

Poly(*N,N*-dimethylacrylamide) Hydrogels Obtained by Frontal Polymerization

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Received 29 October 2008; accepted 9 December 2008

DOI: 10.1002/pola.23251

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Frontal polymerization (FP) has been used as an alternative technique for the preparation of poly(*N,N*-dimethylacrylamide) hydrogels. Samples were synthesized in bulk, water, or dimethyl sulfoxide (DMSO), and the obtained materials were characterized and compared in terms of their yield, swelling behavior, thermal properties, and morphology. It was found that their features are dependent on the presence and type of the solvent used. Samples prepared in bulk are characterized by the lowest yields and the highest front temperatures (T_{\max}) and velocities (V_f), whereas those synthesized in water have the highest yields and the lowest values of T_{\max} and V_f . No significant differences have been found in terms of T_g among the three series of samples. By contrast, the reaction conditions influenced the porous morphology of the samples and, consequently, their swelling capability in water. The swelling ratio ranges from about 670–700% for some samples prepared in water up to 3500% for a sample obtained in DMSO, thus indicating that this parameter can be properly tuned by using the most suitable FP conditions. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 1422–1428, 2009

Keywords: free radical polymerization; frontal polymerization; hydrogels; polyacrylamides; SEM

INTRODUCTION

Hydrogels are polymeric materials, generally crosslinked, that swell in aqueous media or in biological fluids without dissolving.^{1,2} Their architecture can be described as a three-dimensional network in which polymeric chains are physically or chemically bounded with each other and partially solvated.³ Hydrogels have aroused great interest

especially in biomedical applications because of their 3D structure, high water content, good biocompatibility, and good mechanical properties.^{4,5}

Most of the hydrophilic monomers that are commonly used are (meth)acrylates and (meth)acrylamides and their copolymers.^{6–9}

One of the first hydrogels reported in the literature is a copolymer of ethylene glycol bismethacrylate and 2-hydroxyethyl methacrylate.⁶ The resulting material has been used as a reservoir for drug delivery and for the production of soft contact lenses. Moreover, crosslinked copolymers of acrylamide and methylene bisacrylamide have

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 47, 1422–1428 (2009)
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been used to prepare gels for electrophoresis. Other applications of hydrogels are in the fabrication of artificial tendons and tissues, in the reconstruction of cartilage, and so forth.^{10,11}

In 2001, Washington and Steinbock¹² prepared poly(*N*-isopropylacrylamide) gels by frontal polymerization (FP). The latter is a technique that allows the conversion of a monomer into a polymer as a consequence of the formation and subsequent propagation of a polymerization front.

Three types of FP have been reported:

- (Thermal) Frontal Polymerization, in which front propagates because of the exothermicity of the polymerization reaction itself^{1,2,13},
- Photofrontal Polymerization, in which a localized reaction is driven by an external UV source^{10,14–17},
- Isothermal Frontal Polymerization, which is based on the gel effect^{18,19} that occurs when monomer and initiator diffuse into a preformed polymer.²⁰

In this article, we will refer to the thermal FP only.

Since the first pioneering work performed by Chechilo and Enikolopyan,²¹ an even increasing number of monomers have been polymerized by this technique. In detail, Pojman and coworkers polymerized epoxy resins,²² ionic liquid,²³ and acrylic monomers^{24–27}; the design and synthesis of glycidyl ethers that undergo FP^{28,29} were studied by Crivello; Chen and coworkers frontally polymerized 2-hydroxyethyl acrylate³⁰ and *N*-methylolacrylamide³¹; moreover, they studied the obtainment of epoxy resins/polyurethane networks,³² polyurethane-nanosilica hybrid nanocomposites,³³ and poly(*N*-vinylpyrrolidone).³⁴ Our group obtained poly(dicyclopentadiene),³⁵ polyurethanes^{36,37} interpenetrating polymer networks,³⁸ unsaturated polyester/styrene resins,³⁹ and poly(diurethane diacrylates).⁴⁰ We also prepared polymer-dispersed liquid crystal films⁴¹ and applied FP to the consolidation of porous materials^{42,43}; recently, we prepared polymer-based nanocomposites with montmorillonite⁴⁴ and polyhedral oligomeric silsesquioxanes,⁴⁵ and we have synthesized a new class of ionic liquid-based initiators to be used in both classic and frontal radical polymerization.⁴⁶

In this work, FP was applied to the preparation of poly(*N,N*-dimethylacrylamide) [poly(DMAAm)] hydrogels, and the obtained materials were char-

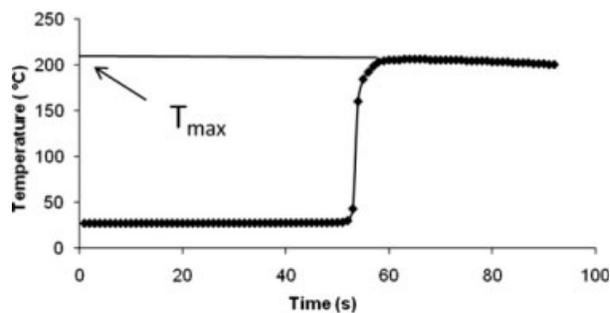


Figure 1. Typical temperature profile of a FP run (sample FP1.4).

acterized and compared in terms of their swelling behavior, thermal properties, and morphology.

EXPERIMENTAL

N,N-Dimethylacrylamide (DMAAm, 99%, FW = 99.13, bp = 70 °C) stabilized with 550 ppm of hydroquinone monomethyl ether, ammonium persulfate (AmPS, FW = 228.20), dimethyl sulfoxide (DMSO, FW = 78.13, bp = 189 °C, $d = 1.101$ g/mL), and *N,N*-methylenebisacrylamide (BIS, FW = 154.17, mp = 300 °C) were purchased from Sigma Aldrich and used as received.

At room temperature, pot-lives were always longer than 1 h. This is the time occurring between the preparation of the mixture and its spontaneous, fast reaction.

Front temperature measurements were performed by using a K-type thermocouple connected to a digital thermometer (Delta Ohm 9416, ± 1.0 °C; Fig. 1) used for temperature reading and recording (sampling rate: 1Hz). Heating of samples immersed in water for swelling studies was performed in an ISCO GTR 90 thermostatic bath. DSC measurements were carried out by a Q100 Waters TA Instruments calorimeter, with a TA Universal Analysis 2000 software.

After freeze-drying, hydrogel morphology was studied by scanning electron microscopy (SEM, Leo Stereoscan-440). Prior to examination, the samples were fractured in liquid nitrogen and the fractured surface was coated with gold.

To determine the swelling ratio (SR%) of hydrogels in water, they were heated from 26 to 43 °C, by increasing temperature at a rate of 1 °C/day. SR% was calculated by applying the following equation:

$$\text{SR\%} = \frac{M_s - M_d}{M_d} \times 100 \quad (1)$$

where M_s and M_d are the hydrogel masses in the swollen and in the dry state, respectively.

Thermal characterization of all samples was performed by DSC analysis. Two heating ramps, from -100 to 350 °C, with a heating rate of 10 °C/min, were carried out. The first scan was performed to eliminate possible residual solvent; the second was done to determine the glass transition temperature (T_g).

Frontal Polymerization Runs

A common glass test tube (i.d. = 1.5 cm, length = 16 cm) was filled with a mixture of DMAAm (5 g, 0.050 mol), BIS (0.05 g, 3.24×10^{-4} mol) and various amount of AmPS (from 0.4 to 2.0 wt % with respect to the total weight of monomer and crosslinker). Moreover, in Series 2 and 3, water and DMSO were respectively added (2.5 mL). Test tubes were kept open during polymerization. A thermocouple junction was located at about 1 cm from the bottom of the tube and connected to a digital temperature recorder. Front started by heating the external wall of the tube in correspondence of the upper surface of the monomer mixture, until the formation of the front becomes evident. The position of the front (easily visible through the glass wall of test tubes) against time was measured. For all samples, front temperature (T_{\max} , ± 10 °C) and front velocity (V_f , ± 0.5 cm/min) were measured.

After polymerization, all samples were washed in water for several days to eliminate the residual monomer and DMSO (only for Series 3), and to allow them to swell.

It should be underlined that, since DMAAm boils only at 70 °C and in all runs T_{\max} was higher than this temperature, in several cases a large part of the monomer evaporated thus resulting in quite low yields. Tubes were not sealed because one of the aims of this work was to perform syntheses following very simple procedures, which could be easily applied in future practical applications.

RESULTS AND DISCUSSION

T_{\max} (Fig. 1) and V_f are the main parameters generally monitored in FP experiments. Figure 1 shows a typical temperature profile recorded during a FP run. It displays the temperature variation in correspondence of the thermocouple junction as time goes. Before the sudden temperature

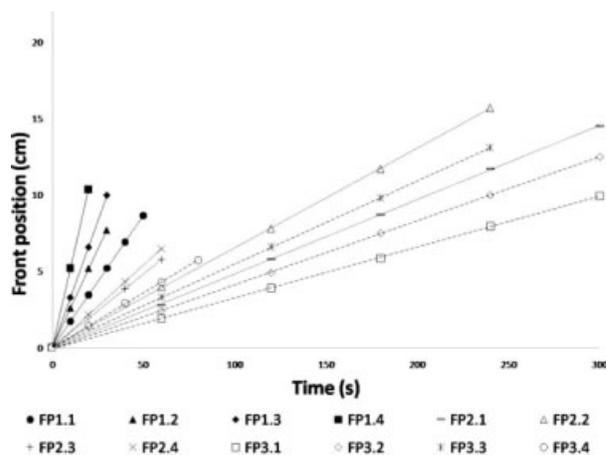


Figure 2. Front position as a function of time for FP runs.

increase observed when the propagating front crossed the junction, this parameter remained constant, thus indicating that no other endo- or exothermal phenomena were taking place simultaneously. This finding confirms that only FP occurred; namely, no spontaneous polymerization occurred. Indeed, at room temperature, pot-lives were always longer than 1 h, which is a time much longer than that necessary for FP runs to occur.

V_f values were calculated by the slope of the curves as that reported in Figure 2 and are listed in Table 1.

Because of the high reactivity, it was not possible to perform traditional batch syntheses (prolonged heating at a given temperature) because spontaneous acceleration and sudden increase of temperature were always observed. In particular, in unstirred reactors, “spontaneous FP,” with a front starting from the upper layer of the monomer mixture, occurred. This phenomenon was already observed and reported by us in a previous paper with the name of *Rainstorm Effect*.⁴⁷

Three different series of poly(DMAAm) hydrogels were synthesized (Table 1): the first one deals with FP runs performed without solvent (Series 1), while the other two collected samples prepared in the presence of water and DMSO (Series 2 and 3, respectively). For each series, four samples were synthesized by varying the AmPS concentration (0.4 , 0.7 , 1.2 , and 2.0 wt % with respect to the total amount of monomer and crosslinker), while DMAAm, BIS, and solvent concentrations were kept constant.

In all series, T_{\max} remains almost constant by varying the amount of AmPS. However, the presence of a solvent and its type influence these

Table 1. Reaction Parameters of the Samples Prepared in This Work

| Sample | Series | AmPS (wt %) | Solvent | V_f (cm/min) | T_{max} (°C) | Yield (%) |
|--------|--------|-------------|------------------|----------------|----------------|-----------|
| FP1.1 | 1 | 0.4 | None | 10.4 | 206 | 37 |
| FP1.2 | | 0.7 | None | 15.6 | 217 | 41 |
| FP1.3 | | 1.2 | None | 19.7 | 215 | 39 |
| FP1.4 | | 2.0 | None | 31.2 | 219 | 35 |
| FP2.1 | 2 | 0.4 | H ₂ O | 2.9 | 124 | 92 |
| FP2.2 | | 0.7 | H ₂ O | 3.9 | 128 | 93 |
| FP2.3 | | 1.2 | H ₂ O | 5.8 | 136 | 92 |
| FP2.4 | | 2.0 | H ₂ O | 6.5 | 138 | 90 |
| FP3.1 | 3 | 0.4 | DMSO | 2.0 | 149 | 85 |
| FP3.2 | | 0.7 | DMSO | 2.5 | 150 | 58 |
| FP3.3 | | 1.2 | DMSO | 3.3 | 151 | 53 |
| FP3.4 | | 2.0 | DMSO | 4.3 | 160 | 44 |

parameters although in different extent depending on the solvent used. Indeed, bulk FP runs (Series 1) are characterized by T_{max} from 206 to 219 °C; when DMSO was used (Series 3), T_{max} values were around 150–160 °C, whereas when H₂O was present (Series 2), T_{max} values did not exceed 138 °C.

By comparing Series 1 with the other two, the former trend can be easily explained by considering the dilution effect and the amount of dissipated heat. Moreover, the difference of T_{max} between Series 2 and 3 can be mainly attributed to the latent evaporation heat of water, which is responsible for further heat dissipation.

As previously mentioned, to operate in the simplest practical conditions, monomers were used as received and test tubes were kept open. This resulted in partial DMAAm evaporation and, consequently, in relatively low yields. Apart from a few exceptions, the lower T_{max} was as higher as the yield was, ranging from 35% for $T_{max} = 219$ °C to 92–93% for $T_{max} = 124$ –136 °C.

As expected, Series 1 is characterized by the fastest front propagation with V_f ranging from 10.4 to 31.2 cm/min. These values are an order of magnitude larger than those typically found in most of the FP experiments, also performed on other systems.⁴⁶ Namely, $V_f = 31.2$ cm/min is one of the largest values reported so far. On the other hand, solvent addition resulted in a dramatic decrease of front velocity to values that, although relatively high, are now located in the common range of most of other FP syntheses.⁴⁸

Based on these findings, by comparing the three series, the use of water as the solvent seems to be the most advantageous in that it allows obtaining the resulting polymer gel in high yields

and short times. Besides, since the corresponding T_{max} values are the lowest, possible material degradation processes are now limited. Moreover, the purification procedure is very easy: the final product is already swollen in water thus facilitating the unreacted monomer removal.

To study and compare the SR% of all samples, they were swollen and equilibrated in water at various temperatures; the resulting trends, reported in Figure 3, were determined by applying eq 1. Even if the prepared materials do not show any critical solution temperature, all of them deswell as temperature increases. However, significant differences characterize each series when compared with the others.

Along Series 1 and 2 [Fig. 3(a,b)], a relationship between the amount of radical initiator and the extent of swelling seems to be present. Indeed, an increase of AmPS results in an SR% decrease. Conversely, this trend is almost inverted by considering Series 3 [Fig. 3(c)]. However, it should be highlighted that, in any series, SR% decreases as temperature increases, at least up to about 39 °C, but with different values and dependence between these two parameters.

In detail as follows:

- Series 1: At 26 °C, SR% of these samples is comprised between about 2270 and 2600%, but FP1.4 (synthesized in the presence of the largest AmPS concentration) behaves differently when compared with FP1.1–3. While SR% values of these latter are only poorly influenced by temperature variations, FP1.4 dramatically changes its volume from SR% = 2270% at 26 °C, down to 1900% at 43 °C.

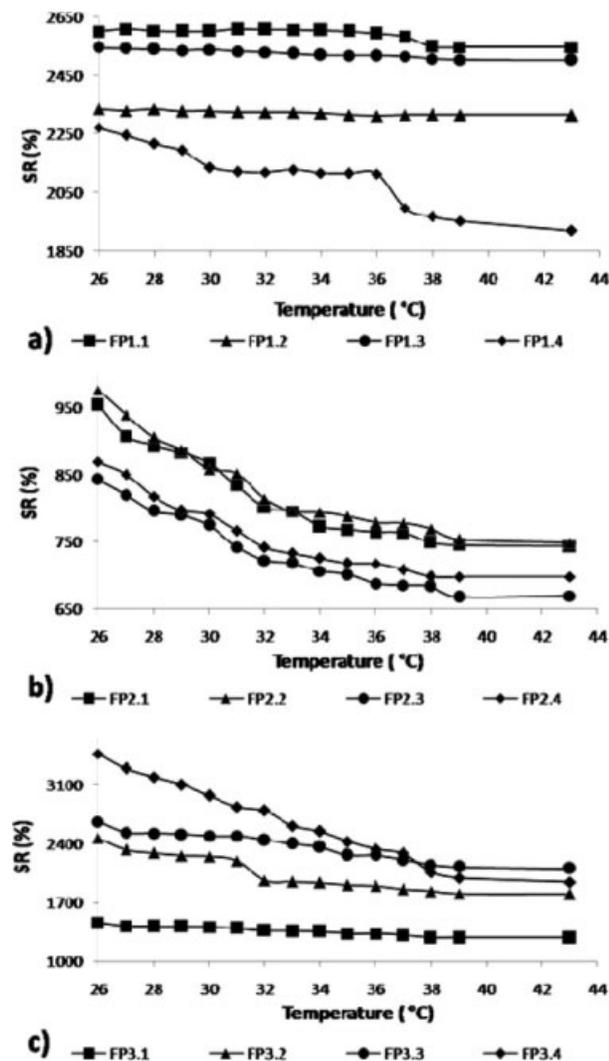


Figure 3. SR% as a function of temperature for the three series: (a) series 1, (b) series 2, (c) series 3.

Moreover, the extent of swelling of this material is always lower than that of the other samples of the same series.

- Series 2: By increasing the temperature, all these samples considerably deswell.

Namely, FP2.1 and FP2.2 SR% goes from about 960 to 750%, whereas the swelling ratio of FP2.3 and FP2.4 ranges from about 850 to 670–700%.

- Series 3: At 26 °C, FP3.4 exhibits an SR% as high as 3500 %, the largest of all samples. This material is also the only one that shows large temperature dependence in Series 3.

For all synthesized polymers, T_g was found to be almost the same and equal to about 126 °C. It is noteworthy that the T_g of these frontally obtained samples is significantly higher than that reported in literature for the same classical polymerization (89 °C).^{25,48} No explanation can be given for such evidence.

Polymers prepared by FP have been examined in detail by SEM to investigate their morphology, pore structure, and distribution. Figure 4 shows SEM micrographs of the samples containing 1.2 wt % of AmPS synthesized in the absence of solvent, in water, and in DMSO. Unlike the sample synthesized in water [Fig. 4(b)], which is characterized by a very dense structure, both the systems prepared in DMSO [Fig. 4(c)] and in bulk [Fig. 4(a)] present a more porous morphology. To find a relationship with the final hydrogel properties, the structure of FP1.3 and FP3.3 will be described in more detail. Indeed, on the micron scale, the aforementioned samples are characterized by polymer aggregates and cavities that are not present in FP1.2. Keeping in mind the swelling mechanism, it is possible to assume that this “free volume” allows these hydrogels to swell more than what the one prepared in water does. On this basis, we can assume that the described structure of the above hydrogels might be responsible for their peculiar behavior in this latter solvent.

CONCLUSIONS

For the first time, the FP technique was exploited to synthesize poly(DMAAm) hydrogels. It was

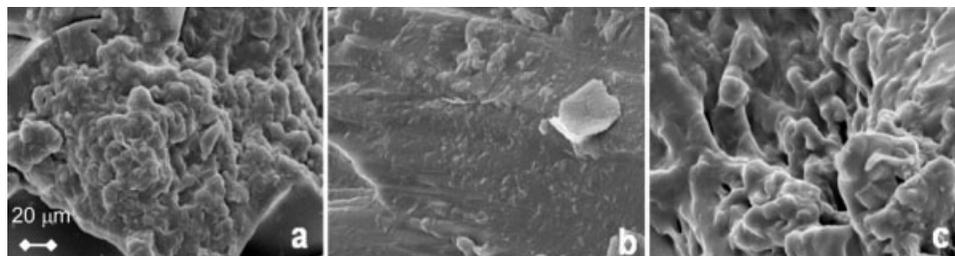


Figure 4. SEM images of samples FP1.3 (a), FP2.3 (b), and FP3.3 (c).

found that many of the features of the prepared samples can be tuned by changing the FP conditions, namely, the presence of a solvent and its type, and initiator concentration.

In particular, because of the exothermicity of the polymerization reaction, samples prepared in bulk were characterized by the highest values of both V_f and T_{max} . Moreover, it is noteworthy that front velocities as high as 31.2 cm/min have been recorded, one of the highest values found so far in FP experiments. However, in bulk FP runs, T_{max} was always higher than 200 °C, thus resulting in low yields because of the large amount of monomer that evaporates before polymerizing. In this respect, water was found to be the best solvent in that, because of its thermal characteristics, kept front temperatures relatively lower, thus permitting to achieve high yields.

In water, all materials do not exhibit any critical solution temperature in the range between 25 and 45 °C, but swelling capability was found to be strongly temperature-dependent. Moreover, SR% was influenced by the presence and type of solvent used during the preparation, with values, at 26 °C, ranging from 850 to 3500% for the samples prepared in water and DMSO, respectively, whereas at 43 °C, it reaches values as low as 600% (sample prepared in water). The above peculiar behavior was explained by taking into account hydrogel morphology.

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