

Microwave Accelerated Synthesis and Characterization of Poly(acrylamide)

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ABSTRACT: Poly(acrylamide) (PAM) was efficiently synthesized under microwave (MW) irradiation using catalytic amount of potassium persulfate. The synthesis does not require any inert atmosphere and could be accomplished in very short time. Microwave power, exposure time, concentration of persulfate, and concentration of the acrylamide were varied to optimize the polymerization in terms of the % conversion (%C). The maximum %C that could be achieved was in 98.5%. The average molecular

weight of the synthesized PAM samples ranged from 4.11×10^4 to 1.30×10^5 , depending upon the MW power used for their synthesis. The representative PAM was characterized by Fourier transform-infrared, SEM, and X-ray diffraction studies. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3702–3707, 2007

Key words: acrylamide; microwave irradiation; polymerization; potassium persulfate

INTRODUCTION

Poly(acrylamide) (PAM) is a synthetic, high molecular weight water soluble organic polymer of wide application. It is used for the treatment of the sludge in water plant,¹ in gel electrophoresis, and capillary gel electrophoresis.² The polymer is also used³ in the field of enhanced oil recovery, paper-making industry, and textile industry. Various redox initiators, like potassium ditelluratoargentate (III) in alkaline medium,⁴ persulfate-bisulfite,⁵ ceric ammonium nitrate-methionine,⁶ and potassium persulfate-2-mercaptoethanol⁷ have been used for the polymerization of the acrylamide. Specific PAM formulations depend on the polymer's chain length and the kinds of functional groups substituted along the chain. A novel route for the polymerization of acrylamide with hydrogen peroxide catalyzed by anionic water-soluble iron (III) 5,10,15,20-tetrakis-(2',6'-dichloro-3'-sulfonatophenyl) porphyrin⁸ and 4'-azobis (4-cyano pentanol)⁹ has been recently reported. Potassium persulfate¹⁰ initiated polymerization has been studied gravimetrically and by dilatometer technique, however, an inert argon atmosphere was required for such polymerization. Polymerization of acrylamide using iron (II) ammonium sulfate/aqueous hydrogen peroxide is also reported,¹¹ where polymerization is done in inert atmosphere at room

temperature in 50% yield. However, the product obtained by precipitation with methanol is colored brown because of contamination of iron (III) hydroxide that has to be removed by ammonia to precipitate the iron (III) hydroxide from the product.

Microwave (MW) irradiation¹² emerging as efficient source thermal energy constitutes a very original procedure of heating materials, and has been exploited in various fields of chemistry including polymers. Under microwave irradiation, homopolymerization^{13,14} and graft copolymerization^{15–20} have been reported without radical initiators or with very low initiator concentration. In the present communication we for the first time report on microwave accelerated synthesis of PAM, where catalytic amount of the persulfate was sufficient for the polymerization and the product had no contamination of colored salt, moreover polymerization could be done in seconds that too under atmospheric conditions. Since microwave promoted polymerization of acrylamide can be done with minimum use of the chemicals under atmospheric conditions in very short time, the present method will be cost effective.

EXPERIMENTAL

A Kenstar (Model No. MOW 9811) domestic microwave oven with a microwave frequency of 2450 MHz and a power output from 0 to 800 W with continuous adjustment was used for all the experiments. The average bulk temperature at the end of the reaction was measured by inserting a thermometer into the reaction mixture and was less than 100°C for all

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the reactions. The polymer sample of maximum % conversion was used for the characterization. For SEM pictures Leo 440 scanning electron microscope was used. Infrared (IR) spectra were recorded on a Nicolet 5700 of FTIR spectrophotometer using KBr pellet. X-Ray Diffraction (XRD) was carried out on Bruker D8 X-ray diffractometer. Brookfield LVDVE viscometer with small sample adapter was used for the viscosity measurements. Acrylamide (E. Merck) was recrystallized with methanol before use. The polymer yield was determined by direct weighing of the PAM produced. The intrinsic viscosity (η) of the polymer solution was measured in water (at $30 \pm 0.2^\circ\text{C}$) using an Ubbelohde viscometer and the number-average molecular weights (M_n) of the polymers synthesized were calculated using the following relationship¹⁰:

$$[\eta] = 6.80 \times 10^{-4} M_n^{0.66} \quad (1)$$

where $[\eta]$ is specific viscosity.

Polymerization under microwave irradiation

To a solution of calculated amount of acrylamide in 25 mL of distilled water in a 100 mL open neck conical flask, calculated amount of the potassium persulfate was added with stirring followed by exposure to microwave field at fixed power for definite time. Reaction mixture after exposure was cooled and precipitated with methanol to obtain PAM. The experiment was repeated with 20 mg of hydroquinone (radical scavenger) under optimal condition.

Polymerization on thermostatic water bath

Acrylamide (1 g) was dissolved in 25 mL water in a two-necked flask, which was purged with purified nitrogen for about 30 min. $\text{K}_2\text{S}_2\text{O}_8$ ($2 \times 10^{-3} \text{ M}$) was added to the reaction flask and the flask was thermostated on a water bath at 35°C . After 1 h the reaction mixture was poured in methanol with stirring, and filtered. The experiment was also repeated at 50°C and 98°C as above. In separate experiments under identical conditions, the polymerization was attempted in presence of air at 35, 50, and 98°C .

Molecular weight determination

The number average molecular weights of the polymer samples (synthesized at different microwave powers) were determined using dilute solution viscosimetry using Ubbelohde viscometer at 30°C . In each case, flow time for the aqueous solutions of the

TABLE I
Water and Saline Retention by Poly(acrylamide) Synthesized under Optimum Conditions (i.e. [Acrylamide] = 0.56 M ; $[\text{K}_2\text{S}_2\text{O}_8] = 2 \times 10^{-3} \text{ M}$; at 80 % MW Power and 50 s Exposure Time, Total Volume 25 mL)

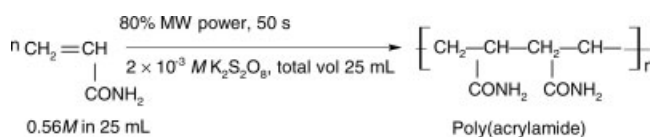
S. No.	Contact time (min)	Water retention (g/g)	Saline retention (g/g)
1.	15	19	14.1
	30	35.20	27.3
	45	58	42.8
	60	73	56.5
	75	84	69.5

polymer samples was measured at five different concentrations.

Determination of water and saline retention

An accurately weighed amount of the dried polymer was placed in a previously dried and weighed sintered glass crucible (G-4), which was then filled with 50 mL of water and after 30 min; suction from a vacuum pump was applied. The glass crucible was then weighed to determine²¹ the amount of water retention per gram of the dried material and this was taken as water retention capacity. Similarly, saline retention capacity was determined by using 1% aqueous sodium chloride solution. Results are summarized in Table I.

RESULTS AND DISCUSSIONS



Using microwave irradiation, PAM samples having average molecular weight of 41,130–1,30,000 have been synthesized. Optimum % conversion (98.5%) was obtained at $2 \times 10^{-3} \text{ M}$ persulfate, 0.56 M acrylamide, 80% microwave power in 50 s exposure. The temperature measured just after the microwave exposure was 98°C . Water and saline retention of the PAM sample synthesized under optimal condition were measured (Table I) and were found to increase with the increase in the contact time and was maximum for 75 min contact (84 g/g and 69.5 g/g, respectively). The PAM solution (1% w/v) of the had viscosity of 6.28 cP at 100 rpm at 25°C and the viscosity remain stable up to 98 h.

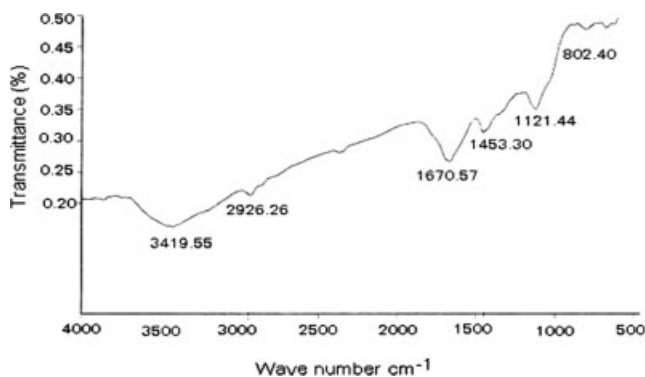


Figure 1 IR spectra of PAM synthesized under microwave irradiation.

Characterization of the PAM

In the IR spectra of the PAM (Fig. 1), N—H stretching vibration is observed at 3419 cm^{-1} . Amide C=O stretching vibration is present at 1670 cm^{-1} while amide II band is masked under the envelope of amide I and is not seen separately. C—H stretching, C—N stretching and out of plane N—H wagging vibrations are observed at 2924 cm^{-1} , 1453 cm^{-1} , and 802 cm^{-1} , respectively.

XRD the PAM (Fig. 2) reveals its crystalline nature. Crystalline peaks are observed at 20° , 14° , 18° , and 25° corresponding to the d values 6.3217 , 4.9242 , and 3.5588 , respectively.

SEM picture of the microwave synthesized PAM (Fig. 3) shows that polymer has a homogeneous web-like interpenetrating porous structure.

Mechanism of polymerization under microwave

Since in presence of radical quencher no polymerization was observed, a plausible free radical mechanism for the grafting under MW may be proposed as below.

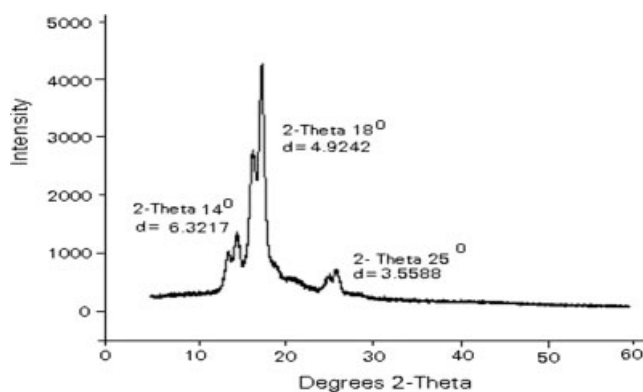


Figure 2 XRD of PAM synthesized under microwave irradiation.

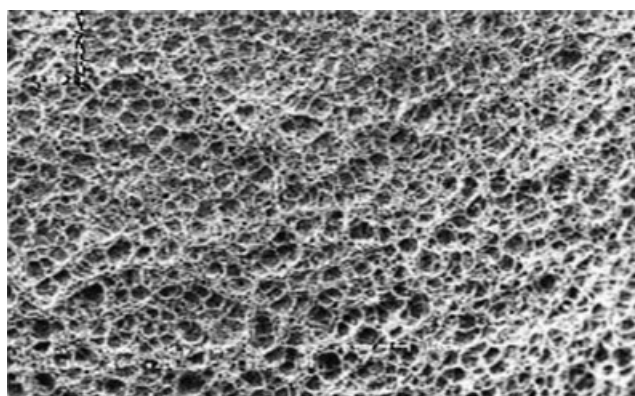
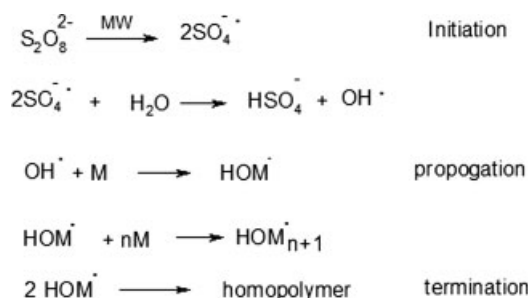


Figure 3 SEM picture of the PAM synthesized under microwave irradiation.

The polymerization is carried out in aqueous medium and water molecules being polar will absorb microwave energy resulting into dielectric heating¹¹ of the reaction mixture. Acrylamide and the persulfate molecules being polar also contribute to the dielectric heating, which results in to easy decomposition of the oxygen-oxygen bond in persulfate²² to yield sulfate radical ion, which after interacting with water gives hydroxyl free radical²³ (primary free radicals). The hydroxyl free radicals are the primary free radicals, which initiate the polymerization of acrylamide. The polymer chain increases until two growing polymer chain unite to terminate the reaction. (Scheme 1). Addition of hydroquinone results in to the formation of stable free radicals out of primary radicals, which are unable to propagate the chain reaction and therefore its presence quenches the reaction and no polymerization is observed.

Maximum % conversion (98.5%) was observed when 0.56 M acrylamide was polymerized in presence of $2 \times 10^{-3}\text{ M}$ persulfate at 80% microwave power and 50 s exposure. However, under identical condition, on thermostatic water bath at 98°C , the

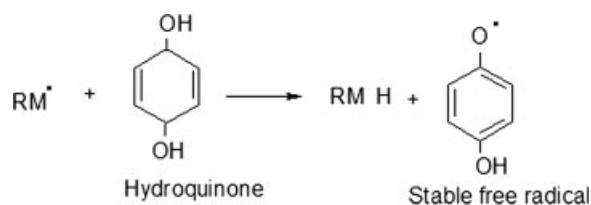


Scheme 1 Mechanism of grafting under microwave irradiation.

TABLE II
% Conversion with Persulfate Concentration
([Acrylamide] = 0.56M, 80% MW Power and 50 s
Exposure Time, Total Volume 25 mL at 98°C)

S. No	[K ₂ S ₂ O ₈]	%C
1.	2 × 10 ⁻³ M	–
2.	4 × 10 ⁻³ M	20
3.	8 × 10 ⁻³ M	35
4.	2 × 10 ⁻² M	49

polymerization was not observed, indicating that 2 × 10⁻³ M persulfate furnishes insufficient amount of the primary radicals under thermal heating. Since microwaves can heat reactants selectively, directly, without thermal inertia and heat exchange with the medium the rate of polymerization under thermal heating is much slower than under microwave irradiation²⁴ and the results under present study are in concurrence with the previous reports²⁵ about the faster polymerization rate under microwave irradiation and the effect of microwave power on the rate of polymerization. However, on increasing the persulfate concentration beyond 2 × 10⁻³ M polymerization was observed. At 2 × 10⁻² M persulfate, 49% conversion was noticed. Table II summarizes the %C at different persulfate concentration. It was observed that on increasing the persulfate %C increases this might be because of formation of more free radicals at higher persulfate concentration.



Scheme 2 Quenching by hydroquinone.

Determination of the optimal conversion

Polymerization conditions were optimized varying different reaction parameters as follows.

Effect of MW power

To the acrylamide (1 g in 25 mL H₂O; 0.56M), K₂S₂O₈ (2 × 10⁻³ M) was added and the reaction mixture was exposed to different microwave powers and exposure time and the resulting polymer samples were precipitated with methanol and the yields were recorded in Table III. It was observed that the yield increases with the increase in the microwave power and was highest at 80% microwave power and 50 s exposure (Fig. 4). Further increasing the MW power decreases the yield; this may be due to some decomposition of the polymer taking place at higher microwave power.

Effect of exposure time

With increase in the exposure time % conversion increases up to 60% microwave power this may be

TABLE III
% Conversion with MW Power and Exposure Time ([Acrylamide] = 0.56M, [persulfate] = 2 × 10⁻³ M, Total Reaction Volume 25 mL)

S. No.	MW power (%)	Exposure time (s)	Yield (mg)	Temperature after exposure (°C)	%C
1	40	25	365	76	36.5
		50	410	90	41
		75	530	98	53
		100	670	98	67
		125	715	98	71.5
2	60	25	450	92	45
		50	580	98	58
		75	695	98	69.5
		100	790	98	79
		125	825	98	82.5
3	80	25	650	95	65
		50	985	98	98.5
		75	890	98	89
		100	830	98	83
		125	745	98	74.5
4	100	25	760	98	76
		50	425	98	42.5
		75	375	98	37.5
		100	310	98	31
		125	285	98	28.5

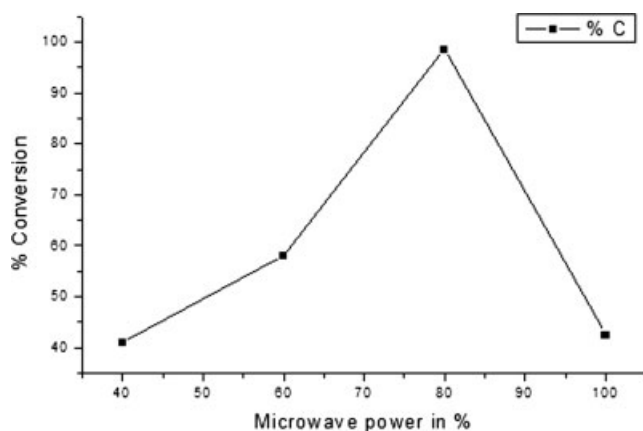


Figure 4 % Conversion with MW power at [acrylamide] = 0.56M, [persulfate] = 2×10^{-3} M; mw exposure 50 s.

due to the formation of more primary radicals with the increasing power. However at 80 and 100% power, % conversion increases with increase in exposure time initially and is greatest for 50 s exposure, exposing beyond this results into decrease of % conversion. Probably prolonged exposure to such high microwave powers results into some depolymerization of the polyacrylamide and therefore % conversion. (Fig. 5; Table III).

Effect of the $K_2S_2O_8$

Effect of the $K_2S_2O_8$ on the polymerization was studied in the concentration range of 1.5×10^{-3} to 3.5×10^{-3} M at the fixed concentration of acrylamide (0.56M) at 80% MW power and 50 s exposure time (Table IV). The % conversion increases with potassium persulphate concentration; this may be due to increase in concentration of the active species ($S_2O_8^{2-}$). Maximum yield was observed at 2×10^{-3} M

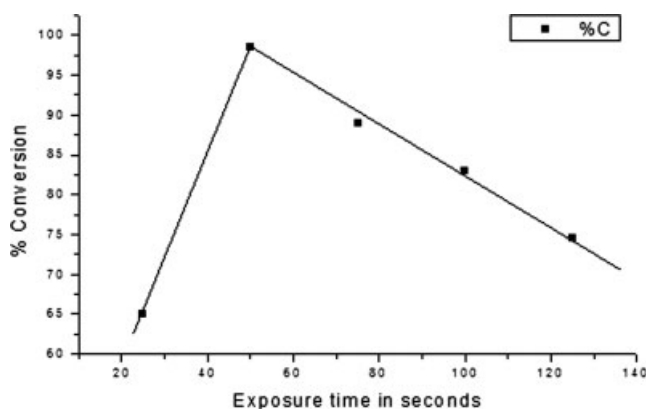


Figure 5 % Conversion with exposure time at [acrylamide] = 0.56M, [persulfate] = 2×10^{-3} M at 80% MW power.

TABLE IV
% Conversion with Potassium Persulfate Concentration ([Acrylamide] = 0.56M, 80% MW Power and 50 s Exposure Time, Total Volume 25 mL)

S. No.	[$K_2S_2O_8$]	Yeild (mg)	Temperature after exposure ($^{\circ}C$)	%C
1.	1.5×10^{-3} M	830	98	83
2.	2×10^{-3} M	985	98	98.5
3.	2.5×10^{-3} M	910	98	91
4.	3.0×10^{-3} M	875	98	87.5
5.	3.5×10^{-3} M	750	98	75

persulphate, increasing concentration beyond this may result in accumulation of large number of free radicals resulting into premature termination of the growing chains and thus the % conversion decreases (Fig. 6).

Effect of acrylamide concentration

Effect of the acrylamide concentration on the polymerization yield was studied in the concentration range 0.56M–1.0M (Table V). It was observed the % conversion decreases with the monomer concentration. Maximum yield was observed at 0.56M acrylamide (Fig. 7). Increase in concentration beyond this decreases the % conversion; this may be due to increased viscosity of the reaction medium on PAM formation.

Molecular weight of the PAM samples

The intrinsic viscosity was calculated by plotting η_{sp} versus C and η_{inh} versus C and then taking the common intercept at C=0 of the best-fitted straight line through the two sets of points. Here C represents polymer concentrations in g/dL. The η_{sp} and η_{inh} are specific and inherent viscosities and were

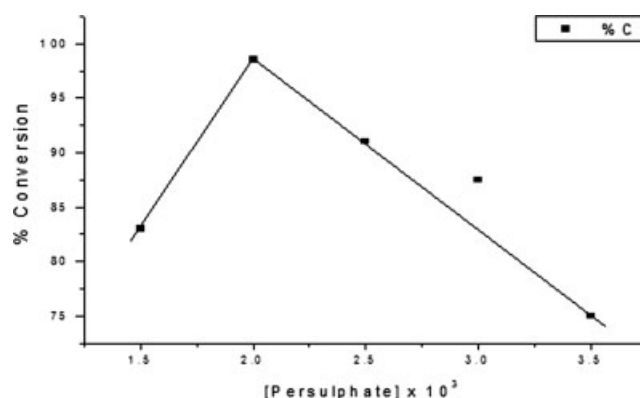


Figure 6 % Conversion with persulfate concentration at [monomer] = (0.56M) at 80% MW power and 50 s exposure.

TABLE V
% Conversion with Monomer Concentration
([Persulfate] = 2×10^{-3} M, 80% MW Power, and 50 s
Exposure Time, Total Volume 25 mL

S. No.	[Acrylamide]	Yield (g)	%C	Temperature after exposure
1.	0.56M	0.985	98.5	98
2.	0.68M	1.070	89.17	98
3.	0.79M	1.130	80.171	98
4.	0.90M	1.275	79.69	98
5.	0.96M	1.380	76.67	98

calculated from the relation $\eta_{sp} = \eta_{rel} - 1$ and $\eta_{inh} = \ln \eta_{rel} / C$.

Using intrinsic viscosity, the number average molecular weight of the polymer samples were calculated according to equation -1 and results are summarized in Table VI. It was observed that with the increase in the microwave power, % conversion and the average molecular weight of the polymer samples increase. However, as the microwave power increases beyond 80%, the average molecular weight of the polymer sample decreases, confirming the earlier conclusion that at high MW power some depolymerization takes place.

CONCLUSIONS

Acrylamide could be polymerized using catalytic amount of potassium persulfate in excellent yield under the influence of microwave irradiation. Moreover, the polymerization under microwave does not require an inert atmosphere. Optimum % conversion could be obtained in 50 s at 80% microwave power keeping acrylamide = 0.56M, $K_2S_2O_8 = 2 \times 10^{-3}$ M in 25 mL water. Average molecular weights of the PAM samples increase with the increase in the MW power used, however increasing power beyond 80%, samples with lower molecular weight were obtained,

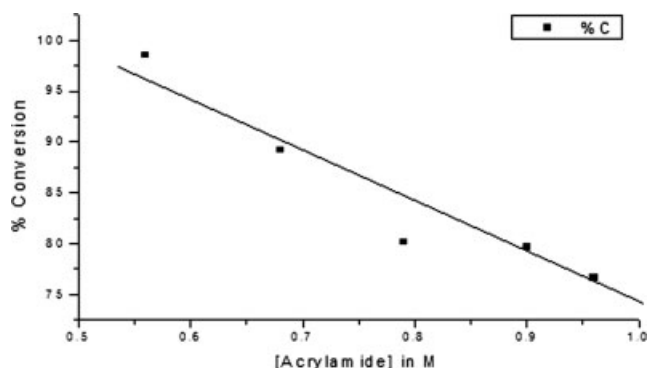


Figure 7 % Conversion with acrylamide concentration at [persulfate] = 2×10^{-3} M at 80% MW power and 50 s exposure.

TABLE VI
Average Molecular Weight of PAM Synthesized at
Different Microwave Power

S. No.	MW power	Intrinsic viscosity	Average molecular weight of PAM
1.	40%	0.755	41,130
2.	60%	1.125	75,300
3.	80%	1.620	1,30,000
4.	100%	1.386	1,03,300

indicating some depolymerization. Under identical conditions no polymerization was observed on thermostatic water bath.

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