

# Gelatin-Based Composite Polymers

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## SYNOPSIS

Composite polymers containing gelatin and polymethyl methacrylate (PMMA) have been prepared by employing a gel pathway. The gels have been obtained by mixing mechanically at 50°C an aqueous solution of gelatin containing a surfactant (sodium dodecylsulphate, SDS) with a monomer (methyl methacrylate, MMA) containing an initiator (AIBN). Two kinds of gels have been identified: high-viscosity liquid gels, which lose their stability after half to two hours at room temperature, and solid-type gels, which maintain their stability for a long time at room temperature. Composite polymer materials have been obtained by the polymerization of MMA in these gels. The polymerization of liquid-type gels has been carried out in two steps: under mixing for the first hour and without mixing for 23 h. The polymerization of the solid-type gels was performed in two different ways: (1) at room temperature for a few days followed by heating at 50°C for 4 h, and (2) the same procedure as for the liquid-type gels (since at 50°C the solid-type gels transform in liquid-type gels). The phase behavior of the gels was investigated and scanning electron microscopy (SEM) was used to examine the morphology of the composite polymers. The swelling experiments have shown that at suitable gelatin concentrations, these composites are insoluble in water, methanol, octane, and cyclohexane but have a relatively high solubility in toluene.

## INTRODUCTION

Composite polymers can be prepared by mechanical blending, solvent casting, or by generating interpenetrating polymer networks.<sup>1-3</sup> There are, in general, difficulties in mixing homogeneously two polymers that exhibit pronounced incompatibility. In recent years emulsion and concentrated emulsion pathways<sup>4-8</sup> have been employed in order to mix at colloidal scale hydrophilic and hydrophobic polymers. It is important to emphasize that the incompatibility of the two monomer phases is a condition for the formation of an emulsion. In the concentrated emulsion pathway, stable emulsions with the appearance of gels have been prepared by dispersing a phase containing a hydrophobic (hydrophilic) monomer into a continuous phase containing a hydrophilic (hydrophobic) monomer and a suitable surfactant. Each of the phases contained an appropriate initiator. The volume fraction of the dispersed

phase is greater than 0.74 (the volume fraction of the most compact arrangement of spheres of equal radius) and can be as large as 0.99.

In the present study a different gel pathway is developed for the preparation of a composite polymer consisting of the incompatible polymer pair of gelatin and PMMA. Gelatin is a natural water-soluble polypeptide (a biopolymer) and PMMA is a rather hydrophobic polymer. Because of their incompatibility, a gel pathway was developed via an emulsion process. It is well known that kinetically or thermodynamically stable oil in water (O/W) or water in oil (W/O) emulsions can be produced by mixing suitable amounts of water and oil with an emulsifier and sometimes a coemulsifier. It was expected that polymerizable stable emulsions could be produced by using MMA (a hydrophobic monomer) instead of oil and an aqueous solution of a surfactant (SDS) and gelatin instead of water. Depending on the gelatin concentration, two types of emulsions with the appearance of a gel have been obtained: high-viscosity liquid-type gels and solid-type gels that exhibit viscoelastic properties. The liquid-type gels are less stable than the solid-type gels. The

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former separate into two phases after about half to two hours at room temperature. The latter are rather stable since their storage for a long time at room temperature does not lead to two separated phases; some of them are transparent at room temperature. The solid-type gels transform, however, into liquid-type gels at 50°C and separate into two phases after about half hour. Composite polymers have been finally obtained by polymerizing MMA in these gels. This work presents the preparation procedure of composite polymers by the new gel pathway, the phase behavior of these gels, and some of the characteristics of the obtained polymers.

## EXPERIMENTAL

### Materials

Methyl methacrylate (Aldrich Chemical Co.) was purified by distillation under reduced pressure. The initiator, azobisisobutyronitrile (AIBN, Alfa Chemical Co.) was purified by recrystallization in methanol. Sodium dodecylsulphate (SDS, Aldrich) and gelatin (300 bloom, Alfa Chemical Co.) were used as received. Water was deionized and double distilled.

### Scanning Electron Microscopy

Scanning electron microscopy (SEM) was employed to examine the morphology of the prepared com-

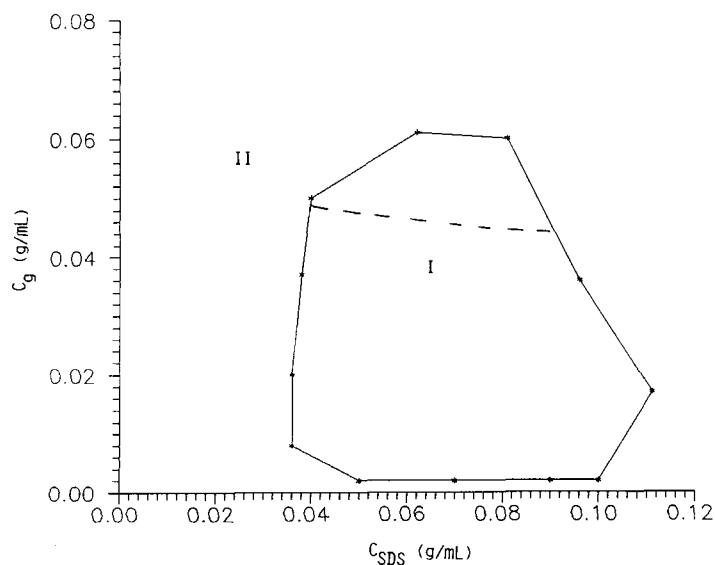
posite polymers. The samples were prepared for SEM by fracturing the composite polymers. The fractured pieces were mounted on SEM stubs using colloidal graphite cement. The samples were sputter-coated with a thin layer of gold before investigation.

### The Swelling Test

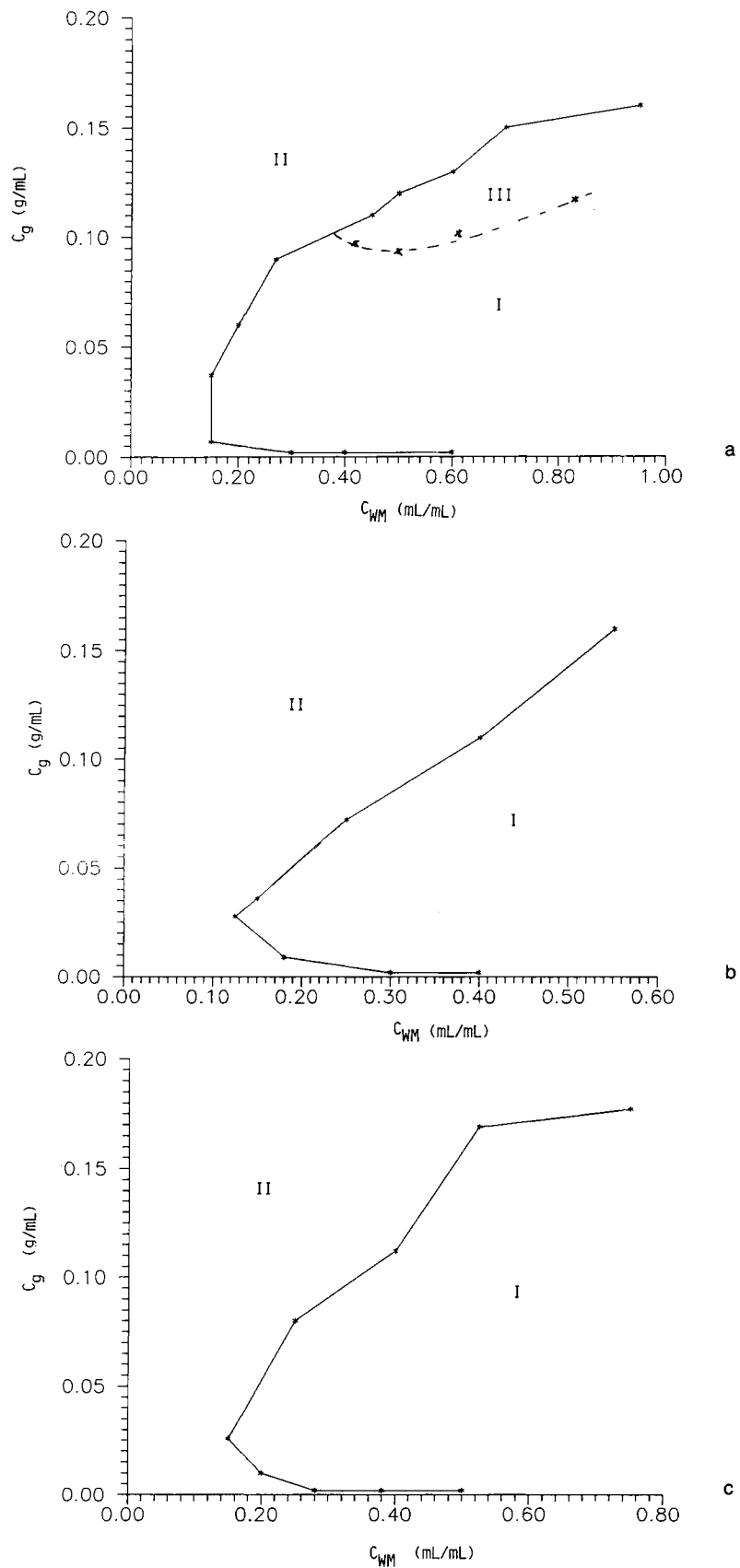
Samples of dried composites were weighed and placed in glass tubes containing the respective solvent. After 24 h, the weights of the swollen samples were determined. The swelling ratio of the samples was calculated using the expression  $S = (W_S - W_0)/W_0$ , where  $W_0$  and  $W_S$  are the weights of the dried (after swelling) and swollen samples, respectively.

### Gel Preparation

For the preparation of the stock solutions, weighted amounts of surfactant (SDS) and initiator (AIBN) were dissolved in water and monomer (MMA), respectively. Further, the aqueous solutions of SDS were introduced in glass tubes containing gelatin. The glass tubes were placed in a water bath at 50°C for 30 min to 1 h and stirred continuously with a mechanical mixer till the solution became homogeneous. The monomer containing AIBN was then introduced in the glass tubes. Gels were finally obtained by the intensive stirring of the aqueous solution of gelatin and SDS with the monomer under



**Figure 1** Phase diagram of the system composed of the monomer MMA and an aqueous solution of SDS and gelatin in the representation gelatin concentration in the entire gel ( $C_g$ ) vs. SDS concentration ( $C_{SDS}$ ) in the entire gel, for a volume ratio 0.15 mL/mL of water to MMA. Region I is the gel region, region II is the two-phase region. The dashed line separates region I in two domains; the solid-type gels (upper domain) and the liquid-type gels.



**Figure 2** Phase diagram of the system composed of the monomer MMA and an aqueous solution of SDS and gelatin in the representation gelatin concentration ( $C_g$ ) in the gel against volume ratio ( $C_{WM}$ ) of aqueous solution of dispersant (SDS) to MMA. Region I is the gel region, region II is the two phase region, and III is the transparent gel domain. In Figures 2 (a), (b), and (c) the concentration of the aqueous solution of SDS is 1.0, 0.5, and 0.15 mol/L, respectively.

heating at 50°C for about 15 min. It should be emphasized that the gels cannot be prepared at room temperature because the aqueous solutions of gelatin and surfactant have a too high viscosity and cannot be mixed with the monomer.

## RESULTS AND DISCUSSION

Figure 1 is a phase diagram for gel formation in which the concentration of gelatin in the system,  $C_g$  (g/mL), is plotted versus the concentration of dispersant (SDS) in the system,  $C_{SDS}$  (g/mL), at a fixed volume ratio of water to monomer. Gels form in region I but do not form in region II. These gels were prepared at 50°C, but after preparation they were kept at room temperature. Region I contains two types of gels: high-viscosity liquid-type gels that lose their stability (separate into two phases) after half to two hours and solid-type gels that maintain their stability for a long time. The dashed curve provides some indications in this direction, the domain above the curve being more likely to lead to solid-type gels. A minimum amount of surfactant is necessary to generate a gel. However, if the concentration of surfactant becomes too large, gels are no longer obtained. This is probably due to the high viscosity of the aqueous surfactant solution, which opposes the dispersion of one phase into the other. Similarly, a minimum amount of gelatin is needed to generate a gel and a too high gelatin concentration has a negative effect. Probably the high rigidity of the aqueous gelatin-surfactant network in these systems does not allow the dispersion of one phase into the other.

The concentration  $C_g$  of gelatin in the system versus the volume ratio  $C_{WM}$  of the aqueous solution of SDS to monomer is plotted at constant SDS concentration in Figure 2. The tongue-like region (I)

in these figures represents the gel-forming domain. Beyond this domain, the system separates into two phases (region II). The figures show that gel does not form at any gelatin concentration when the ratio of the volumes of water (plus SDS) to monomer is too small. The gel-forming domain widens with respect to gelatin concentration upon increasing the amount of water. As in Figure 1, in the gel-forming domain, the gels behave like liquids at lower gelatin concentrations and have a low stability, and like solids when the contents of gelatin and water are high and have a high stability at room temperature. The elastic characteristics of these solid-type gels can be recognized by simple shaking. Transparent gels have been found in the upper right region (III) of Figure 2 (a). The transparent gels are very stable. Their storage for many months at room temperature did not lead to two phases; their melting temperature estimated by a ball-falling method is around 36°C. It is important to emphasize that the gelatin plays a major role in the stability of the gels. Indeed, in the absence of gelatin, the mixtures of MMA and aqueous solution of SDS separate into two phases as soon as the mechanical mixing is stopped.

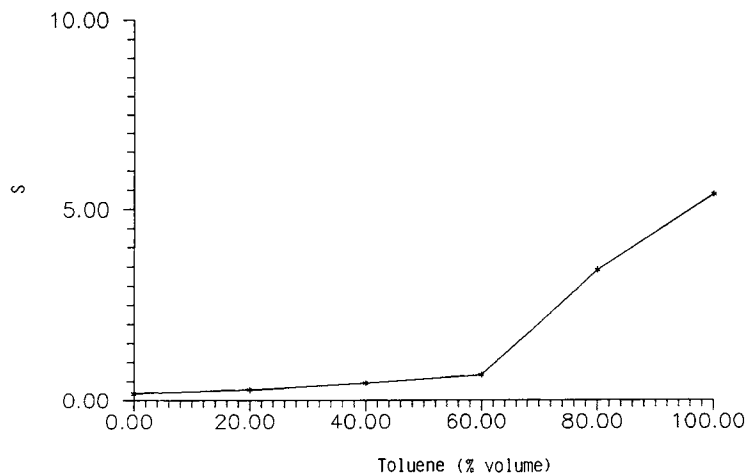
Composite polymers have been finally prepared by the polymerization of the monomer MMA in the gels. For the liquid-type gels a partial polymerization had to be conducted at 50°C for 30–60 min under stirring (in order to prevent phase separation), followed by polymerization at the same temperature for 23 h without stirring. For the solid-type gels, polymerization could be performed in two different ways: (1) at room temperature for 5–7 days followed by heating at 50°C for about 4 h, and (2) at 50°C using the same procedure as for liquid-type gels (since the solid-type gels transform in liquid-type gels at 50°C). During polymerization, no large-scale phase separation, i.e., two-phase separation, has been observed. Phase separation at small scale still

**Table I Swelling of Composites in Different Solvents, in 24 h**

Solvent Sample <sup>a</sup>	Water	Methanol	Octane	Cyclohexane	Toluene
1	0.210	0.250	0.200	0.222	Soluble
2	0.233	0.248	0.209	0.250	Soluble
3	0.256	0.217	0.170	0.177	5.370
4	0.442	0.468	0.365	0.374	1.650 <sup>b</sup>

<sup>a</sup> The compositions of samples 1, 2, 3, and 4 are  $C_g = 0.017, 0.050, 0.062, 0.072$  g/mL, respectively;  $C_{WM} = 0.50$  mL/mL;  $C_{SDSW} = 1.00$  mol/L and  $C_{AIBN} = 0.25$  mol/L.

<sup>b</sup> Sample 4 decreased its weight by 11% during immersion in toluene for 48 h. The immersion of this and the other three samples in the other solvents listed does not decrease the weight of the samples.

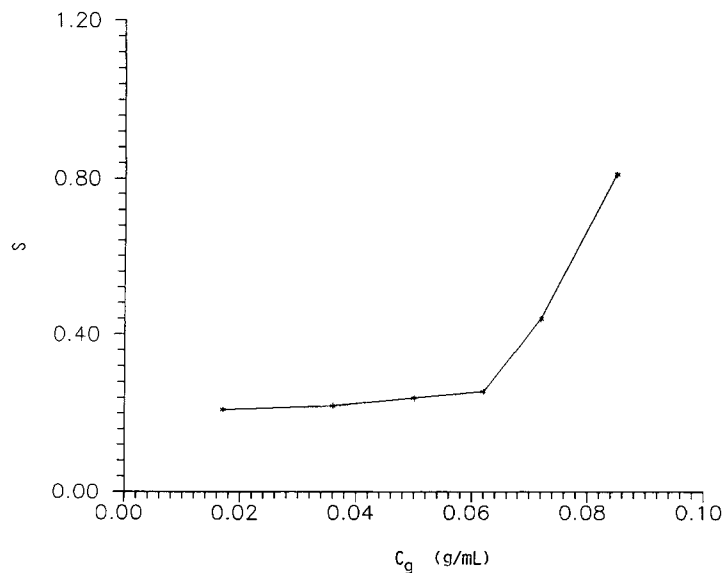


**Figure 3** The swelling of a typical composite sample in cyclohexane–toluene mixtures at room temperature. Composition:  $C_g = 0.062$  g/mL;  $C_{WM} = 0.50$  mL/mL;  $C_{SDSW}$  (the concentration of surfactant in water) = 1.00 mol/L; and  $C_{AIBN}$  (the concentration of AIBN in monomer) = 0.25 mol/L.

might have occurred and may be partly responsible for the transformation of the transparent gels into translucent or opaque solids after the completion of polymerization.

After polymerization, the solid composite polymers have been subjected to drying either in vacuum or in air, at room temperature. Cracks have appeared on the surface of the materials during their drying under vacuum, and the mechanical strength of the

composites dried under vacuum was poor. The occurrence of cracks is probably a result of the fast evaporation of water and of the residual monomer, which destroyed the structure of these materials. Therefore, a mild drying process under ambient conditions is recommended. The mechanical strength of the composite polymers before drying is relatively weak. After drying for several days, at room temperature, in air, the materials became



**Figure 4** The dependence of swelling of the composite in water on the gelatin concentrations. Composition:  $C_{WM} = 0.50$  mL/mL;  $C_{SDSW} = 1.00$  mol/L;  $C_{AIBN} = 0.25$  mol/L.

lighter in weight and stronger. Some of the dried materials are rather strong and can be hardly broken by hand.

The obtained composite polymers have some interesting properties. At suitable gelatin concentrations, they are insoluble in octane, cyclohexane, methanol, and water. In addition, their swelling in these liquids is small. Table I contains swelling data for typical samples in different solvents. These materials absorb small amounts of water, methanol, octane, and cyclohexane. The composite polymers with low content in gelatin are, however, soluble in toluene. Sample 4 of table I, which contains a somewhat larger amount of gelatin, has lost 11% of its weight after being immersed for 48 h in toluene.

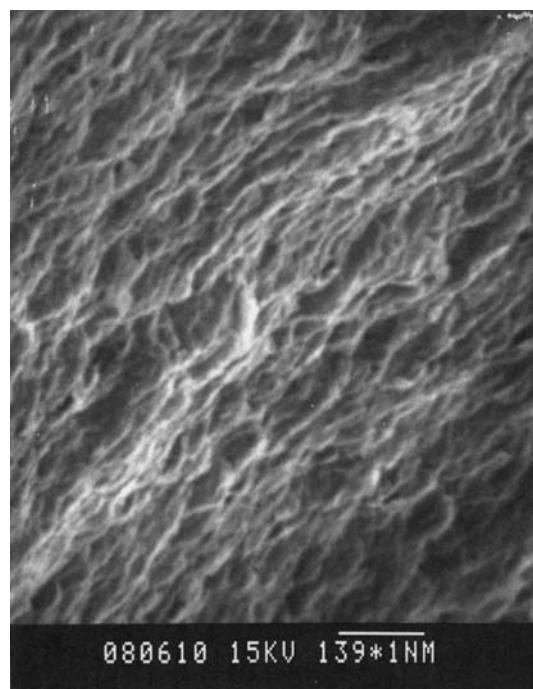
Figure 3 presents the swelling behavior of a sample in a cyclohexane-toluene mixture. The swelling increases as the content of toluene increases. This selective absorption indicates that these materials can be potentially used for membrane separation of aromatics from aliphatics or saturated cyclic solvents if crosslinking could be used to avoid the dissolution of PMMA in aromatics.

Figure 4 shows that the composite materials with high gelatin content absorb water, but the amount absorbed is not too large.

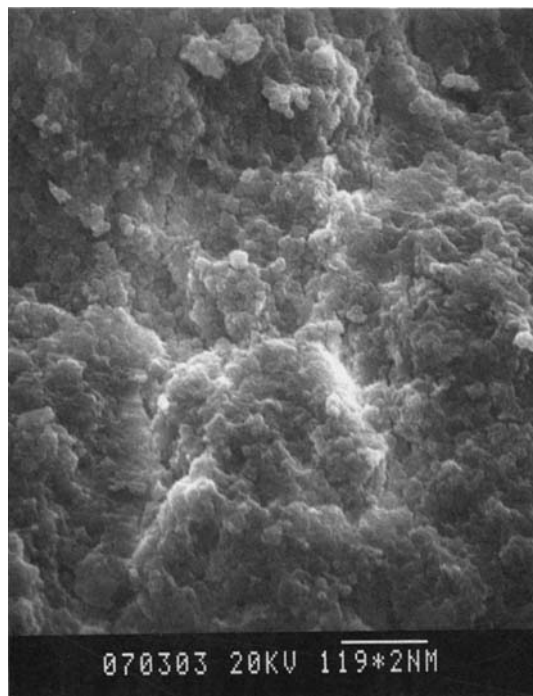
It should be noted that PMMA is soluble in toluene. The present composites, which contain both PMMA and gelatin, become less soluble and exhibit some swelling in toluene. This suggests that interpenetrating networks are formed. Perhaps a gelatin network was generated before and remained even after polymerization at least in the high gelatin content samples. The fact that the composite materials with low gelatin content are soluble in toluene implies that they do not possess a gelatin network.

Scanning electron microscopy (SEM) was used to examine the morphology of the composite polymers. The SEM picture Figure 5(a) of a fractured composite polymer sample indicates a network structure that might be a gelatin network. Most of the PMMA is probably located in the meshes of the gelatin network. The differentiation between the two polymer phases in the composite material cannot be made with SEM (it could probably be made with transmission electron microscopy (TEM) after staining one of the polymer phases selectively). In the SEM picture [Fig. 5(b)], which is for a material with a low gelatin content, one can no longer identify a network; instead, one can identify a large number of small particles in contact.

It is not yet clear whether some of MMA molecules have been chemically grafted to the gelatin



(a)



(b)

**Figure 5** Electron micrographs of some composites before drying. The compositions of specimens (a) and (b) are, respectively,  $C_g = 0.067$  and  $0.032$  g/mL;  $C_{WM} = 0.40$  mL/mL;  $C_{SDSW} = 1.0$  mol/L and  $C_{AIBN} 0.25$  mol/L.

network. It is, however, relevant to note that the composite polymer samples with relatively high gelatin content have lost little weight after their swelling in toluene and drying. This may indicate that at least some MMA molecules have been grafted on the gelatin network.

## CONCLUSION

A gel pathway has been employed to prepare composite polymers containing gelatin and PMMA. The gels have been prepared by mechanical mixing at 50°C an aqueous solution of surfactant and gelatin with the monomer MMA. The gels prepared at 50°C have been kept at room temperature. Two classes of gels have been obtained at room temperature: high-viscosity liquid-type gels at low gelatin concentrations and solid-type gels with melting points around 36°C at higher gelatin concentrations. The liquid gels lose their stability after about half to two hours. For this reason their polymerization had to be carried out at 50°C in two steps: 1 h under stirring followed by 23 h without stirring. For solid-type gels polymerization could be either conducted at 50°C using the same procedure as for the liquid-type gels (since they transform into liquids at this temperature) or without stirring at room temperature for a few days followed by heating at 50°C for 4 h. At suitable gelatin contents, these composite polymers are insoluble in octane, cyclohexane, methanol, and water and have rather strong mechanical strength. At low gelatin contents, they are soluble in toluene; the solubility decreases with increasing gelatin content. A slow ambient drying of these composites is recommended in order to prevent the generation of cracks during the evaporation of water and residual

monomers. The swelling test as well as the SEM pictures suggest that probably a gelatin network is generated in the composite polymers with high gelatin content.

## NOTATIONS

$C_g$	the concentration of gelatin in the entire gel (g/mL)
$C_{SDS}$	the concentration of SDS in the entire gel (g/mL)
$C_{SDSW}$	the concentration of SDS in water (mol/L)
$C_{AIBN}$	the concentration of AIBN in monomer MMA (mol/L)
$C_{WM}$	the volume ratio of aqueous solution of SDS to monomer MMA (mL/mL)

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