far have not shown that a hydrophobic polymer can swell directly in water. In a previous study[5] we found that toluene-modified ethylvinylbenzene (EVB)-DVB copolymers could swell directly in the aque-

ous solutions of ethanol with different concentrations, depending upon the degree of crosslinking and the volume fraction of the monomers in the organic phase; when the DVB content for the EVB-DVB copolymer increased to 98%, the copolymer could swell in the water-ethanol solution with a concentration of ethanol as low as 10% (v/v); however, it still could not swell directly in water.

In the same way of thinking as Davankov et al. for their hypercrosslinked polystyrene,[3,4] we explained the direct swelling of EVB-DVB copolymers in aqueous solutions of ethanol or the indirect swelling of St-DVB copolymer in water by considering the existence of inner strains in the polymer networks.[1,5] As the St (or EVB)-DVB copolymer network is formed in a solvated state and the crosslinking reaction fixes the stretched chains, the inner strain arises and rapidly grows with the removal of the inert diluent after polymerization. Then an increase in volume of the copolymers during swelling will be favorable to the release of the strain, and the strained networks therefore drastically increase the ability of the copolymers to swell in solvents having an extremely small affinity for these copolymers.

However, being different than the hypercrosslinked polystyrene in the structure, the matrix of the porous copolymer, whether it is prepared in the presence of a solvating solvent or a nonsolvent, is composed of highly crosslinked microgel particles or small nodules linked together by less crosslinked networks.[6,7] For the copolymer with a high degree of crosslinking, even if it is prepared by using a solvating solvent as the diluent, the densely crosslinked networks of microgel particles have entirely or partially finished the course of deswelling under the strong elastic retraction during the copolymerization. These rigid microgel particles do not swell much, even in solvating solvents such as toluene. As a result, the inner strain formed inside the microgel particles in the dry state is not significant. On the contrary, less crosslinked networks between the microgel particles become strained during deswelling as a result of the retraction and deformation of the networks, and the strain increases with an increase in the degree of crosslinking to some extent.

As is well known, for the swelling of a crosslinked polymer, the energy of the interaction of the polymer chains with the solvent must be higher than the energy of the interaction between the polymer chains. The strained network, mainly in the less crosslinked domains between the microgel particles mentioned above, is supposed to greatly decrease the energy of interchain interactions as a result of the insertion of the rigid crosslinking bridges or the highly crosslinked microgel particles playing the part of "struts," which hinder the chains from approaching each other. However, for the direct swelling of the St-DVB copolymer in water, this seems to not be enough and the enhanced interaction of the polymer chains with water is needed for a hydrophobic copolymer to swell directly in water.

Therefore, we prepared a series of copolymers based on alkyl methacrylate esters (AMA), which are still hydrophobic but have a higher polarity compared with the St (or EVB)-DVB copolymers. Their swelling properties in water were investigated by measuring the water uptake directly and indirectly. The present article reports the results of these investigations.

EXPERIMENTAL

Synthesis of Copolymers

Methyl MA (MMA), ethyl MA (EMA), n-butyl MA (BMA, Shanghai General Factory of Reagents), and ethylene glycol dimethacrylate (EGDM, Su Zhou An Li Chemical Factory) were vacuum distilled before use. Technical DVB was purified according to the method of Popov and Schwachula[8] to give a purified product with 51.7% p-DVB and 46.3% m-DVB.

The copolymers based on AMA were prepared by the suspension copolymerization method with toluene as the diluent. The monomers AMA and DVB or EGDM were first mixed together with toluene to form an organic phase in which the initiator 2,2′-azobis(isobutyronitrile) was added in the amount of 1 wt % of the monomers used. The organic phase mixture was then added in a 1 : 3 volume ratio to the aqueous phase containing 0.2 wt % hydroxyethyl cellulose and 20 wt % NaCl, and the polymerization was allowed to proceed at 70 and 90°C for 14 and 4 h, respectively. The copolymers obtained were bead shaped and were washed with water and acetone and finally extracted with acetone in a Soxhlet apparatus. The acetone-swollen beads were then dried and those of 28–50 mesh in size were used for the further experiments. The copolymer samples for AMA monomers with DVB or EGDM were expressed as AMA/DVB or AMA/EGDM, respec-

tively. The amount of monomers (including crosslinking agents) for the preparation of these copolymers was all calculated as mole percents of the total monomers, and thus the degree of crosslinking was expressed as a mole percent. The dilution degree was expressed as the volume ratio of diluent to monomers. Except for additional illustrations, the copolymers were prepared with a dilution degree of 2.0.

Characterization

The apparent density (d_a) of the copolymers in the dry state was determined by an improved mercury pycnometric method as described in our previous article,[1] and the relative error of the measurement was less than 1%. The true density (d_t) was also measured by the pycnometric method but with n-heptane as the confining fluid. From the d_a and d_t the pore volume (V_p) was calculated using the equation

$$V_p = 1/d_a - 1/d_t$$

Swelling Experiments

Swelling experiments were carried out by direct contact of the copolymer sample with water in a glass filter tube (rinsing and then immersing the copolymer with water) or by first immersing the copolymer in methanol for 24 h and subsequently washing it with water to remove the methanol. After that the water uptake (V_w, mL/g) was measured with a centrifuge method also described in the previous article,[1] and the relative error was 3% or less for samples with a water uptake value of greater than 0.3 mL/g. The swelling equilibrium for direct swelling in water at 25°C was usually achieved in 2 days; but for a few samples the equilibrium time extended up to 2 weeks or more, depending upon the copolymer composition. The water uptakes of the copolymer in equilibrium with water measured directly or indirectly were denoted by V_{dw} and V_{iw}, respectively. In the dynamic swelling experiments the degree of swelling Q (%) at different times was calculated as $Q = V_{wt}/V_{dw} \times 100\%$, where V_{wt} was the water uptake at swelling time t and V_{dw} the equilibrium water uptake; both of them were measured by direct contact of the copolymer with water.

RESULTS AND DISCUSSION

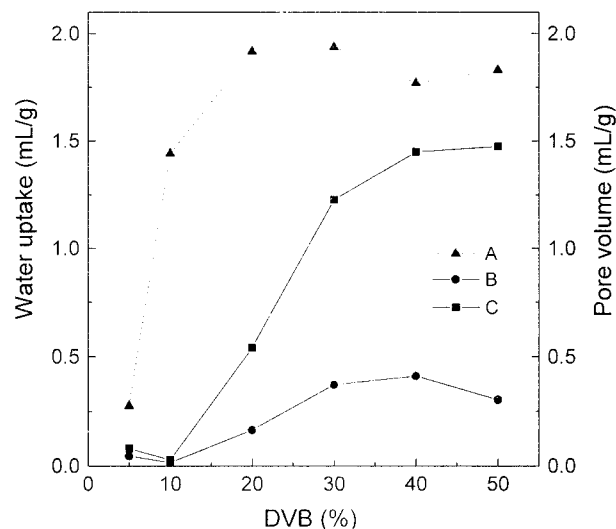The equilibrium swelling behavior of AMA-based copolymers with DVB as the crosslinking agent in

Figure 1 The dependence of the water uptakes (V_{iw} and V_{dw}) and pore volume of MMA/DVB copolymers on the DVB content: water uptake V_{iw} (curve A), water uptake V_{dw} (curve B), and pore volume (curve C).

water was first investigated by measuring the water uptake directly (V_{dw}) and indirectly (V_{iw}). As an example, Figure 1 shows the dependence of the water uptakes (V_{iw} and V_{dw}) and pore volume of MMA/DVB copolymers on the DVB content. It can be seen that, very similar to the St-DVB copolymers reported in our previous article,[1] the water uptake (V_{iw}) of MMA/DVB copolymers measured by displacing methanol from the swollen polymer (curve A) is very limited at the low DVB percentage of 5%, but beyond this degree of crosslinking the value of V_{iw} abruptly increases and the plot of V_{iw} becomes well above that of the pore volume, indicating that the water not only fills into the existing air-filled pores but also causes the expansion of the pores or the formation of new pores in the copolymer, which must be accompanied by the deformation of the polymer matrix or the relaxation of the crosslinked networks. On the contrary, the water uptake (V_{dw}) measured by direct contact of the copolymer with water (Fig. 1, curve B) just shows a small increase with the degree of crosslinking increasing to a relatively high range of DVB content and it is much less than the corresponding pore volume. The similar experiment for EMA/EGDM copolymers shows still less of an increase in water uptake (V_{dw}) than for MMA/EGDM copolymers at a high degree of crosslinking, and for BMA/EGDM copolymers the value of V_{dw} is completely negligible over the whole range of degrees of crosslinking studied.
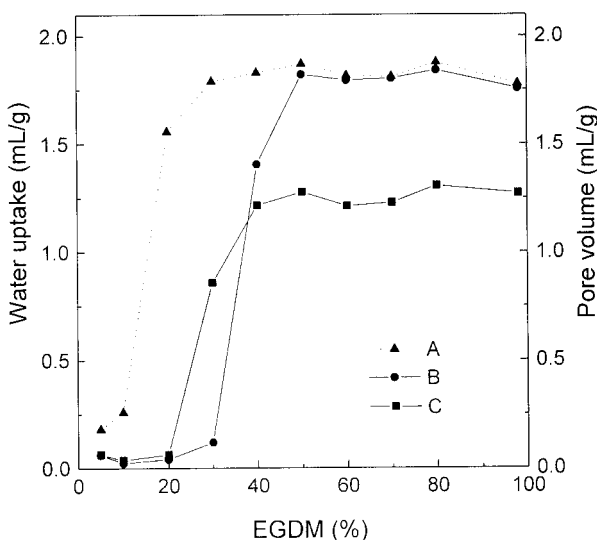
Figure 2 The dependence of the water uptakes (V_{iw} and V_{dw}) and pore volume of MMA/EGDM copolymers on the EGDM content: water uptake V_{iw} (curve A), water uptake V_{dw} (curve B), and pore volume (curve C).

Figure 2 shows the dependence of the water uptakes (V_{iw} and V_{dw}) and pore volume of MMA/EGDM copolymers on the EGDM content. As shown, when the water uptake is measured indirectly, the EGDM-dependence of the water uptake (V_{iw}) in Figure 2 (curve A) is very similar to the DVB-dependence of the water uptake (V_{iw}) in Figure 1 (curve A), and there is just a little shift of the degree of crosslinking at which the water uptake increases drastically (we call this the swelling transition degree of crosslinking later) from 5% DVB in Figure 1 to 10% EGDM in Figure 2. However, when the water uptake is measured directly, the dependence of the water uptake (V_{dw}) on the degree of crosslinking in Figure 2 (curve B), as compared with that in Figure 1 (curve B), changes greatly. At 5, 10, and 20% EGDM, the MMA/EGDM copolymers still do not swell in water by direct contact of the copolymer with water; even at 30% EGDM, the water cannot fill the pores of the copolymer. This is expected on the basis of the classical concept of the swelling of networks, because the hydrophobic MMA/EGDM copolymers present a water repellant surface and the interaction between polymer chains and water is very weak. However, for the same reason the swelling presented at a higher degree of crosslinking is striking. Note that, once the EGDM content is over a value of 30%, the water uptake (V_{dw}) increases sharply to the value that is nearly the same as that of the V_{iw} at EGDM

content of 40% or higher. Clearly, with the replacement of DVB in the MMA/DVB copolymers by EGDM, the obtained MMA/EGDM copolymers become swellable directly in water at a relatively high degree of crosslinking.

EGDM, with the component nearly the same as MMA, is less hydrophobic compared to DVB, but it still forms a hydrophobic polymer and its polarity should be very close to that of MMA; that is to say, an increase in the EGDM content in MMA/EGDM copolymers essentially does not change the interaction of the polymer chains with water. Therefore, the direct swelling in water at the degree of crosslinking beyond 30% EGDM in this case should be still sought in the structure peculiarities and the formation history of porous copolymers,[1,5] which were briefly mentioned in the Introduction of this article. Because the crosslinking reaction to form the MMA/EGDM copolymers was also conducted here in the presence of a great amount of solvating diluent (toluene), the crosslinked network formed was strained in the dry state and the strained network greatly decreased the energy of interaction between the polymer chains as mentioned earlier. With an increase in the amount of EGDM in the copolymerization system, the formed network became more rigid and therefore more strained, which led to a stronger trend of the copolymers to recover the volume where the structurization process was completed. Once the degree of crosslinking of the MMA/EGDM copolymers was over a certain value, the abrupt increase in the swelling in water occurred. In contrast to St-DVB or MMA/DVB copolymer, the fact that the MMA/EGDM copolymer becomes swellable directly in water at a relatively high degree of crosslinking shows that there are at least two factors that cause the hydrophobic copolymers to swell directly in water: one is the formation of the sufficiently strained network of the copolymers and the other is the polarity of the copolymers, even though it may be weak. With the replacement of St by MMA in St-DVB copolymers, the obtained MMA/DVB copolymers are less hydrophobic than St-DVB copolymers and the water uptake (V_{dw}) of these copolymers (see Fig. 1, curve B) thus shows a small increase with an increase in the DVB content, but the balance of forces that determines the swelling equilibrium still does not cause the MMA/DVB copolymer to swell in water directly. With a further replacement of DVB by EGDM in the MMA/DVB copolymer, the still hydrophobic matrix of the MMA/EGDM copolymer prefers a
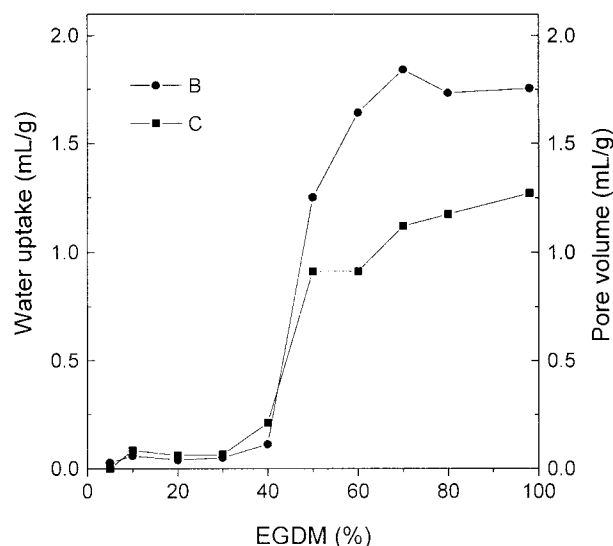
Figure 3 The dependence of the water uptake (V_{dw}) and pore volume of EMA/EGDM copolymers on the EGDM content: water uptake V_{dw} (curve B) and pore volume (curve C).

partially expanded conformation when it contacts the water directly.

From a comparison of curve B with curve A in Figure 2 we can see the relationship between the swelling capacities of MMA/EGDM copolymers in water that were measured directly and indirectly. Both the values of water uptakes V_{dw} and V_{iw} present the swelling transition but beyond different degrees of crosslinking of 30 and 10% EGDM, respectively. In the region of EGDM content below the transition degree of crosslinking, the inherent hydrophobic nature of the MMA/EGDM copolymer dominates the direct or indirect swelling in water, causing the copolymer matrix to prefer a collapsed state with the resulting exclusion of water. It is uncertain, at present, why the swelling transitions in water for the same copolymer of MMA/EGDM do not take place at the same degree of crosslinking when the swelling capacity in water was measured directly and indirectly. However, it is still noteworthy that both of the swelling curves above the swelling transitions enter nearly the same plateau where the value of V_{dw} is nearly the same as that of V_{iw}. This fact suggests that the swelling capacity in water that was measured by displacing methanol from the swollen copolymer essentially reflects a true equilibrium of the hydrophobic polymer network with water, at least in the relatively high degree of crosslinking region. The swelling experiments carried out with EMA/EGDM and BMA/EGDM

copolymers showed the same results: the value of V_{dw} was very close to that of V_{iw} in the degree of crosslinking region above the swelling transitions.

Figures 3 and 4 show the dependence of the water uptake (V_{dw}) and pore volume of EMA/EGDM and BMA/EGDM copolymers, respectively, on the EGDM content. As shown, the swelling behaviors in water for the EMA/EGDM and BMA/EGDM copolymers, which were investigated by directly measuring the water uptake, are all similar to that for the MMA/EGDM copolymers presented in Figure 2, curve B. The swelling at a lower degree of crosslinking is negligible, and the water cannot fill in the pores of the copolymers; but, beyond a certain percentage of EGDM at a relatively high degree of crosslinking, the swelling transition occurs and the water uptake (V_{dw}) reaches a value much greater than the corresponding pore volume. Because the EMA and BMA monomers in the EMA/EGDM and BMA/EGDM copolymers are more hydrophobic than the MMA in MMA/EGDM copolymers, the above results provide further evidence in favor of the finding in Figure 2 that the hydrophobic copolymers could swell in water directly in some conditions.

However, if we make a comparison of Figures 2–4 we can find that the swelling transition degrees of crosslinking are clearly different for these three kinds of copolymers. The transition degrees
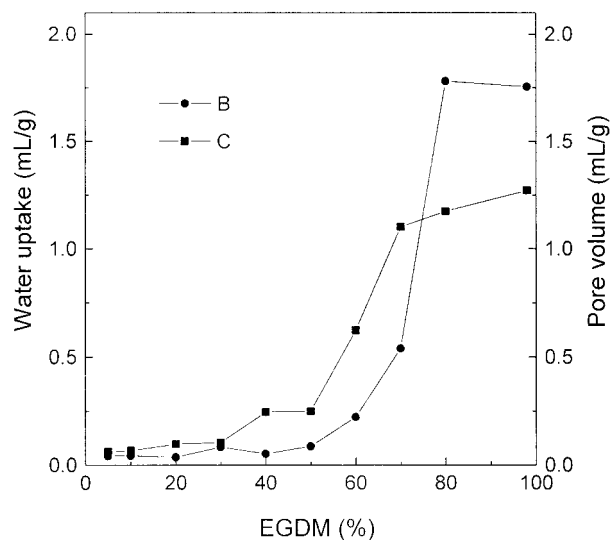

Figure 4 The dependence of the water uptake (V_{dw}) and pore volume of BMA/EGDM copolymers on the EGDM content: water uptake V_{dw} (curve B) and pore volume (curve C).

of crosslinking shift systematically from 30 to 60% EGDM as the alkyl side chain lengths of the AMA monomers increase from C_1 to C_4. We could probably first attribute this shift to the hydrophobicity or the polarity of the copolymers; the hydrophobicity of these three kinds of copolymers is in the order BMA/EGDM > EMA/EGDM > MA/EGDM. On the basis of the knowledge that an increase in the hydrophobicity of the copolymers reduces the interaction of polymer chains with water and, on the other hand, the inner strain is thought to increase with an increase in the degree of crosslinking that is in favor of the swelling of hydrophobic copolymers in water as mentioned earlier, it is reasonable that the swelling transition degree of crosslinking shifts from low to high EGDM percentage with an increase in the alkyl side chain lengths of AMA monomers.

Our opinion is that another cause of the upward shift of the transition degree of crosslinking from 30 to 60% EGDM for AMA/EGDM copolymers should be sought in the additional structure difference of these AMA-based copolymers. As we know, the n-alkyl ester side chain in the methacrylic esters is a flexible one, which functions as a plasticizer and contributes to the flexibility of the polymer chains of the copolymers. Because the volume occupied by the alkyl side chain is n-butyl > ethyl > methyl, the rigidity of the polymer chains for the copolymers with the same crosslinking degree should be in the order MMA/EGDM > EMA/EGDM > BMA/EGDM, which agrees well with the value of the glass-transition temperature (T_g) of the corresponding homopolymers of MMA, EMA, and BMA. The T_gs for PMMA, PEMA, and PBMA are 105, 65, and 21°C, respectively). The rigidity of the crosslinked networks for the copolymers is known to exert an important influence on the inner strain in the networks and, in turn, on the swelling of the copolymers in solvents.[3,4] Therefore, the swelling transition in water for MMA/EGDM copolymers with the most rigid networks occurs at a lower degree of crosslinking than the other two kinds of copolymers in question, and the transition degree of crosslinking for BMA/EGDM copolymers is the highest among the three. In an additional experiment we investigated the swelling behavior of AMA/EGDM copolymers in the organic solvent methanol. In this case the difference of the hydrophobicity among MMA/EGDM, EMA/EGDM, and BMA/EGDM copolymers is not an important factor influencing their swelling behavior, but the transition degree of crosslinking in methanol also
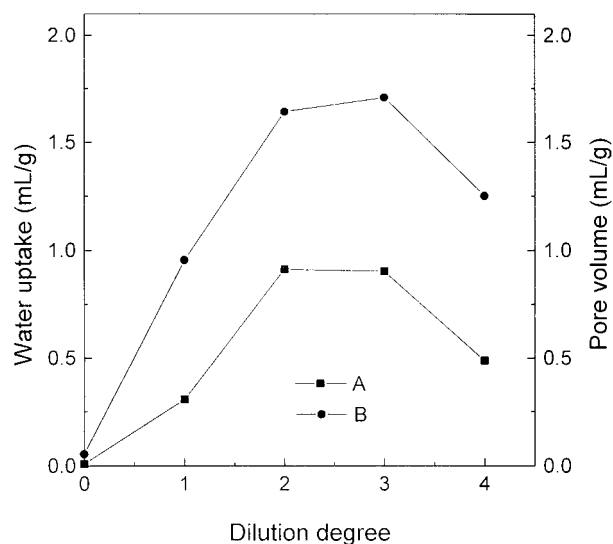

Figure 5 The dependence of the water uptake (V_{dw}) and pore volume of EMA/EGDM copolymers with 60% EGDM on the EGDM content: water uptake V_{dw} (curve A) and pore volume (curve B).

shifts from 10 to 30% EGDM as the alkyl side chain length of the AMA monomers increases from C_1 to C_4. Such a shift must be attributed to the different rigidity of the polymer chains between the AMA-based copolymers and thus supports the interpretation of the shift of the swelling transition degree of crosslinking in water mentioned above. Of course, because of the effect of the hydrophobicity, the shift of the transition degree of crosslinking in water is greater than that in methanol.

The swelling capacity of a porous copolymer is usually affected by the amount of diluent used in the copolymerization. A similar effect of the amount of diluent on the direct swelling of the hydrophobic copolymers in water was also observed. Figure 5 shows the dependence of the water uptake (V_{dw}) and pore volume of 60% EGDM EMA/EGDM copolymers on the dilution degree. It is seen that the water uptake and pore volume increase rapidly with an increase in the dilution degree up to 2.0, and at the dilution degree beyond 3.0 they tend to also decrease rapidly. Except when the copolymer is prepared in the absence of toluene as the diluent (dilution degree = 0), the value of the water uptake (V_{dw}) is much greater than the corresponding pore volume of copolymers at other dilution degrees, indicating that a direct swelling in water occurs for all these EMA/EGDM copolymers. The differences between the water uptake (V_{dw}) and pore volume at
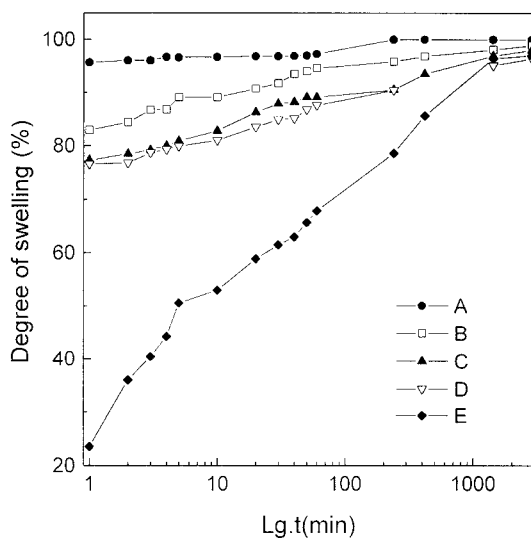
Figure 6 The dynamic swelling behavior of MMA/
EGDM copolymers with different degrees of crosslink-
ing in water. The degree of swelling was measured by
direct contact of the copolymer with water, and it was
plotted against the logarithmic contact time. EGDM
content (%) 80 (curve A), 70 (curve B), 60 (curve C), 50
(curve D), and 40 (curve E).

dilution degrees of 0, 1.0, 2.0, 3.0, and 4.0 are
0.019, 0.404, 0.486, 0.561, and 0.520, respectively.
The decrease in the difference value, as well as
the water uptake (V_{dw}) and pore volume, at a
dilution degree beyond 3.0 is supposed to be
caused by the formation of a less rigid network in
the presence of an excess of solvating diluent;
thus, it is expected that the difference between
the water uptake (V_{dw}) and pore volume will in-
crease with a further increase in the degree of
crosslinking.

The direct swelling of AMA/EGDM copolymers
in water also shows a difference in the dynamic
swelling behavior of the copolymers with different
crosslinking degrees and different alkyl side
chain lengths of the AMA monomers. Figure 6
shows the dynamic swelling behavior of MMA/
EGDM copolymers with different degrees of
crosslinking in water. The degree of swelling was
measured by direct contact of the copolymer with
water (as mentioned in the Experimental section)
and was plotted against the logarithmic contact
time. As shown, just as with the equilibrium
swelling in water presented in Figure 2 (curve B),
the dynamic swelling in water in Figure 6 is also
dependent on the degree of crosslinking; with an
increase in the content of EGDM, the rate of
swelling increases. In addition, the swelling rate

shows a transition in this figure. For the copoly-
mer with 40% EGDM the swelling is very slow; it
takes 420 min (7 h) for the degree of swelling to
reach a value of 85.6%. The corresponding water
uptake at this degree of swelling is 1.204 mL/g,
which is very close to the 1.217 mL/g pore volume
of this copolymer. Because the MMA/EGDM co-
polymers usually present a water repellant sur-
face, it is expected that the water cannot pene-
trate into the pores of the copolymer at a signifi-
cant rate and much more time is needed for this
polymer to reach an equilibrium value of the wa-
ter uptake of 1.406 mL/g. However, beyond the
degree of crosslinking of 40%, the swelling rate
rapidly increases, showing a swelling transition
between 40 and 50% EGDM, which correlates
well with the equilibrium swelling transition in
Figure 2 (curve B). However, by making a further
comparison between curve B in Figure 2 and the
curves in Figure 6 we can see that, although the
swelling capacity at 50% EGDM and higher in
Figure 2 (curve B) is essentially the same, the
swelling rate in the same range of EGDM content
in Figure 6 is very different. The time for copoly-
mers with 80 and 70% EGDM to reach the swell-
ing equilibrium (degree of swelling = 100%) is
240 min (4 h) and 2880 min (48 h), respectively,
and for copolymers with 60 and 50% EGDM more
than 48 h is needed.

It is more interesting to see that, at the con-
tact time with water of just 1 min, the degrees
of swelling for the MMA/EGDM copolymers
with 50–70% EGDM reached high values from
76.6 to 82.9% and with 80% EGDM the degree of
swelling reached a value of 95.7%, which is very
close to the equilibrium value of 100%. In brief,
the swelling of these MMA/EGDM copolymers
in water takes place and reaches the very high
degree of swelling the moment the copolymers
contact the water. It is a common phenomenon
for porous copolymers to swell very quickly in
organic solvents. However, for the direct swell-
ing of the hydrophobic copolymers in water, the
result is really striking. The water uptakes cor-
responding to the degrees of swelling of 76.6,
77.3, 82.9, and 95.7% for MMA/EGDM copoly-
mers with EGDM contents of 50, 60, 70, and
80% are 1.395, 1.387, 1.494, and 1.762 mL/g,
respectively; all of these water uptake values
are greater than the corresponding pore vol-
umes of 1.278, 1.214, 1.229, and 1.307 mL/g for
the same copolymers. We think this fact could
also be interpreted by taking into account the
structure peculiarities of the copolymers and

the existence of the inner strain in the polymer networks formed in the presence of a great amount of the solvating solvent toluene. The matrix of the porous copolymers (as mentioned in the Introduction) is composed of highly crosslinked microgel particles linked together by less crosslinked networks, and the volume variation of the swelling copolymers could be considered to mainly result from the expansion of the less crosslinked domains. Because the strained networks (mainly between the highly crosslinked microgel particles) have a strong tendency to release the strain and because the interaction between the polymer chains is strongly weakened as a result of the insertion of the rigid crosslinking bridges or the highly crosslinked microgel particles, it is easy to understand that the swelling in the less crosslinked domains is easy and fast and therefore most of the swelling of the copolymers is achieved in a very short contact time of the copolymers with water. Because the densely crosslinked networks of microgel particles entirely or partially finished the course of deswelling during the copolymerization, the swelling in the highly crosslinked domains would not be significant and should be slow, which therefore gives the interpretation of the characteristic feature of these swelling curves (other than the curve of 40% EGDM) in Figure 6 that, once most of the swelling is rapidly achieved, the swelling progresses thereafter at a very slow rate.

Figure 7 shows the dynamic swelling behavior of AMA/EGDM copolymers with different alkyl side chain lengths of AMA monomers in water. The degree of swelling for copolymers with an EGDM content of 80% was also plotted against the logarithmic contact time. In a comparison of the equilibrium swelling behaviors of AMA/EGDM copolymers in Figures 2–4, a systematic shift of the swelling transition degree of crosslinking from 30 to 60% EGDM was previously observed as the alkyl side chain length of AMA monomers increased from C_1 to C_4. In Figure 7 we can see that the swelling rate changed with the same trend of it being the highest for the MMA/EGDM copolymer followed by the EMA/EGDM copolymer, and it is the lowest for the BMA/EGDM copolymer. Here we can also attribute the difference in the swelling rate to the difference in the hydrophobicity among the different kinds of AMA-based copolymers and to the rigidity of AMA monomers with different alkyl side chain lengths. Among the three kinds of copolymers, the
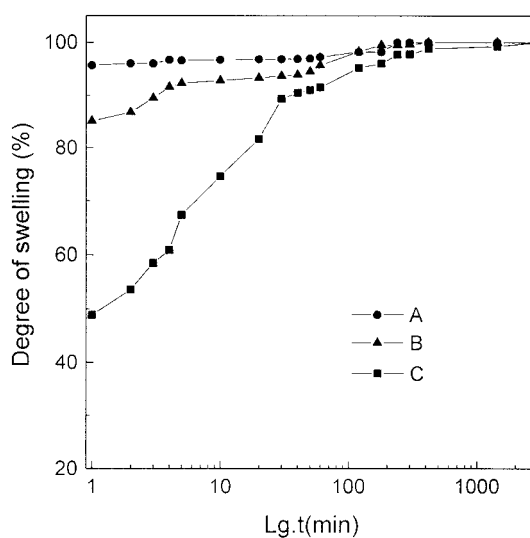

Figure 7 The dynamic swelling behavior of AMA/EGDM copolymers with different alkyl side chain lengths of AMA monomers in water. The degree of swelling for copolymers with 80% EGDM was measured by direct contact of the copolymer with water, and it was plotted against the logarithmic contact time. Copolymers: MMA/EGDM (curve A), EMA/EGDM (curve B), and BMA/EGDM (curve C).

BMA/EGDM copolymer is the one with the strongest hydrophobicity and the lowest rigidity of the polymer chains and therefore the lowest rate of swelling.

CONCLUSIONS

When AMA/EGDM copolymers are prepared in the presence of a large amount of solvating solvent as the diluent, they can swell in water directly at a relatively high degree of crosslinking. In the lower EGDM content region, the inherent hydrophobicity of the copolymers dominates the swelling, causing the matrix of the copolymer to prefer a collapsed state with the resulting exclusion of water. However, once the degree of crosslinking increases and reaches a certain percentage of EGDM, regardless of the hydrophobic nature of the copolymers, the swelling transition occurs. The swelling curves for MMA/EGDM, EMA/EGDM, and BMA/EGDM copolymers enter their respective final plateaus where the water uptake measured directly for these three kinds of AMA/EGDM copolymers is nearly the same as that measured indirectly. The swelling transition degree of

crosslinking is different for the different kinds of AMA/EGDM copolymers, and the order is MMA/EGDM < EMA/EGDM < BMA/EGDM. The studies on the dynamic swelling of AMA/EGDM copolymers show that, with an increase in the degree of crosslinking, the swelling rate also presents a transition at a certain EGDM percentage. Above this percentage the swelling is very fast at the beginning, rapidly reaches a high degree of swelling value, and then progresses at a very low rate. The swelling rate is highest for the MMA/EGDM copolymer followed by the EMA/EGDM copolymer and the BMA/EGDM copolymer, which is the lowest. The direct swelling of AMA/EGDM copolymers in water was also attributed to the structure peculiarities of the copolymers and the existence of the inner strain in the polymer networks formed in the presence of a great amount of solvating solvent.

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